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March 2003

WTP
Project
Report

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Test Specification: TSP-W375-01-00002 Rev. 0
Test Plan: TP-RPP-WTP-066 Rev. 0
Test Exceptions: None
R&T Focus Area: Pretreatment
Test Scoping Statement(s): B-39

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Completeness of Testing

This report describes the results of work and testing specified by TSP-W375-01-00002 Rev. 0 and TP-RPP-WTP-066 Rev 0. The work and any associated testing followed the quality assurance requirements outlined in the Test Specification and Test Plan. The descriptions provided in this test report are an accurate account of both the conduct of the work and the data collected. Test plan results are reported. Also reported are any unusual or anomalous occurrences that are different from expected results. The test results and this report have been reviewed and verified.

Approved:

Gordon H. Beeman, Manager
WTP R&T Support Project

Date

Manager
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Date

Summary

The River Protection Project-Waste Treatment Plant baseline for pretreating Envelope C low-activity waste (LAW) at Hanford includes a precipitation step for removing radioactive strontium (Sr-90) and transuranic (TRU) isotopes before the waste is vitrified. The resulting solids, designated as high-level waste (HLW), are removed, washed, and concentrated by cross-flow filtration. The Sr/TRU removal process is based on precipitation by adding strontium nitrate for Sr-90 removal and permanganate for TRU removal. Section 5 of the *Research and Technology Plan* (BNI 2002) identifies further research needs, which are illustrated in Figure 5-14, Precipitation Test Matrix, of that report.

One need shown in this matrix is optimization of the Sr/TRU precipitation reaction conditions [SOW Ref: Sec. C.6 Std.2 (a)(3)(ii)(B)]. One action included is determining the gas generation and chemical energetics release from Sr/TRU precipitates (WBS No: 1.2.08.02 and 1.2.10.1). The gas generation and energetics testing of Sr/TRU precipitate is addressed in Scoping Statement B-39, which is included in Appendix C of the *Research and Technology Plan* (BNI 2002). Experiments for the study discussed here were conducted in accordance with the approved Test Plan, TP-RPP-WTP-066, which implements the requirements set forth in Test Specification TSP-W375-01-00002.

Objectives

The objective of this work, performed by Battelle – Pacific Northwest Division (PNWD), was to measure the gas generation and energetics of actual solid samples from the Sr/TRU removal treatment of Tank 241-AN-102 (AN-102) waste mixed with leach solutions from pretreatment of Tank 241-C-104 (C-104) sludge (solids referred to as “AN-102/C-104 Sr/TRU precipitate”). This waste blending was performed by Lumetta et al. (2002), and the Sr/TRU treatment was performed by Hallen et al. (2002). The AN-102/C-104 Sr/TRU precipitate was washed using inhibited water (0.01 M NaOH) and dewatered to dryness using vacuum filtration. A subsample of the vacuum-dried solids was used for energetics testing. The remaining solids were resuspended in inhibited water for gas generation testing to better mimic the slurry expected from cross-flow filtration. Gas generation from the AN-102/C-104 Sr/TRU precipitate was measured as a function of temperature with and without the application of an external radiation source (^{137}Cs gamma capsule).

Experiments were conducted to determine the quantity and composition of gases generated from actual Sr/TRU precipitate by chemical and radiolytic processes as a function of temperature. The gas generation tests focused first on the effect of temperature on the composition and rate of gas generation. Generation rates of hydrogen, nitrous oxide, nitrogen, and methane increased with temperature, and the composition of the product gas mixture varied with temperature. The gas generation rate was examined at 45°, 60°, 75°, 90°, and 105°C.

It is important to understand the potential reactivity of Hanford HLW because several of the stored wastes contain fuels (organic compounds) and oxidants (nitrates and nitrites) that are thermally sensitive (Scheele et al. 1995; Wahl et al. 1996; Meacham et al. 1997). To assess the potential reactivity hazard of the washed AN-102/C-104 Sr/TRU precipitated sludge, we used a strategy similar to that of Babad et al. (1995). Enthalpy-calibrated differential thermal analysis (DTA) from room temperature to 500°C was used to measure the heat of reaction of the AN-102/C-104 Sr/TRU precipitated sludge.

Conduct of Testing

Gas generation tests on actual radioactive Sr/TRU precipitate were conducted at the High-Level Radiochemistry Facility (HLRF) in the 325 Building. Measurements were made using reaction vessels and a gas manifold system similar to those used in earlier studies with simulated waste (Bryan and Pederson 1995) and described in earlier reports detailing work with actual waste.^(a,b) The self-dose rates from the radionuclide inventory of AN-102/C-104 Sr/TRU precipitate samples were calculated to assess the amount of radiolytically induced gas from internal radiation sources.

To assess the potential reactivity hazards of washed Sr/TRU solids, energetics testing was conducted using enthalpy-calibrated DTA from room temperature to 500°C. In addition, a single supplemental DSC analysis was performed to help identify reaction events. This strategy is similar to that used by Babad et al. (1995) to assess the reactivity hazards of stored organic-bearing HLW (Meacham et al. 1997). The DTA and DSC were calibrated before testing using known melting point standards. If an exothermic reaction producing more than 480 J/g were to be observed, PNWD has the capability to further evaluate the energetics of the material using the reactive system screening tool, subject to concurrence by the contractor.

Results and Performance Against Objectives

Arrhenius treatment of the rate data yielded the thermal activation parameters (E_a) for gas generation shown in Table S.1. These parameters (E_a , kJ/mol) were measured as 64 (± 62) for hydrogen, 79 (± 26) for nitrous oxide, 14 (± 7) for nitrogen, 147 (± 82) for methane, and 60 (± 32)

(a) Bryan SA, CM King, LR Pederson, and SV Forbes. 1996. *Thermal and Radiolytic Gas Generation from Tank 241-SY-103 Waste: Progress Report*. TWSFG96.17, Pacific Northwest National Laboratory, Richland, WA.

(b) King CM and SA Bryan. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-S-106 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.

Table S.1. Thermal and Radiolytic Rate Parameters for Gas Generation from AN-102/C-104 Sr/TRU Precipitate Samples^(a)

Parameter	H ₂	N ₂ O	N ₂	CH ₄	Overall rate
E _a , kJ/mol ^(b)	64(±62)	79(±26)	14(±7)	147(±82)	60(±32)
A, mol/kg/day ^(c)	7.9E+2	6.9E+5	2.3E-3	3.6E+14	2.0E+3
ln(A)	7(±21)	13(±9)	-6(±2)	34(±27)	8(±11)
R ²	0.458	0.902	0.934	0.861	0.699
G-value at 32,000 R/h ^(d)	0.18 (±0.02)	0.0041 (±0.004)	-- ^(e)	0.0006 (±0.001)	0.19 (±0.023)
G-value at 687 R/h	0.025 (±0.016)	0.004 (±0.004) >45°C 0.053 (±0.002) 45°C	-- ^(e)	0.005 (±0.003)	0.04 (±0.03)

(a) Values in parentheses indicate 95% confidence interval.
(b) Thermal activation parameter.
(c) Arrhenius pre-exponential factor.
(d) G-value is radiolytic activation value, defined as molecules produced per 100 eV absorbed dose.
(e) Indicates values not determined, as explained in text.

for total gas generated. Gases produced from irradiation with a 31,000 R/h (¹³⁷Cs) external gamma source were measured to determine the radiolytic G-values for gas generation and are summarized in the table. The effects of temperature and radiation were examined at ambient cell temperature, ~33°C, as well as at 45°, 60°, 75°, 90°, and 105°C. The radiolytic G-values, in molecules per 100 eV, were determined to be 0.18 (±0.02) for hydrogen, 0.0041 (±0.004) for nitrous oxide, 0.0006 (±0.001) for methane, and 0.19 (±0.023) for total gas generated. The scatter in the nitrogen data precluded an accurate assessment for the nitrogen G-value.

Using the DTA and DSC, we found only two or three endothermic reactions requiring from +5 to +36 J/g waste and no exothermic reactions for the AN-102/C-104 Sr/TRU precipitate. Because the Sr/TRU washed solids did not exhibit exothermic behavior exceeding the Hanford reactive waste criterion of an exothermic 480 J/g dry waste (e.g., -480 J/g dry waste) as measured by DSC (Babad et al. 1995), these solids would not be classified as reactive waste. The DTA and DSC measured results indicating heat production of <480 J/g dry waste are consistent with the estimated theoretical maximum enthalpy production of 210 J/g dry waste for these solids containing organic carbon as 3.6 wt% oxalate. Because the oxidation of oxalate will only result in a nominal maximum 2 wt% loss, the total mass loss observed by the TGA of 8.6 wt% after 100°C indicates that other slow endothermic reactions, such as decomposition of hydrates and hydrous oxides, must be postulated to explain the greater mass loss. In addition, it appears that any heat absorbed during dehydration and/or decomposition more than compensates for heat released by any organic oxidation by nitrite or nitrate.

Quality Requirements

PNWD implemented the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP quality assurance (QA) organization. Experimental work

was initiated in May 2001 and extended through August 2002. Experimental work conducted prior to September 2001 was performed in accordance with PNWD's quality assurance project plan CHG-QAPjP Rev. 0, which invoked PNWD's Standards Based Management System (SBMS), compliant with DOE Order 414.1A Quality Assurance and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A—Quality Assurance Requirements. Due to a change in the contract QA requirements in September 2001, the experimental work performed after that date was conducted in accordance with PNWD's quality assurance project plan RPP-WTP-QAPjP Rev. 0, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990 Part 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP). The quality of the data gathered during the earlier experiments was not affected by the change in requirements.

PNWD addressed verification activities by conducting an Independent Technical Review of the final data report in accordance with procedure QA-RPP-WTP-604. This review verified that the reported results were traceable, that inferences and conclusions were soundly based, and the reported work satisfied the Test Plan objectives. The review procedure is part of PNWD's WTPSP Manual.

Issues

The test plan stated gas generation tests were to be performed in duplicate at five temperatures (60°, 75°, 90°, 105° and 120°C). The temperature range used during testing included ambient hot cell temperature, ~33°C, in addition to 45°, 60°, 75°, 90°, and 105°C. Due to the added experiments at lower temperatures, which more closely resemble normal operating conditions, the originally planned highest temperature experiment (120°C) was not conducted.

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1.0 Introduction

The River Protection Project-Waste Treatment Plant baseline for pretreating Envelope C low-activity waste (LAW) at Hanford includes a precipitation step for removing radioactive strontium (Sr-90) and transuranic (TRU) isotopes before the waste is vitrified. The resulting solids, which are designated as high level waste (HLW), are removed, washed, and concentrated by cross-flow filtration. The Sr/TRU removal process is based on precipitation by addition of strontium nitrate for Sr-90 removal and permanganate for TRU removal. Section 5 of the *Research and Technology Plan* (BNI 2002) identifies further research needs, as illustrated in Figure 5-14, Precipitation Test Matrix, of that report.

One issue or need shown in this matrix is optimization of the Sr/TRU precipitation reaction conditions [SOW Ref: Sec. C.6 Std.2 (a)(3)(ii)(B)]. One action included under this need is to determine the gas generation and chemical energetics release from Sr/TRU precipitates [WBS No: 1.2.08.02 and 1.2.10.1]. The gas generation and energetics testing of Sr/TRU precipitate is addressed in Scoping Statement B-39, which is included in Appendix C of the *Research and Technology Plan*. Experiments were conducted in accordance with the approved Test Plan, TP-RPP-WTP-066, which implements the requirements set forth in the Test Specification, TSP-W375-01-00002.

The objective of the work reported here was to measure gas generation and energetics of actual solid samples from the Sr/TRU removal treatment of samples of Tank 241-AN-102 (AN-102) waste mixed with leach solutions from pretreatment of 241-C-104 (C-104) sludge (solids referred to as “AN-102/C-104 Sr/TRU precipitate”). This waste blending was performed by Lumetta et al. (2002) and the Sr/TRU treatment was performed by Hallen et al. (2002). The AN-102/C-104 Sr/TRU precipitate was washed using inhibited water (0.01M NaOH) and dewatered to dryness using vacuum filtration. A subsample of the vacuum-dried solids was used for the energetics testing. The remaining solids were re-suspended in inhibited water for gas generation testing to better mimic the slurry expected from cross-flow filtration. Gas generation from the AN-102/C-104 Sr/TRU precipitate was measured as a function of temperature with and without the application of an external radiation source (¹³⁷Cs gamma capsule). These tests will help address safety concerns and provide information on potential emissions to the off-gas ventilation system of the pretreatment vessel.

PNWD implemented the RPP-WTP quality requirements in a quality assurance project plan (QAPjP) as approved by the RPP-WTP quality assurance (QA) organization. Experimental work was initiated in May 2001 and extended through August 2002. Experimental work conducted prior to September 2001 was performed in accordance with PNWD's quality assurance project plan CHG-QAPjP Rev. 0, which invoked PNWD's Standards Based Management System (SBMS), compliant with DOE Order 414.1A, Quality Assurance, and 10 CFR 830, Energy/Nuclear Safety Management, Subpart A–Quality Assurance Requirements. Due to a

change in the contract QA requirements in September 2001, the experimental work performed after that date was conducted in accordance with PNWD's quality assurance project plan RPP-WTP-QAPjP Rev. 0, which invoked NQA-1-1989 Part I, Basic and Supplementary Requirements, and NQA-2a-1990 Part 2.7. These quality requirements were implemented through PNWD's Waste Treatment Plant Support Project Quality Assurance Requirements and Description Manual (WTPSP). The quality of the data gathered during the earlier experiments was not impacted by the change in requirements.

Section 2 of this report describes the gas generation test samples and the experimental conditions and equipment used for the tests. Section 3 presents the results and discusses the gas generation experiments. Section 4 provides the energetics measurements of AN-102/C-104 Sr/TRU precipitate. Overall conclusions are given in Section 5, and Section 6 contains the cited references. The appendix contains the test plan outlining the work scope for this report.

2.0 Experimental Methods for Gas Measurements

The gas generation tests on AN-102/C-104 Sr/TRU precipitate samples focused first on finding the effects of temperature and second on the results of irradiating AN-102/C-104 Sr/TRU precipitate samples with an external source (^{137}Cs gamma capsule). The samples and radiation source were contained in a hot cell. Gas measurement equipment is contained in an adjacent hood attached to the reaction vessels by small-diameter (0.0058-cm inside diameter) stainless steel tubing. The tests established gas generation rates from actual samples as a function of temperature with and without irradiation. From these results, thermal activation energies were determined that allowed gas generation rates at other temperatures to be calculated. G-values for the radiolytic gas generation component were also derived from these data.

To assess the effects of temperature on the gas generation from AN-102/C-104 Sr/TRU precipitate, experiments were performed in duplicate ambient hot cell temperature as well as at 45°, 60°, 75°, 90°, and 105°C. Due to the small initial volume of sample material, two test vessels were used for all thermal tests; the samples were tested at increasingly higher temperatures for all temperatures tested. The effects of radiation on gas generation were assessed by repeating the thermal experiment in the presence of an external ^{137}Cs gamma capsule, using the original thermal tests as well as two fresh samples not previously heated. The irradiation experiments (original two samples plus additional two new samples) were performed at the same temperatures, for a total for four samples tested under irradiation conditions. The thermal tests provided activation energies for gas generation (Laidler 1987); the radiolytic experiments provided G-values for gas generation (Spinks and Woods 1990). These parameters allowed the gas generation rates of the principal gas components of AN-102/C-104 Sr/TRU precipitate to be estimated for current and future storage conditions.

Gas generation tests were conducted in the 325 Building High-Level Radiation Facility (HLRF). A description of the experimental conditions is presented in Section 2.1. A description of the AN-102/C-104 Sr/TRU precipitate test material is given in Section 2.2. The self-dose rates from the radionuclide inventory of AN-102/C-104 Sr/TRU precipitate samples was calculated to assess the amount of radiolytically induced gas from internal radiation sources. These calculations are given in Section 2.3.

2.1 Experimental Conditions and Equipment

Gas generation measurements were made using reaction vessels and a gas manifold system similar to those used in earlier studies with simulated waste (Bryan and Pederson 1995) and in subsequent work with actual waste (Bryan et al. 1996; King et al. 1997; Bryan et al. 2002).^(a)

(a) Bryan SA, CM King, LR Pederson, and SV Forbes. 1996. *Thermal and Radiolytic Gas Generation from Tank 241-SY-103 Waste: Progress Report*. TWSFG96.17, Pacific Northwest National Laboratory, Richland, WA.

Figure 2.1 is a drawing of the reaction vessel showing placement of the thermocouples within and at various locations outside the reaction vessel. Each vessel has a separate pressure transducer on the gas manifold line. The entire surface of the reaction system exposed to the sample is stainless steel except for a gold-plated copper gasket sealing the flange at the top.

The location of reaction vessels within a carousel-style holder is depicted in Figure 2.2. The arrangement of the reaction vessels near the ^{137}Cs gamma capsule (in the center of the carousel) and Fricke dosimeters (Spinks and Woods 1990) (when used) are also shown. Figure 2.3 is a schematic diagram of the gas manifold system. Temperatures and pressures are recorded every 10 seconds on a Campbell Scientific CR10 datalogger; an average of the data is taken every 20 minutes and saved in a computer file.

The reaction vessels are cylinders of 316L stainless steel. The reaction space of the vessel is approximately $\frac{3}{4}$ inch in diameter and 5 inches in height. Each vessel was wrapped in heating tape and insulated. Two thermocouples were attached to the external body of the reaction vessel,

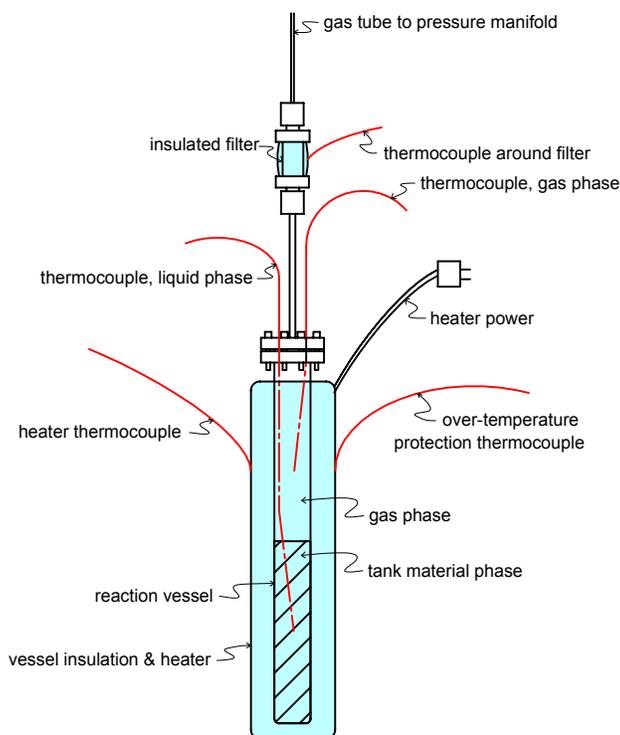


Figure 2.1. Reaction Vessel Used in Small-Scale Gas Generation Tests

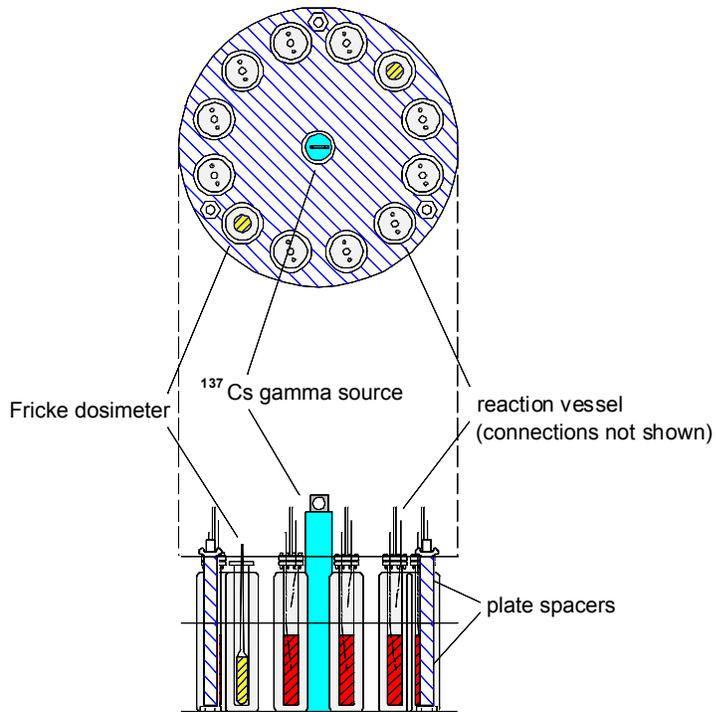


Figure 2.2. Diagram of Reaction Vessel Holder with Gamma Source Used in Gas Generation Tests

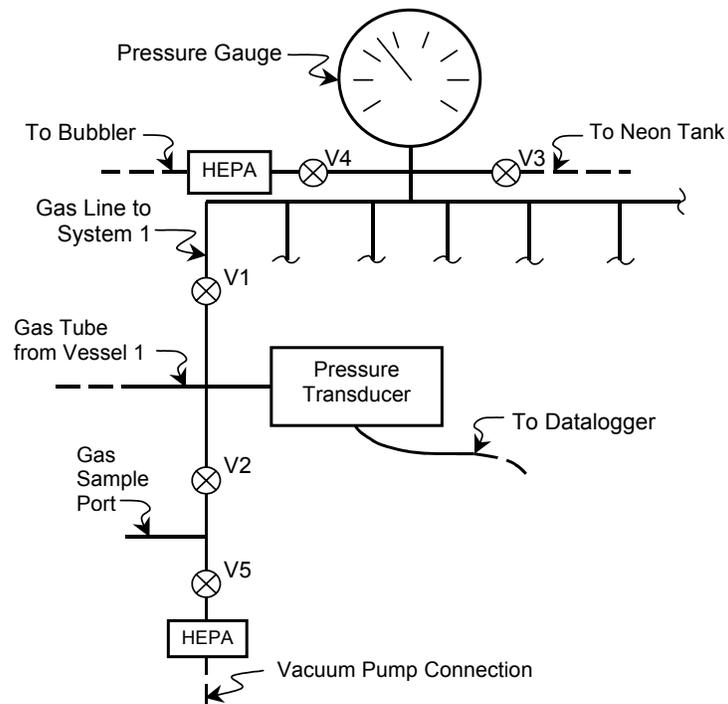


Figure 2.3. Diagram of Pressure Manifold System Used in Gas Generation Tests

one for temperature control and one for over-temperature protection. Two thermocouples were inserted through the lid. The thermocouple centered in the lower half of the vessel monitored the temperature of the liquid phase, and the one centered in the upper half monitored the gas phase temperature within the reaction vessel. The reaction vessels were placed in a hot cell and connected by small-diameter (0.1016 cm inner diameter) stainless steel tubing to the gas manifold outside the hot cell. A stainless steel filter (60-micrometer pore size, Nupro[®]) protected the tubing and manifold from contamination. A thermocouple was attached to this filter as well.

The total gas in the system was calculated using the ideal gas law relationship from the pressure, temperature, and volume of the parts of the apparatus having different gas phase temperatures: $\text{moles}_{\text{total}} = \text{moles}_{\text{vessel}} + \text{moles}_{\text{filter}} + \text{moles}_{\text{manifold and tubing}}$. The manifold and filter volumes were determined from pressure/volume relationships using a calibrated gas manifold system. The manifold volume (the pressure sensor, valves, and miscellaneous fittings) was 3.99 mL, the filter volume 1.34 mL, and the tubing volume 4.45 mL (calculated based on the known length and inside diameter of the tubing). The cap stem (tube from vessel to filter) had a volume of 0.20 mL to adequately account for pressure and temperature effects of the gas within the cap stem. Half of that volume was added to the filter volume for a total of 1.44 mL; and half of that volume was added to the vessel volume. The volume of each vessel was determined gravimetrically by filling it with water. These volumes are recorded in Table 2.1 along with the mass of sample added to each vessel and the gas-phase volume in the vessel after the sample was added. The reproducibility of the molar gas determination using this manifold system has been determined experimentally. The relative error for measuring moles of gas with the system was determined by Bryan et al. (1996). The relative standard deviation for quantitative gas phase measurements conducted over time and temperature ranges similar to that of the gas generation tests typically has been less than 2%.

Table 2.1. Sample Masses and Vessel Volumes Used in Small-Scale Gas Generation Tests with Washed AN-102/C-104 Sr/TRU Precipitate Samples

System	1	2		
Reaction Vessel ID	HC-21	HC-22		
Temperature	45 to 105°C	45 to 105°C		
Sample mass, g	10.25	10.32		
gas phase, mL	22.73	22.72		
total, mL	32.49	32.55		
System	1	2	3	4
Reaction Vessel ID	HC-21	HC-22	HC-23	HC-24
Temperature	45 to 105°C	45 to 105°C	~32 to 105°C	~32 to 105°C
Sample mass, g	10.25	10.32	9.58	10.42
gas phase, mL	22.73	22.72	23.44	22.61
total, mL	32.49	32.55	32.56	32.53

An atmospheric pressure gauge was attached to the datalogger. The pressure in each system was given as the sum of atmospheric pressure and gauge pressure in each system. Neon was used as the cover gas because it leaks more slowly from the system than helium. The neon was analyzed independently by mass spectrometry and determined to contain no impurities in concentrations significant to warrant correction.

At the start of each run, each system was purged at least three times by pressurizing with neon at 45 psi (310 kPa) and venting to the atmosphere. The systems were sealed initially at atmospheric pressure (~745 mm or 99.3 kPa Hg). The sample portion of the manifold was isolated (valves V1 and V2 closed) (see Figure 2.2) for the remainder of the run. The vessels were then heated to keep the material within 1°C of the desired liquid phase temperature. The gas phase was 5°–25°C lower than the temperature of the sample liquid phase.

At the end of each run, the vessels were allowed to cool overnight, then a sample of the gas was taken for mass spectrometry analysis. The metal gas collection bottles were equipped with a valve and had a volume of approximately 75 mL (about four times the volume of the gas reaction system). The bottle, after being evacuated overnight under high vacuum, was attached to the gas sample port. Air was removed from the region between valves V2 and V5 (Figure 2.3) using a vacuum pump, then the gas sample was taken. After the collection bottle was removed, the bottle and sample port were surveyed for radioactive contamination. No contamination was found during these experiments. The reaction vessel was purged again with neon after each sampling event and before the next reaction sequence. For the irradiation experiments, the gamma source was removed from the gas generation apparatus during gas sampling events so that the duration heating was the same as the duration under irradiation.

Analysis of the composition of the gas phase of each reaction vessel after each run was performed according to analytical procedure PNNL-MA-599 ALO-284 Rev. 1. The amount of a specific gas formed during heating is given by the mole percent of each gas multiplied by the total moles of gas present in a system. Duplicate samples, which were run in separate reaction vessels and sampled independently at each temperature, were used to assess the reproducibility and uncertainty of the rate parameters.

Gases in the reaction system have been shown to be well mixed.^(a) The measured amount of argon in gas samples is an indicator of how much nitrogen from air has leaked into the system (the N₂:Ar ratio in air is 83.6:1). The nitrogen produced in the vessel was the total nitrogen minus atmospheric nitrogen. The solubilities of nitrogen, hydrogen, methane, and nitrous oxide gases have been measured on simulated waste systems similar in composition to the liquid in

(a) Bryan, SA, CM King, LR Pederson, and SV Forbes. 1996. *Thermal and Radiolytic Gas Generation from Tank 241-SY-103 Waste: Progress Report*. TWSFG96.17, Pacific Northwest National Laboratory, Richland, Washington.

AN-102/C-104 Sr/TRU precipitate (Pederson and Bryan 1996). Less than 0.01% of these gases dissolve in the condensed phase, so their loss due to solubility was negligible.

2.2 AN-102/C-104 Sr/TRU Precipitate Test Material

PNWD received 27 bottles of tank waste from the 222-S Laboratory in Hanford's 200 West Area. The waste material was taken by grab sampling in Tank AN-102 from riser 022 between August 7 and 11, 2000 and shipped to the 222-S Laboratory. The sample material was transferred to 500-mL bottles before being shipped to the Radiological Processing Laboratory (RPL) in the 300 Area, where the bottles were inspected upon receipt (Lumetta et al. 2002, Appendix A). All of the samples contained a settled layer of light brown solids with a dark brownish/black standing liquid. Eight of the samples were designated for process testing. The eight as-received AN-102 samples were homogenized to form a slurry and characterized (Urie et al. 2002a). Supernatant and solids from jars of homogenized AN-102 waste were mixed to make a waste material consisting of 2 wt% undissolved solids. Permeate, leachate, and wash solutions from processing Tank C-104 sludge (Brooks et al. 2000) were blended with the 2 wt% solids containing AN-102 waste to produce the AN-102/C-104 waste blend. The AN-102 and C-104 materials were then blended together. No visible gel formation or net solids increase occurred during the blending process.

Subsamples of the vacuum-dried AN-102/C-104 Sr/TRU precipitate was received (Hallen et al. 2002) for gas generation and energetics testing. The chemical and radiochemical composition of the as-received precipitate is listed in Table 2.2. This material was used as-received in the energetics testing (see Section 4). The sample was modified according to the test specification (Reynolds and Johnson 2001) for gas generation testing by adding 41.08 g of inhibited water (0.01 M NaOH) to 8.73 g of the as-received Sr/TRU material. Table 2.3 contains the chemical and radiochemical composition of the diluted sample used for gas generation tests.

Table 2.2. Chemical and Radiochemical Composition of As-Received AN-102/C-104 Sr/TRU Material Used in Energetics Testing (wet basis)

Analyte Composition, wt%														
F	Cl	NO ₂	Br	NO ₃	PO ₄	SO ₄	C ₂ O ₄	TOC	Al	Na	Cr	Fe	Mn	Sr
3.795	0.119	1.085	DL	2.705	0.204	0.289	3.615	0.820	8.230	19.750	0.527	0.823	6.695	9.665
Radionuclide Composition, μCi/g														
⁹⁹ Tc	⁹⁰ Sr	⁶⁰ Co	¹³⁷ Cs	¹⁵⁴ Eu	¹⁵⁵ Eu	²³⁴ U + ²³⁷ Np	²³⁹ Pu + ²⁴⁰ Pu	²³⁸ Pu + ²⁴¹ Am	²⁴³ Cm + ²⁴⁴ Cm	²⁴² Cm	²⁴¹ Am	Total Alpha		
9.20E-02	1.58E+03	5.96E-02	1.43E+02	4.15E+00	2.38E+00	8.33E-03	2.39E-01	4.04E+00	1.61E-01	1.45E-02	3.72E+00	4.45E+00		

Table 2.3. Calculated Chemical and Radiochemical Composition of Diluted AN-102/C-104 Sr/TRU Precipitate Material Used in Gas Generation Testing (wet basis)

Analyte Composition, wt%													
F	Cl	NO ₂	Br	NO ₃	PO ₄	SO ₄	C ₂ O ₄	Al	Na	Cr	Fe	Mn	Sr
0.665	0.021	0.190	DL	0.474	0.036	0.051	0.634	1.442	3.461	0.092	0.144	1.173	1.694
Radionuclide Composition, μCi/g													
⁹⁹ Tc	⁹⁰ Sr	⁶⁰ Co	¹³⁷ Cs	¹⁵⁴ Eu	¹⁵⁵ Eu	²³⁴ U + ²³⁷ Np	²³⁹ Pu + ²⁴⁰ Pu	²³⁸ Pu + ²⁴¹ Am	²⁴³ Cm + ²⁴⁴ Cm	²⁴² Cm	²⁴¹ Am	Total Alpha	
1.61E-02	2.76E+02	1.04E-02	2.51E+01	7.27E-01	4.17E-01	1.46E-03	4.18E-02	7.07E-01	2.82E-02	2.53E-03	6.52E-01	7.80E-01	

2.3 Self-Dose Rate from Radionuclide Inventory in AN-102/C-104 Sr/TRU Precipitate Samples

The self-dose rate for the AN-102/C-104 Sr/TRU precipitate sample used in the gas generation reaction vessel was calculated using the measured chemical and radiochemical content of the sample. The self-dose rate is needed to correct for radiolytic generation from self-radiolysis of the sample. (The measured chemical and radionuclide inventories for the gas generation samples are given in Table 3.2.)

The dose rate in a reaction vessel was calculated using MCNP version 4B (Monte Carlo N-Particle Transport Code System) (Briesmeister 1997). This program uses the Monte Carlo method, in which radiation is emitted in random directions from random locations in the sample. The probability of the radiation being absorbed or scattered by the sample and being reflected from the container wall back into the sample is known. The reaction vessel (316L stainless steel) was modeled as a cylinder with 0.035-inch-thick steel walls, 680-inch inside diameter, 5.5-inch height, 0.185-inch base thickness, and 0.210-inch lid thickness. Input to the program includes the composition of the walls, the composition of the bulk of the sample, and the radionuclides present. The output is the amount of radiation absorbed by the sample averaged over its entirety. Table 2.4 contains the calculated dose rates for the waste sample in the small reaction vessel (~32.5 mL). Using the same waste volume for comparison, the dose rate was calculated for a much larger vessel, a tank 10 m high and 10 m in diameter (758 m³). A big difference exists in the gamma dose rate term due to edge-loss of gamma in the small reaction vessel configuration. Because essentially all the beta and alpha radiation is absorbed (or reflected back) in the sample and most of the dose is from beta sources, the total dose rate from the small vessel (685.7 R/h) is fairly close to that calculated for the much larger vessel (716.7 R/h).

Table 2.4. Calculated Self-Radiolysis Dose Rates from AN-102/C-104 Sr/TRU Precipitate Samples in a Small Reaction Vessel and Large Tank (R/h)

	Gamma	Beta	Alpha	Total
Vessel	1.0	676.6	9.0	685.7
Tank	31.1	676.6	9.0	716.7

The dose rate in a reaction vessel with the ^{137}Cs capsule placed in the middle of the vessel holder was determined by Fricke dosimetry, as described in King et al. (1997). The dose rate received from the ^{137}Cs capsule by the solution within the reaction vessel was 31,300 R/h (average of four determinations) with a relative standard deviation of 18%. Correcting for the half-life of ^{137}Cs (30 yr), this measurement is consistent with that taken by King et al. (1997) for the same ^{137}Cs gamma capsule.

3.0 Gas Generation from AN-102/C-104 Sr/TRU Precipitate Samples

To assess the relative contributions of thermal and radiolytic components of Hanford tank waste, gas generation was measured from AN-102/C-104 Sr/TRU precipitate material in the presence and absence of external radiation. By isolating and measuring the components of gas generation, the gas generation behavior of the Sr/TRU precipitate can be predicted under different storage conditions and different vessel sizes.

The percent composition and rates for gas generation under thermal and radiolytic conditions are described in Section 3.1. Thermal activation parameters from standard Arrhenius treatment of the thermal experiments and G-value determinations from the radiolytic experiments are reported in Section 3.2.

3.1 Composition and Rates of Gas Generation from AN-102/C-104 Sr/TRU Precipitate Samples

Measurements were made on AN-102/C-104 Sr/TRU precipitate material in the presence and absence of external radiation. The thermal measurements were run in duplicate, and the radiolytic experiments were run in quadruplicate, at five temperatures. Due to a limited amount of material, the duplicate thermal samples were tested at the initial low temperature and gas generation rates measured. Then the samples were heated to the next higher temperature to measure the gas generation rate at that temperature. The samples were then heated to the next subsequent temperatures in turn, until the gas generation rates were measured for all temperatures (45°, 60°, 75°, 90°, and 105°C). For vessels HC-23 and HC-24, an additional measurement was made at ambient temperature. Gas samples were taken from the vessels periodically. After each gas sample was taken, the vessel was purged with neon gas to remove previously generated gases before resuming gas generation. Gas generation rates were determined for each gas sample from the heating time, the percent composition of the gas, the total moles of gas in each system when the sample was taken, and the mass of tank material present in each reaction vessel. Section 3.1.1 presents the thermal results, and Section 3.1.2 presents the radiolytic results.

3.1.1 Thermal Gas Generation from AN-102/C-104 Sr/TRU Precipitate Samples

This section contains the thermal gas generation data produced by heating material in duplicate reaction vessels at 45°, 60°, 75°, 90°, and 105°C in the absence of external radiation. The total amount of gas produced versus heating time was calculated for the experiments. To obtain separate rates for each gas present, gas samples were analyzed by mass spectroscopy. The mole percent composition of these gas samples is given in Table 3.1. Of more interest are

the relative amounts of gases generated; the composition of gas formed during heating is derived from the composition of sampled gas by excluding the neon cover gas and argon, nitrogen, and oxygen from atmospheric contamination. For example, if analysis found 80% neon, 15% nitrous oxide, and 5% hydrogen, the composition of gas formed by excluding neon would be 75% N₂O and 25% H₂. Unless otherwise stated, the uncertainties in all the entries in this table are approximately plus or minus one in the last reported digit.

In the tables of percent composition (Table 3.1) and rates (Table 3.2), a run number and a vessel identification number are assigned for each reaction vessel and the gas sampling event. For example, entries for runs 1, 2, 3, 4, and 5 give data for reaction vessel HC-21 under thermal conditions, which are experiments performed at 45.0°, 60.1°, 75.2°, 90.2°, and 104.6°C, respectively.

Argon was used to indicate atmospheric contamination because it was not present in the cover gas and was not produced from the waste. Any nitrogen present could have been generated by the waste or stemmed from atmospheric contamination. The percent nitrogen generated is given by the percent nitrogen found minus 83.6 times the percent argon in the sample (the ratio of nitrogen to argon in dry air is 83.6). The uncertainty of approximately 0.001 in argon values translates to an uncertainty of 0.08 in the percent nitrogen produced. The argon-corrected percent nitrogen in the runs at 60°C is only about 50% higher than this value. The rate of oxygen generation cannot be determined by the present experiment because tank material consumes oxygen when it is heated (Person 1996). The uncertainty in the argon values translates to an

Table 3.1. Mole Percent Composition of Thermal Gas Sampled (including Ne) and Heating Times of Reaction Systems at Various Temperatures (no external radiation source)

Mole Percent of Gas Formed in Reaction Vessel HC-21 Under Thermal Conditions^(a)											
Run	Temp (°C)	Ne	Ar	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other Hydrocarbons	Time (hr)
1	45.0	97.8	0.02	0.009	--	1.77	0.367	0.01	--	--	496
2	60.1	97.9	0.019	0.005	0.012	1.63	0.386	0.004	--	--	312
3	75.2	97.7	0.02	0.012	0.004	1.79	0.413	0.013	0.002	0.005	317
4	90.2	97.7	0.02	0.005	0.005	1.82	0.403	0.026	0.004	0.002	316
5	104.6	97.3	0.021	0.018	0.027	1.92	0.423	0.234	0.020	0.003	312
Mole Percent of Gas Formed in Reaction Vessel HC-22 Under Thermal Conditions											
Run	Temp (°C)	Ne	Ar	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other Hydrocarbons	Time (hr)
6	45.0	98.3	0.009	0.005	--	0.47	0.098	0.02	--	--	496
7	60.3	99.9	0.002	0.004	0.013	0.105	0.017	0.005	--	--	312
8	75.5	99.9	0.001	0.007	0.006	0.059	0.016	0.011	0.001	0.003	317
9	90.6	99.9	0.001	0.02	0.005	0.068	0.008	0.022	0.003	0.002	316
10	105.3	99.8	0.001	0.037	0.013	0.069	0.009	0.058	0.020	0.013	312

(a) Values listed as -- in the tables are below the detection limit.

Table 3.2. Gas Generation Rates from Thermal Treatment of AN-102/C-104 Sr/TRU Precipitate Material in the Absence of an External Radiation Source^(a)

Gas Generation Rate in Reaction Vessel HC-21 Under Thermal Conditions, mol/kg/day									
Run	Temp (°C)	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other Hydrocarbons	Time (hr)
1	45.0	5.2E-7	--	1.1E-5	--	7.5E-7	--	--	496
2	60.1	4.7E-7	1.06E-06	1.2E-5	--	3.7E-7	--	--	312
3	75.2	1.1E-6	2.99E-07	1.8E-5	--	1.2E-6	1.82E-07	4.6E-7	317
4	90.2	4.5E-7	3.89E-07	2.1E-5	--	2.4E-6	3.64E-07	1.8E-7	316
5	104.6	1.6E-6	2.4E-06	2.3E-5	--	2.1E-5	1.46E-06	2.7E-7	312
Gas Generation Rate in Reaction Vessel HC-22 Under Thermal Conditions, mol/kg/day									
Run	Temp (°C)	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other Hydrocarbons	Time (hr)
6	45.0	3.2E-7	--	--	--	1.2E-6	--	--	496
7	60.3	4.0E-7	1.31E-06	2.2E-6	--	5.1E-7	--	--	312
8	75.5	7.0E-7	5.97E-07	--	--	1.1E-6	9.95E-08	3.0E-7	317
9	90.6	2.0E-6	5.01E-07	--	--	2.2E-6	3.01E-07	2.0E-7	316
10	105.3	3.9E-6	1.38E-06	--	--	6.1E-6	2.22E-06	1.4E-6	312

(a) Values listed as -- in the table are below the detection limit.

uncertainty of 0.02 in the percent oxygen produced. The percent oxygen found in the samples was always less than this value and often negative after correction using the argon value, indicating that it was indeed being consumed.

3.1.2 Radiolytic Gas Generation from AN-102/C-104 Sr/TRU Precipitate Samples

This section contains the data from enhancing radiolytic gas generation by placing a ¹³⁷Cs source (gamma capsule) next to the reaction vessels while heating the material in the reaction vessels to temperatures of 45°, 60°, 75°, 90°, and 105°C. Two vessels were tested at ambient hot-cell temperature. Two gas samples were taken from each of the 10 reaction vessels. The mole percent composition of the gas sampled at the end of each run is given in Table 3.3. The rates of gas generation from each run are given in Table 3.4.

Table 3.3. Mole Percent Composition of Radiolytic Gas Sampled (including Ne) and Heating Times of Duplicate Systems at Five Temperatures^(a)

Mole Percent of Gas Formed in Reaction Vessel HC-21 Under Radiolytic Conditions											
Run	Temp, °C	Ne	Ar	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	other hydrocarbons	Time, hr
11	46.1	94.3	0.03	1.55	0.008	3.33	0.61	0.108	0.003	0.002	291
12	45.1	96.4	0.023	0.74	0.07	2.2	0.419	0.028	--	--	150
13	60.1	96.8	0.018	0.72	0.024	1.74	0.51	0.024	--	--	140
14	75.3	96.8	0.019	0.77	0.004	1.86	0.52	0.023	0.001	--	162
15	90.3	97.1	0.016	0.79	0.025	1.58	0.49	0.018	0.002	--	161
16	104.7	97.2	0.014	0.98	0.053	1.43	0.299	0.013	0.010	--	170
Mole Percent of Gas Formed in Reaction Vessel HC-22 Under Radiolytic Conditions											
Run	Temp, °C	Ne	Ar	H ₂	CO ₂	N ₂	O ²	N ₂ O	CH ₄	Other hydrocarbons	Time, hr
17	44.8	97.6	0.001	1.44	0.006	0.72	0.01	0.124	0.007	0.004	291
18	44.7	98.2	0.001	0.67	0.008	0.167	0.065	0.031	0.001	--	150
19	60.1	98.5	0.001	0.63	0.005	0.14	0.094	0.024	0.001	--	140
20	75.3	99.1	0.001	0.68	0.004	0.131	0.046	0.023	0.001	--	162
21	90.4	99.1	0.001	0.72	0.037	0.125	0.022	0.019	0.003	0.004	161
22	105.0	98.8	0.001	0.92	0.023	0.125	0.036	0.016	0.01	0.010	170
Mole Percent of Gas Formed in Reaction Vessel HC-23 Under Radiolytic Conditions											
Run	Temp, °C	Ne	Ar	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other hydrocarbons	Time, hr
23	33.9	94.5	0.035	1.03	0.004	2.86	0.84	0.03	0.002	--	291
24	45.3	98.5	0.001	0.58	0.015	0.099	0.098	0.018	0.002	--	150
25	60.5	99.0	0.001	0.57	0.008	0.112	0.092	0.023	0.002	0.001	140
26	75.8	99.1	0.001	0.62	0.005	0.102	0.094	0.031	0.004	0.005	162
27	89.6	99.0	0.002	0.62	0.045	0.153	0.056	0.04	0.020	0.039	161
28	105.0	98.7	0.002	0.8	0.061	0.183	0.013	0.046	0.050	0.102	170
Mole Percent of Gas Formed in Reaction Vessel HC-24 Under Radiolytic Conditions											
Run	Temp, °C	Ne	Ar	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other hydrocarbons	Time, hr
29	30.8	97.9	0.003	1.37	0.009	0.29	0.279	0.037	0.002	--	291
30	44.8	99.0	0.001	0.65	0.006	0.127	0.14	0.019	--	--	150
31	60.0	99.1	0.001	0.62	0.005	0.108	0.111	0.023	0.001	--	140
32	75.2	99.0	0.001	0.69	0.002	0.133	0.07	0.027	0.002	--	162
33	90.0	99.0	0.002	0.72	0.03	0.117	0.028	0.025	0.010	0.026	161
34	104.5	98.9	0.001	0.81	0.047	0.124	0.019	0.024	0.010	0.011	170

(a) Values listed as -- in the table are below the detection limit.

Table 3.4. Gas Generation Rates from Radiolytic Treatment of AN-102/C-104 Sr/TRU Precipitate Material in the Presence of an External Radiation Source. Rates expressed in moles of gas generated per kg of total wet AN-102/C-104 Sr/TRU precipitate sample per day.^(a)

Gas Generation Rate in Reaction Vessel HC-21 Under Radiolytic Conditions, mol/kg/day									
Run	Temp, °C	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other hydrocarbons	Time, hr
11	46.1	1.6E-4	8.5E-07	9.6E-5	--	1.1E-5	3.19E-07	2.1E-7	291
12	45.1	1.5E-4	1.41E-05	7.3E-5	--	5.6E-6	--	--	150
13	60.1	1.5E-4	5.05E-06	6.7E-5	2.7E-5	5.1E-6	--	--	140
14	75.3	1.4E-4	7.27E-07	6.5E-5	2.1E-5	4.2E-6	1.82E-07	--	162
15	90.3	1.4E-4	4.49E-06	5.8E-5	2.8E-5	3.2E-6	3.59E-07	--	161
16	104.7	1.7E-4	9.31E-06	6.0E-5	1.3E-6	2.3E-6	1.05E-06	--	170
Gas Generation Rate in Reaction Vessel HC-22 Under Radiolytic Conditions, mol/kg/day									
Run	Temp, °C	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other hydrocarbons	Time, hr
17	44.8	1.7E-4	6.96E-07	--	--	1.4E-5	8.17E-07	4.7E-7	291
18	44.7	1.5E-4	1.73E-06	1.8E-5	9.2E-6	6.7E-6	2.17E-07	--	150
19	60.1	1.5E-4	1.21E-06	1.4E-5	1.7E-5	5.8E-6	2.43E-07	--	140
20	75.3	1.4E-4	8.18E-07	9.7E-6	4.8E-6	4.7E-6	2.05E-07	--	162
21	90.4	1.5E-4	7.58E-06	8.5E-6	--	3.9E-6	6.15E-07	8.2E-7	161
22	105.0	1.8E-4	4.49E-06	8.1E-6	2.6E-6	3.1E-6	1.95E-06	2.0E-6	170
Gas Generation Rate in Reaction Vessel HC-23 Under Radiolytic Conditions, mol/kg/day									
Run	Temp, °C	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other hydrocarbons	Time, hr
23	33.9	1.4E-4	5.52E-07	2.4E-6	1.1E-5	4.1E-6	2.76E-07	--	291
24	45.3	1.2E-4	3.23E-06	3.3E-6	1.6E-5	3.9E-6	4.3E-07	--	150
25	60.5	1.3E-4	1.83E-06	6.5E-6	1.6E-5	5.3E-6	4.58E-07	2.3E-7	140
26	75.8	1.2E-4	9.84E-07	3.6E-6	1.4E-5	6.1E-6	7.87E-07	9.8E-7	162
27	89.6	1.2E-4	8.83E-06	1.4E-5	6.6E-6	7.9E-6	3.53E-06	7.7E-6	161
28	105.0	1.5E-4	1.14E-05	1.9E-5	--	8.6E-6	1.01E-05	1.9E-5	170
Gas Generation Rate in Reaction Vessel HC-24 Under Radiolytic Conditions, mol/kg/day									
Run	Temp, °C	H ₂	CO ₂	N ₂	O ₂	N ₂ O	CH ₄	Other hydrocarbons	Time, hr
29	30.8	1.4E-4	9.17E-07	1.3E-5	2.4E-5	3.8E-6	2.04E-07	--	291
30	44.8	1.3E-4	1.17E-06	8.5E-6	2.3E-5	3.7E-6	--	--	150
31	60.0	1.3E-4	1.03E-06	5.0E-6	1.8E-5	4.8E-6	2.07E-07	--	140
32	75.2	1.2E-4	3.58E-07	8.8E-6	8.5E-6	4.8E-6	3.58E-07	--	162
33	90.0	1.3E-4	5.35E-06	6.0E-6	9.9E-7	4.5E-6	1.96E-06	4.6E-6	161
34	104.5	1.4E-4	7.98E-06	6.9E-6	--	4.1E-6	1.7E-06	1.9E-6	170

(a) Values listed as -- in the table were below the detection limit.

3.2 Thermal and Radiolytic Rate Parameters for Gas Generation from AN-102/C-104 Sr/TRU Precipitate

The three most important mechanisms for gas generation from wastes contained in Hanford tanks have been determined to be 1) radiolytic decomposition of water and some organic species; 2) thermally driven chemical reactions, mainly involving organic complexants, solvents, and other solution species; and 3) chemical decomposition of the steel tank walls (Johnson et al. 1997). The total gas generation rate is the sum of the radiolytic, thermal, and corrosion rates:

$$\text{Total Rate} = \text{Radiolytic Rate} + \text{Thermal Rate} + \text{Corrosion Rate} \quad (3.1)$$

Because radiolytic and thermal rates dominate (Johnson et al. 1997), they are the focus of these experiments.

The thermal rate varies with temperature. The relation between thermal rate constant, k , at different temperatures is given by the Arrhenius equation:

$$k = Ae^{\left(\frac{-E_a}{RT}\right)} \quad (3.2)$$

where R is the gas constant, 8.314 J/K-mol, T is the temperature in Kelvin, E_a is the activation energy, and A is the pre-exponential factor. The initial thermal rate is assumed to be zero-order (Espenson 1981), in which the rate constant is equivalent to the observed rate. Values of E_a and A can then be determined from the rates measured in the reaction vessels. The equation allows the thermal rate to be calculated at temperatures where the rate is so slow it is difficult to measure directly.

The radiolytic rate at a given temperature is determined experimentally by measuring the difference between rates measured in the presence and absence of external radiation. The G-value is related to the radiolytic rate by Equation 3.3:

$$\text{G-value(molecules/100 eV)} = \frac{\text{Radiolytic rate (mol/kg/day)}}{\text{Dose rate (R/h)}} \times (4.02 \times 10^7) \quad (3.3)$$

The constant 4.02×10^7 is a unit conversion factor. The 95% confidence interval for the thermal rates is obtained from the thermal data. The 95% confidence interval rates measured in the presence of external radiation are estimated at given temperatures as half the range of the duplicate measurements. Radiolytic rates have been observed to be essentially temperature

independent over the temperature range studied both in water radiolysis (Draganic and Draganic 1971) and in the Hanford waste tank material (King and Bryan 1999).^(a,b)

The activation energy for the initial rate of gas formation for each thermal gas reaction system was estimated from gas composition and generation data from each run, corresponding to approximately the initial 300-hour reaction time for the thermal reactions and 150 hours for the radiolytic reactions (Tables 3.3 and 3.4). A plot of the total gas generated is shown in Figure 3.1. This figure shows the total gas generated from AN-102/C-104 Sr/TRU precipitate under self-radiolysis and high dose conditions. The calculated fits of the data use thermal activation energies (E_a) and G-values from Table 3.5. The activation energy for total gas formation was found to be $60(\pm 32)$ kJ/mole (95% confidence level).

Generation rates of the major gas components from AN-102/C-104 Sr/TRU precipitate under self-radiolysis conditions are shown in Figure 3.2. Based on the formation rate of each gas component in the reaction vessel, thermal Arrhenius activation parameters and radiolytic G-values can be calculated for the major components. The gas generation rate data for self-radiolytic generation at various temperatures for H_2 , N_2O , CH_4 , and total gas are shown in Figure 3.2. The

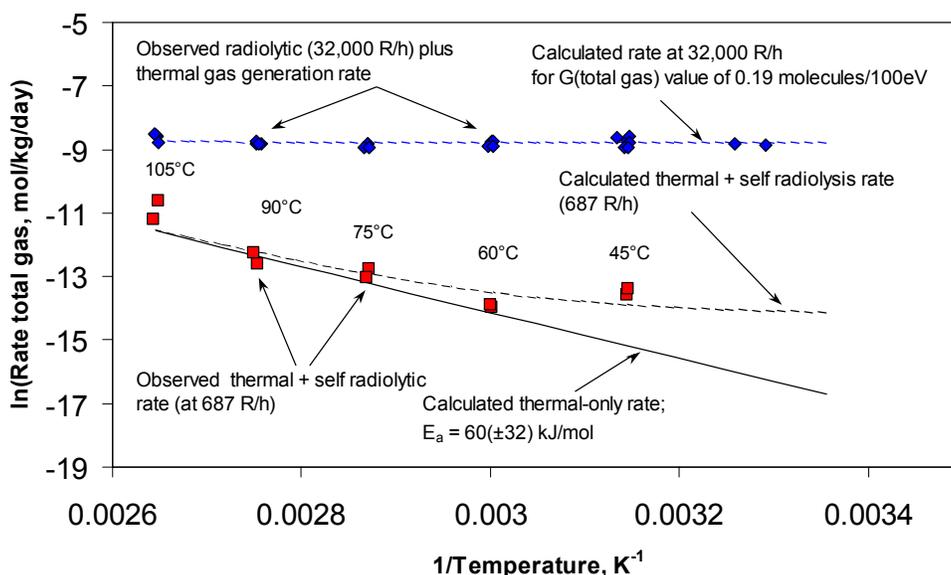


Figure 3.1. Rates of Total Gas Generated from AN-102/C-104 Sr/TRU Precipitate under Self-Radiolysis and High-Dose Conditions

(a) Bryan SA and CM King. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-AW-101 Waste: Status Report*. TWS98.39, Pacific Northwest National Laboratory, Richland, WA.

(b) Bryan SA and CM King. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-A-106 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.

Table 3.5. Thermal and Radiolytic Rate Parameters for Gas Generation from AN-102/C-104 Sr/TRU Precipitate Samples

	H ₂	N ₂ O	N ₂	CH ₄	Total Gas
E _a , kJ/mol	64(±62)	79(±26)	14(±7)	147(±82)	60(±32)
A, mol/kg/day	7.9E+2	6.9E+5	2.3E-3	3.6E+14	2.0E+3
ln(A)	7(±21)	13(±9)	-6(±2)	34(±27)	8(±11)
R ²	0.458	0.902	0.934	0.861	0.699
G-value at 32,000 R/h	0.18 (±0.02)	0.0041 (±0.004)	--	0.0006 (±0.001)	0.19 (±0.023)
G-value at 687 R/h	0.025 (±0.016)	0.004 (±0.004) >45°C 0.053 (±0.002) 45°C	--	0.005 (±0.003)	0.04 (±0.03)

(a) Values listed as -- in the table are values not determined. See text.

fits of the data use thermal activation energies (E_a) and G-values from Table 3.5. The activation energies (E_a) for formation of these components are 64 (±62) kJ/mole (95% confidence interval) for H₂, 79 (±26) kJ/mole for N₂O, 14 (±7) kJ/mole for N₂, 147 (±82) for CH₄, and 60 (±32) for total gas generated.

The experimental thermal and radiolytic rates for duplicate runs for hydrogen, nitrous oxide, and methane generation, represented by symbols, are shown in Figures 3.3, 3.4, and 3.5, respectively. The curved lines are predicted temperature-independent radiolytic rates, which are thermal rates plus a constant representing a G-value. The radiolytic G-values, listed in Table 3.5 in molecules per 100 eV, were determined to be 0.18 (±0.02) for hydrogen, 0.0041 (±0.004) for nitrous oxide, 0.0006 (±0.001) for methane, and 0.19 (±0.023) for total gas generated. The scatter in the nitrogen data precluded an accurate assessment for the nitrogen G-value.

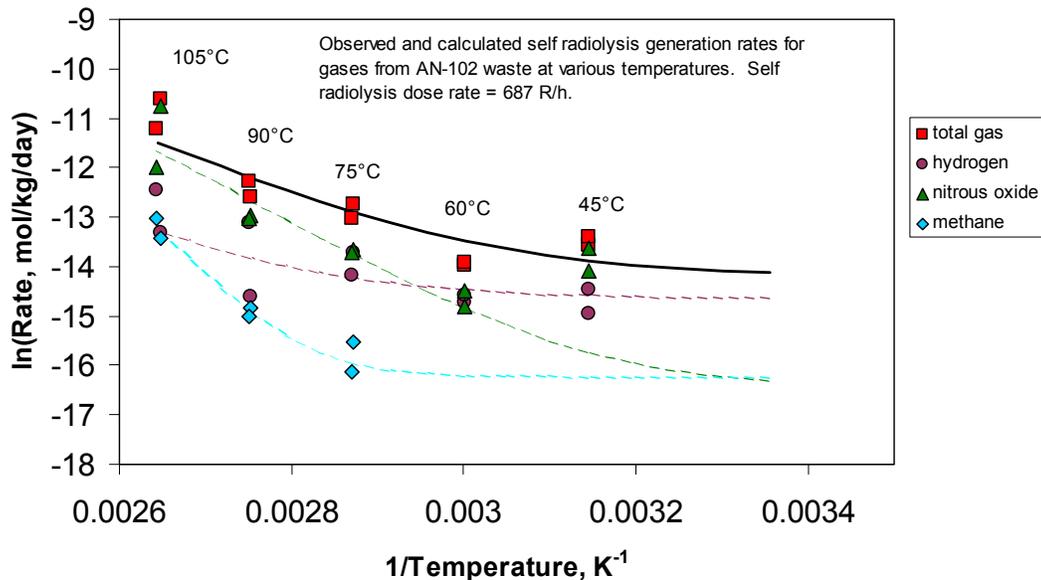


Figure 3.2. Formation of Major Gas Components from AN-102/C-104 Sr/TRU Precipitate Samples under Self-Radiolysis Conditions

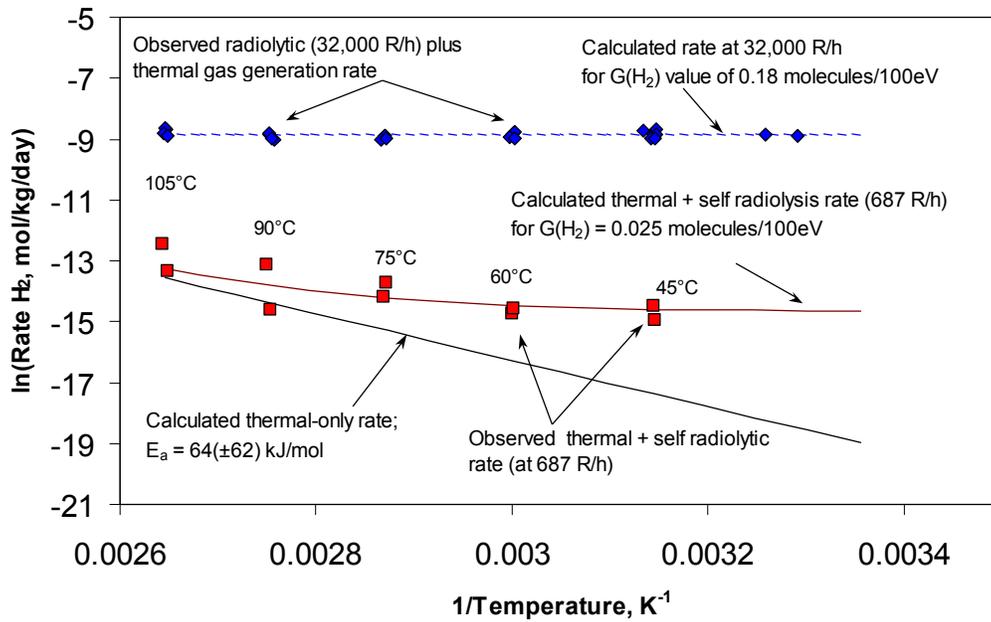


Figure 3.3. Thermal and Radiolytic Gas Generation Rates for Hydrogen from AN-102/C-104 Sr/TRU Precipitate Samples

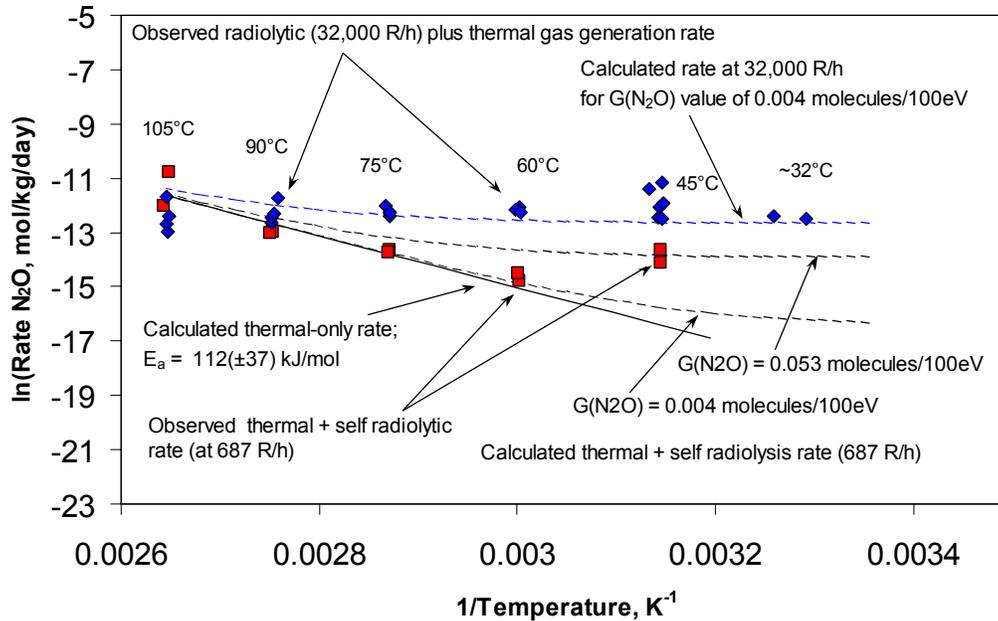


Figure 3.4. Thermal and Radiolytic Gas Generation Rates for Nitrous Oxide from AN-102/C-104 Sr/TRU Precipitate Samples

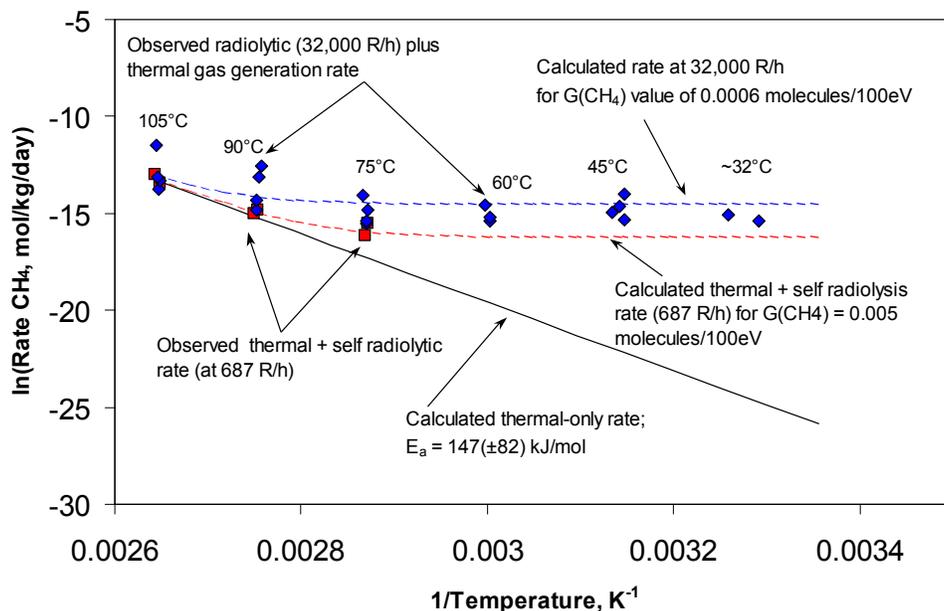


Figure 3.5. Thermal and Radiolytic Gas Generation Rates for Methane from AN-102/C-104 Sr/TRU Precipitate Samples

Table 3.6 compares the thermal and radiolytic gas generation activation parameters measured for AN-102/C-104 Sr/TRU precipitate with those values determined for other Hanford waste materials. Of particular interest is the comparison of the activation parameters between the AN-102/C-104 Sr/TRU sample and the AN-102 washed solids; the activation energies for hydrogen generation between these two samples are essentially identical, 64 and 63 kJ/mol, respectively.

The G-value for hydrogen generation is higher in the AN-102/C-014 Sr/TRU sample (0.18 molecules/100eV using 32,000 R/h external gamma source) than in the AN-102 washed solids (0.055 molecules/100eV). This increased G-value for the AN-102/C-104 Sr/TRU sample using the external gamma source is most likely due to the addition of inhibited water to the matrix prior to the experiment. With the addition of inhibited water (0.01 M NaOH) as a large fraction of the total sample (see Section 2.2), the $G(\text{H}_2)$ value from gamma radiolysis would approach that expected for a dilute aqueous stream containing low concentrations of nitrate and nitrite. The $G(\text{H}_2)$ value of 0.18 molecules/100eV is consistent with the measured $G(\text{H}_2)$ value from pure water radiolysis using identical experimental equipment [$G(\text{H}_2) = 0.196$ molecules per 100 eV absorbed dose] (Arm et al. 2003) and is consistent with literature for pure water systems in a closed reaction system (i.e., H_2 product not allowed to escape).

Table 3.6. Comparison of Gas Generation Parameters^(a) in Tank Wastes Previously Tested

	H ₂			N ₂ O			N ₂			CH ₄		
	E _a	ln(A)	G-value	E _a	ln(A)	G-value	E _a	Ln(A)	G-value	E _a	ln(A)	G-value
AN-102/C-104 ^(b)	64(62)	7(21)	0.18(2)	79(26)	13(9)	0.004(4)	14(7)	-6(2)	---	147(82)	34(27)	0.0006(10)
AN-102, washed ^(c)	63(16)	8(5)	0.055(18)	111(28)	26(10)	0.062(13)	58(29)	8(10)	0.0495(16)	71(155)	7(51)	0.0005(2)
A-101, top ^(d)	101(8)	22(3)	0.0051(4)	77(27)	13(9)	0.0038(4)	118(18)	28(6)	0.0020(4)	125(32)	28(10)	0.00021(4)
AW-101,cv ^(d,e)	102(3)	25(1)	0.101(1)	131(20)	33(7)	0.0189(1)	126(15)	31(5)	0.011(1)	138(6)	33(2)	0.00106(2)
S-102 ^(f)	80(19)	15(6)	0.017(4)	87(7)	17(2)	0.009(3)	65(39)	9(12)	0.010(3)	127(33)	29(11)	0.0005(2)
S-106 ^(g)	73(6)	12(2)	0.0048(6)	62(47)	8(16)	0.00013(8)	95(28)	19(9)	0.0049(4)	104(8)	21(3)	0.00031(3)
SY-103, ^(h) cv	91(9)	21(3)	0.14	117(9)	29(3)	0.036	84(10)	17(3)	0.036	146(18)	34(6)	0.003(1)
U-103 ⁽ⁱ⁾	91(24)	20(8)	0.006	108(22)	24(7)	0.019(3)	88(34)	18(11)	0.012(3)	156(8)	40(3)	0.0022(3)

(a) Units: E_a, kJ/mol; A, mol/kg/day; G-value, molecules/100 eV. Values in parentheses indicate 95% confidence interval.
 (b) Results of this study.
 (c) Bryan et al. 2002.
 (d) Bryan SA and CM King. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-AW-101 Waste: Status Report*. TWS98.39, Pacific Northwest National Laboratory, Richland, WA.
 (e) The letters cv indicate convective layer.
 (f) King et al. 1997.
 (g) Bryan SA and CM King. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-A-106 Waste: Status Report*. TWS98.78, Pacific Northwest National Laboratory, Richland, WA.
 (h) Bryan et al. 1996.
 (i) King and Bryan 1999.

The fate of radical and molecular products in irradiated water depends a great deal on substances present in solution with which they may react. In the absence of such substances and in a closed system (which retains molecular hydrogen), the radicals will react with the hydrogen and hydrogen peroxide to reform water. The net result of continuous irradiation is to set up a steady-state equilibrium in which the water contains an equilibrium concentration of hydrogen and hydrogen peroxide. The equilibrium concentrations depend on the yields of radical and molecular products. Low-LET (linear energy transfer) radiation, where the radical yield is high and the molecular product yield low, produces a small equilibrium concentration of molecular products. Gamma-radiation, for example, produces very little change in pure de-aerated water irradiated in a closed system (Spinks and Woods 1964). Good agreement between theoretical and measured values for $G(\text{H}_2)$ is obtained for such closed systems only when it is assumed that there is a small primary yield of molecular hydrogen [$G(\text{H}_2)^\circ$] produced within the spur, which is little affected by contaminants or scavengers (Draganic and Draganic 1971). The lower threshold for $G(\text{H}_2)$ based on the “in-spur” molecular hydrogen yield is established as 0.175 (Schwarz 1969).

The activation energies and G-values determined for the production of N_2O and CH_4 from AN-102/C-104 Sr/TRU material are within the range of activation energies observed for other tank waste materials (Table 3.6). The activation energy determined for N_2 production from AN-102/C-104 Sr/TRU material is much lower than those reported for other tank materials. The reason for this is not understood. The scatter in the nitrogen radiolytic data precluded an accurate assessment for the nitrogen G-value.

4.0 Energetics of AN-102/C-104 Sr/TRU Precipitate Samples

4.1 Background

It is important to understand the potential reactivity of Hanford HLW because several of the stored wastes contain fuels (organic compounds) and oxidants (nitrates and nitrites) that are thermally sensitive (Scheele et al. 1995; Wahl et al. 1996; Meacham et al. 1997). Because of this, thousands of waste samples have been screened using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to determine whether the thermally induced heat produced exceeded 480 J/g dry waste (Babad et al. 1995). If the DSC-measured energetics of a sample exceeded this criterion, the waste was further characterized using the reactive system screening tool (RSST).

4.2 Composition of Washed Sr/TRU Solids

Hallen et al. (2002) reported the measured composition of the washed Sr/TRU solids used for the energetics testing reported here. The fuel and oxidant concentrations are important in identifying the energetic potential. Table 4.1 provides the concentrations of measured oxidants and potential oxidants nitrite, nitrate, manganese (assumed as the dioxide), and chrome (as chromate) as well as selected components of the AN-102/C-104 Sr/TRU precipitate samples. The only organic compound listed is oxalate ($C_2O_4^{2-}$) at 0.41 mmol/g, or 0.82 mmol C/g, or 3.6 wt%. This analysis indicates that oxalate is the only organic present when compared with the TOC-measured 0.68 mmol C/g. Compared with other organic compounds, sodium oxalate has reduced energetics (Meacham et al. 1997; Wahl et al. 1996; Burger 1995). After washing, the soluble oxidants nitrate and nitrite were present in the solids at 0.436 and 0.236 mmol/g, respectively.

Table 4.1. Measured Composition of AN-102/C-104 Sr/TRU Precipitate Samples

Waste Constituent	Concentration wt%	Concentration mmol/g
NO_2^-	1.85	0.24
NO_3^-	2.70	0.44
$C_2O_4^{2-}$ (C)	3.62 (0.99)	0.41 (0.82)
Total organic carbon (TOC) ^(a)	0.82	0.68
Cr	0.53	0.10
Mn	6.70	1.22
(a) TOC recommended by analyst based on results of hot persulfate and furnace methods.		

The molar stoichiometric ratios for the maximum enthalpy producing reactions between oxalate and nitrate or nitrite are 1:0.4 and 1:0.67, respectively (Burger 1995). There is nearly a stoichiometric amount of nitrite in the solids (86.6%) as well as a large excess of nitrate. There is sufficient nitrate and nitrite for full oxidation of oxalate via the most energetic reaction path.

The AN-102/C-104 Sr/TRU precipitate samples have the potential to produce a theoretical maximum exothermic heat of -120 J/g waste or -210 J/g dry waste based on the measured 3.6 wt% oxalate, which represents the TOC, and sufficient nitrate and nitrite to completely oxidize the oxalate. This estimated heat production was calculated using Burger's (1995) reported enthalpies for reactions of oxalate in the presence of hydroxide with all available nitrite and with the remaining oxalate reacting with nitrate. If MnO₂ were the oxidant, we would predict slightly lower maximum enthalpies based on Burger's observation that, for his considered reactions, reaction enthalpies with MnO₂ are slightly less than with sodium nitrate.

4.3 Measurement Strategy

Following the strategy used by Babad et al. (1995) to assess the reactivity hazards of stored organic-bearing HLW (Meacham et al. 1997), the Sr/TRU washed solids were evaluated using enthalpy-calibrated DTA rather than DSC from room temperature to 500°C. We also performed a single supplemental DSC analysis to help with the identification of reaction events. The enthalpy-calibrated DTA was used for energetics testing of washed AN-102 sludge/entrained solids samples (Bryan et al. 2002). The DTA and DSC was calibrated before using known melting point standards. In the event that an exothermic reaction produced energy >480 J/g dry waste or <-480J/g dry waste, the material would have been analyzed using the RSST after concurrence of BNI. [See Scheele et al. (1995), Wahl et al. (1996), and CCPS (1995) for descriptions of the thermo-analytic methods.]

For the AN-102/C-104 Sr/TRU precipitate sample, the DTA/TGA instrument was programmed to heat to 100°C at 5°C/min, hold at 100°C for 30 minutes to evaporate any free water, and then heat to 500°C at 5°C/min. An argon purge gas was used to eliminate oxygen and any of its reactions with organics in the sample during the analysis. The Sr/TRU washed solids were analyzed four times using the DTA/TGA and once by DSC after drying at 80°C.

4.4 Results of Energetics Testing

The observed thermal behavior of the washed Sr/TRU solids is provided in Figure 4.1 as measured by DTA, TGA, differential thermogravimetric (DTG) analysis, and DSC between 100 and 500°C. DTG is another method to help identify where reactions begin and end. DTG has the advantage over the normal TGA presentation of an appearance similar to the DTA or DSC curve. The drying reaction at 100°C is not presented in the figure to enhance presentation of the reactions between oxalate and nitrate or nitrite.

Based on the mass at 100°C after heating for 30 minutes, as shown by TGA in Figure 4.1, the original samples contained an average of 57 wt% solids (43 wt% water). The TGA indicates that an additional average 8.6 wt% is lost between 100° and 500°C. Assuming that the 3.6 wt% oxalate reacted with nitrate to release CO₂ and N₂, the maximum total mass loss would be 1.8 wt%. The reactions producing N₂O result in about the same mass loss, indicating that additional reactions are responsible for at least half of the mass loss. It is speculated that chemical decompositions of hydrates and hydrous oxides are responsible for some of the mass loss. Analyzing the off-gas could confirm postulated reactions and facilitate enthalpy measurements

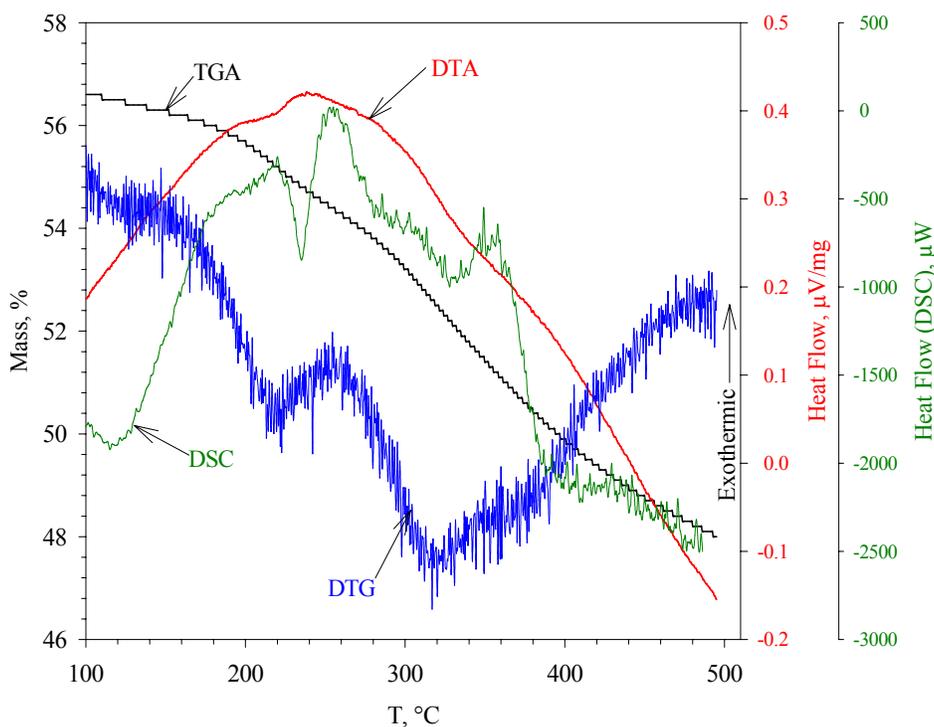


Figure 4.1. Average Thermal Behavior of AN-102/C-104 Sr/TRU Precipitate Samples Measured by Simultaneous DTA/TGA and DSC

from exothermic reactions. The off-gas was not analyzed because this capability is not available for radioactive samples. It is recommended that this capability be added before any additional analyses are performed.

Using the DTG for guidance to identify reactions in the DTA curve, endothermic reactions occurred between 1) 190° and 250°C and 2) 250° and 400°C. As seen in Table 4.2, the average respective enthalpies required for these two endothermic reactions were +5 and +13 J/g dry waste. Based on this interpretation of the DTA curve, there are no thermally induced exothermic events occurring in the washed solids, at least none that produce sufficient heat to compensate for the heat required for the other competing reactions. This indicates that the Sr/TRU washed solids do not exhibit exothermic behavior that exceeds the Hanford reactivity criterion of 480 J/g dry waste and is consistent with the theoretical -210 J/g dry waste maximum heat production based on the oxalate and TOC content. Based on the Babad et al. (1995) criteria, the DTA results indicate that the Sr/TRU washed solids would not be classified as reactive wastes.

Table 4.2. Thermal Behavior of AN-102/C-104 Sr/TRU Precipitate Samples Measured by DTA/TGA^(a)

Sample	Event Temperature Range (°C)	Mass Loss wt%	Enthalpy Change J/g dry waste ^(a)
Analysis #1	25–100	43.0	NM
	190–240	1.1	+4
	290–400	3.6	+15
	Total (100–500)	8.4	+19
Analysis #2	25–100	42.5	NM
	100–190	1.2	+6
	290–400	3.7	+8
	Total (100–500)	9.0	+14
Analysis #3	25–100	43.3	NM
	190–240	1.1	+4
	290–400	3.7	+18
	Total (100–500)	8.5	+22
Analysis #4	25–100	43.1	NM
	190–240	1.2	+4
	290–400	3.6	+13
	Total (100–500)	8.5	+17
Average	25–100	43.0	+5
	100–400	6.7	+13
	Total (100–500)	8.6	+18

(a) NM = not measured.

The DSC provides two possible sets of results. The first is consistent with the DTA/DTG-observed results, with endotherms observed at 1) 219°–255°C and 2) 255°–360°C. Alternatively, three endothermic events may be present at 1) 219°–255°C 2) 255°–360°C, and 3) 360°–430°C. The measured enthalpy on a dry mass basis (water content based on DTG-measured mass loss $\leq 100^\circ\text{C}$) for the first endotherm is +9 J/g, +36 J/g for the second, and +36 J/g for the third in the second interpretation. The presence of a third endotherm is not strongly supported by the DTG. The first endotherm is near the melting point of the equimolar sodium nitrate/nitrite eutectic (210°C) and may be attributable to that reaction. As with the DTA results, based on the Babad et al. (1995) criteria for reactive wastes, the DSC results indicate that the washed Sr/TRU solids would not be classified as reactive wastes.

5.0 Conclusions

This report summarizes work performed to evaluate thermal and radiolytic activation parameters for gas generation of AN-102/C-104 Sr/TRU precipitate samples and to measure the energetics of thermal reactions from these samples.

Arrhenius treatment of the rate data yielded thermal activation parameters (E_a) for gas generation. The thermal activation parameters (E_a , kJ/mol) were measured to be 64 (± 62) for hydrogen, 79 (± 26) for nitrous oxide, 14 (± 7) for nitrogen, 147 (± 82) for methane, and 60 (± 32) for total gas generated. Gases produced from irradiation with a 31,000 R/h (^{137}Cs) external gamma source were measured to determine the radiolytic G-values for gas generation. The effect of temperature and radiation were examined at ambient cell temperature, $\sim 33^\circ\text{C}$, in addition to 45° , 60° , 75° , 90° , and 105°C . The radiolytic G-values, in molecules per 100 eV, were determined to be 0.18 (± 0.02) for hydrogen, 0.0041 (± 0.004) for nitrous oxide, 0.0006 (± 0.001) for methane, and 0.19 (± 0.023) for total gas generated. The scatter in the nitrogen data precluded an accurate assessment for the nitrogen G-value.

Of interest is the comparison of the activation parameters between AN-102/C-104 Sr/TRU sample and the AN-102 washed solids; the activation energies for hydrogen generation between these two samples is essentially identical, 64 and 63 kJ/mol, respectively. The G-value for hydrogen generation is higher in the AN-102/C-014 Sr/TRU sample (0.18 molecules/100eV, using 32,000 R/h external gamma source) than for AN-102 washed solids (0.055 molecules/100eV). This increased G-value for the AN-102/C-104 Sr/TRU sample using the external gamma source is most likely due to the addition of inhibited water to the matrix prior to the gas generation experiment. With the addition of inhibited water (0.01 M NaOH) as a large fraction of the total sample, the $G(\text{H}_2)$ value from gamma radiolysis would approach that expected for a dilute aqueous stream containing low concentrations of nitrate and nitrite. The $G(\text{H}_2)$ value of 0.18 molecules/100eV is consistent with the measured $G(\text{H}_2)$ value from pure water radiolysis using identical experimental equipment [$G(\text{H}_2) = 0.196$ molecules per 100 eV absorbed dose] (Arm et al. 2003) and is consistent with literature for pure water systems in a closed reaction system (i.e., H_2 product not allowed to escape).

The AN-102/C-104 Sr/TRU precipitate exhibited only endothermic thermal reactivity and thus did not exhibit exothermic behavior exceeding the Hanford reactive waste criteria of an exothermic 480 J/g dry waste as measured by DSC (Babad et al. 1995). Using this criterion the washed AN-102/C-104 Sr/TRU precipitate would not be classified as a reactive waste. The DTA and DSC measured results indicating energetics of < 480 J/g dry waste are consistent with the estimated maximum enthalpy production of 210 J/g dry waste for these solids containing organic carbon as 3.6 wt% oxalate. Because the oxidation of oxalate will only result in a nominal maximum 2 wt% loss, the total 8.6 wt% mass loss observed by the TGA above 100°C indicates that other slow endothermic reactions, such as decomposition of hydrates and hydrous

oxides, must be postulated to explain the greater mass loss. In addition, it appears that any heat absorbed during dehydration and/or decomposition overshadows any heat released by any organic oxidation by nitrite or nitrate.

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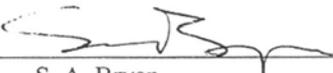
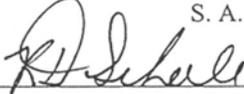
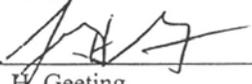
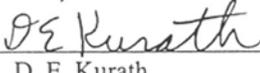
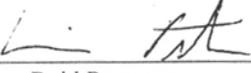
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Appendix

PNNL Test Plan TP-RPP-WTP-066: Energetics and Gas Generation Tests

Battelle Test Plan		Document No.: TP-RPP-WTP-066 Rev. No.: 0
Title: Energetics and Gas Generation Tests		
Work Location: RPL/Variou	Page 1 of 9	
Author: S.A. Bryan/R. D. Scheele	Effective Date: March 2001 Supersedes Date: New	
Identified Hazards: <input checked="" type="checkbox"/> Radiological <input checked="" type="checkbox"/> Hazardous Materials <input checked="" type="checkbox"/> Physical Hazards <input type="checkbox"/> Hazardous Environment <input type="checkbox"/> Other:	Required Reviewers: <input checked="" type="checkbox"/> Author <input checked="" type="checkbox"/> Technical Reviewer <input checked="" type="checkbox"/> Quality Engineer <input checked="" type="checkbox"/> Project Manager <input checked="" type="checkbox"/> Client	
Approval	Signature	Date
Author	 S. A. Bryan	5/1/01
Author	 R. D. Scheele	5/1/01
Technical Reviewer	 J. G. H. Geeting	5-1-01
Quality Engineer	 T. L. Almeida	5/2/01
Project Manager	 D. E. Kurath	5/1/01
Client	 Reid Peterson	5/16/01

Applicability

This test plan applies to the:

- 1) Washing of Tank 241-AN-102 waste materials for use in this task.
- 2) Gas generation measurements on heat treated and irradiated, washed Tank 241-AN-102 waste materials, and Sr/TRU precipitated AN-102 solids (if quantity of solids permits).
- 3) Screening of the washed AN-102 high level waste (HLW) solids and Sr/TRU precipitated solids using a differential scanning calorimeter (DSC) or differential thermal analyzer (DTA) to determine if there are energetic exothermic reactions.
- 4) Determination of water content in the washed AN-102 high level waste (HLW) solids using thermogravimetric analysis (TGA).
- 5) Supplemental measurement of exothermic behavior, using the Reactive System Screening Tool (RSST) and a larger sample, if the DSC- or DTA-measured exotherm(s) are greater than 480 J/g dry waste. The RSST provides additional data including an improved measure of exothermic energetics and thermal behavior.

Irradiation of the Hanford tank waste materials and collection of the gases will be performed within PNNL's High Level Radiation Facility (HLRF) in the Radiochemical Processing Laboratory (RPL). The other activities will be performed in various laboratories in the RPL. This test plan applies to staff working on these activities at PNNL's Gamma Irradiation Facility (GIF) and in the RPL and includes laboratory technicians, scientists and engineers.

DRD and Other References

Test specifications for this activity were provided by CH2M Hill Hanford Group, Inc. (CHG) in document TSP-W375-01-00002, Rev. 0, "Energetics and Gas Generation Studies", (DA Reynolds and M.E. Johnson, 2/27/01).

Definitions

None.

Justification

This activity provides information on gas generation capacity and reactivity of Tank 241-AN-102 waste material. The energetic tests evaluates potential for runaway reactions, the gas generation studies explore the rate gases will be generated under thermal and radiolytic conditions. These tests will assist in understanding certain process safety concerns and provide information on potential emissions to the pretreatment vessel off-gas ventilation system.

Test Objectives

The RPP-WTP is evaluating gas generation rates and potential for exothermic reaction of the washed solids from Hanford Tank 241-AN-102 to provide information for assessing safe storage conditions. The objectives are:

- Prepare washed solids from Tank 241-AN-102 suitable for use within this task.

- Perform thermal and radiolytic experiments on washed solids from Hanford Tank 241-AN-102 under the following conditions.
 - Thermal treatments at 5 temperatures (in duplicate);
 - Irradiation treatments at same temperatures as thermal treatment (in duplicate);
 - Measure gases evolved during thermal and radiolytic treatments;
 - Determine thermal and radiolytic activation parameters for gas generation
 Also perform identical testing on Sr/TRU precipitated AN-102 solids if the quantity of solids allows.
- Screen the washed AN-102 HLW solids and AN-102 Sr/TRU precipitated solids using a DSC or DTA to determine if there are exothermic reactions. If the DSC- or DTA-measured exotherms are greater than 480 J/g dry waste, then;
- The RSST apparatus will be used with a much larger sample to better quantify the exotherm and provide additional data.

Hanford wastes are known to produce gases and have shown exothermic behavior under certain situations. Hydrogen gas generation will be measured for washed sludge to simulate conditions found in the HLW melter feed tank. The energetics testing outlined in this test specification will provide semi-quantitative measures of the thermally induced exotherms encountered within these wastes.

Success Criteria

The RPP-WTP will consider this test successful when the gas composition and gas generation rates versus thermal and radiation exposure are accurately determined for the washed Hanford AN-102 waste. The gas generation and energetics data as measured will provide information for safe storage.

Background

The product of the ultrafilter is a solids-bearing stream. This stream will be accumulated in a tank in the pretreatment area of the plant. The solids have the potential for gas generation and for energetic reactions.

Energetics of the waste has been a concern. The waste contains fuel (organics molecules) and oxidizers (nitrate and nitrite ions). The potential for an organic/nitrate reaction has been studied extensively in the tank farm. The conclusion is that an energetic reaction in the waste storage mode in the tank farms is not credible (Meacham et. al. 1997). This is based on thousands of samples from the tanks that were screened using a DSC/TGA method (Babad et. al. 1995). Those wastes that exhibited an exothermic reaction greater than 480 J/g dry waste were further tested with the RSST to identify propagating reactions. No propagating reactions were found. It should be noted that AN-102 was tested a number of times (TWINS3 Database). The highest DSC-measured energetics on a solid sample was 488 J/g on a dry weight basis.

The solid waste stored in the Pretreatment Plant will be washed in the ultrafiltration step. This should remove nearly all of the organics species from the solids. The only organic shown to be in the solid form is sodium oxalate, $\text{Na}_2\text{C}_2\text{O}_4$ which has been shown to have reduced reactivity compared to other organic compounds. Also the washing should remove nearly all of the oxidizer (nitrate/nitrite). This should leave the solids in a less reactive mode than when in Hanford's HLW storage tanks. Mixtures of oxalate and nitrate/nitrite are reactive, however the amount of heat produced depends on the oxalate concentration. Theoretically a 6 wt% carbon mixture of sodium oxalate and sodium nitrate can produce a maximum of 420 J/g mix, however, PNNL measurements by DSC and DTA have observed reaction heats of 5 and 20% of maximum theoretical (Wahl et. al. 1995).

This test specification is to determine the reactivity of the washed solids. The approach will be a graded approach. The first step will be to test the material using a DSC and/or DTA/TGA. This step uses little waste. If the DSC or DTA shows that the sample may have greater than 480 J/g dry waste, then the larger more complicated RSST test will be performed upon approval.

There have been a number of tests on actual wastes for gas generation done at PNNL (Bryan et al 1996; Bryan and King 1998a, 1998b; King and Bryan 1998; King et al 1999). These tests were used with other information to derive an estimate of the generation rate of gas (Pederson and Bryan 1996; Hu 2000). It is recognized that radiation will produce gas from the radiolysis of water. The washed sludge that is stored in the Pretreatment facility will have most of the organic compounds washed out. The lower organic content should greatly diminish the amount and rate of gas generation of the sludge. However, the reduced nitrate and nitrite content – which when present, acts as a scavenger for hydrogen generation – may have the affect of increasing the gas generation capacity. The tests will determine the gas generation capacity of the low organic wastes with relatively high radiation doses.

Description of Tests

Hanford waste samples from Tank 241-AN-102 have been received, composited, and prepared for use by this task under “Washed BNFL Ultrafiltration Physical Testing: Feed Characterization” task (Paul Bredt, BNFL-TP-41500-015).

The sludge washing will be performed by adding approximately equal volumes of 0.01 M NaOH solution with the solids, mixing for 1 hour, followed by a settle-decant. The washing will be repeated three times. The washed solids will be the starting mixture for the gas generation and energetics studies. The washing will simulate the washing that the solids will receive in the pretreatment plant. It is expected that this washing step will remove organics that promote gas generation. However, it is expected to remove nitrate ion that protects against radiolysis of water.

Two samples of the solids prepared in the previous step will be analyzed for: sodium, aluminum, TOC, nitrate, nitrite, hydroxide, and oxalate. Rad-chem analysis will also be performed for the flowing constituents: ^{90}Sr , ^{241}Am , and ^{244}Cm .

Energetics

PNNL will measure the exothermic reaction potential of wet, washed AN-102 solids and AN-102 Sr/TRU precipitated solids (if quantity of solids permits) using DSC or DTA/TGA. The samples will be analyzed by DSC or DTA/TGA at least in duplicate. For any observed exotherm, its enthalpy will be calculated. If the exotherm(s) are less than 350 J/g wet waste, no further analyses. If the exotherm(s) are greater than 350 J/g wet waste, the water content will be measured using TGA if not already measured. If the DSC- or DTA-measured exothermic enthalpy exceeds 480 J/g dry waste, RPP-WST will be consulted for guidance on the decisions on what material will be analyzed by RSST in a single analysis. Results of the thermal analyses will be reported.

Gas Generation Testing

The effects of temperature and radiation on gas generation from washed Tank 241-AN-102 entrained solids material will be assessed. Gas generation testing of Sr/TRU precipitated solids will also be performed if the quantity of solids is sufficient (~600 g). For AN-102 tank waste, material will come from a composite core samples taken from AN-102. Gas will be generated at five temperatures: 60, 75, 90, 105, and 120°C, in the presence and absence of external gamma radiation (supplied by a ^{137}Cs

capsule), for a total of 10 experimental variations. Each experiment will be performed in duplicate, giving a total of 20 experiments. Each reaction will use approximately 20-30 g of tank material. A total of approximately 600g of washed Tank 241-AN-102 material will be required for testing. The rate of gas generation in the presence of external radiation is the sum of radiolytic and thermal rates. The radiolytic rate will be determined by subtracting the thermal-only rate from the rate in the presence of external radiation.

Gas generation measurements will be made using the gas manifold system and procedures developed in the study of Tank 241-SY-103 (Bryan et al 1996) and 241-S-102 (King et al 1997). New reaction vessels will be used for this test and are constructed of 316-L stainless steel. Pressures of each reaction vessel will be measured independently using pressure transducers connected to the gas manifold line of each reaction vessel. The schematic diagram of the gas manifold system with the placement of the reaction vessels relative to the gas manifold system is shown in Figure 1.

Figure 2 illustrates the small-scale reaction vessel and shows where the thermocouples are placed within and outside the vessel. The reaction vessels are 316-L stainless steel cylinders, each internally ~1.75 cm diameter and 14 cm high (internal volume ~33 cm³). For the gas generation testing, each vessel will be wrapped in heating tape and insulated. Two thermocouples are attached to the external body, one for temperature control and one for over-temperature protection. Two thermocouples are inserted through the flange. The thermocouple centered in the lower half of the vessel monitored the temperature of the liquid phase; the one centered in the upper half monitored the gas phase temperature within the reaction vessel. The reaction vessels are placed in the hot cell connected by a thin (0.0058-cm inside diameter) stainless steel tube to the gas manifold outside the hot cell. A stainless steel filter (60-micrometer pore size, Nupro) protected the tubing and manifold from contamination. A thermocouple is attached to this filter as well.

Total moles of gas produced will be calculated based on the measured pressure and temperature and the known volume of the gas phase of the reaction vessel. The volumes of the reaction vessels have been determined gravimetrically using water. The volumes of the pressure sensor, valves, and miscellaneous fittings have been determined from pressure/volume relationships using a calibrated gas manifold system.

Gas samples from the reaction vessels will be withdrawn through the capillary line into an evacuated bulb. The volume of the capillary line is small, less than 2 mL, whereas the gas phase of the reaction vessel volume is ~33 mL in all cases, and the collection bulb volume is ~30 mL. Because gases will move by viscous flow through the capillary tube in this pressure regime, no significant fractionation of the gas is expected.

Analyses to determine the mole percent of the components within the gas phase of each reaction vessel will be performed using the Mass Spectroscopy Facility operated by PNNL in the 325 Building. The amounts of specific gases generated will be calculated from the total moles of gas generated and the mole percent data.

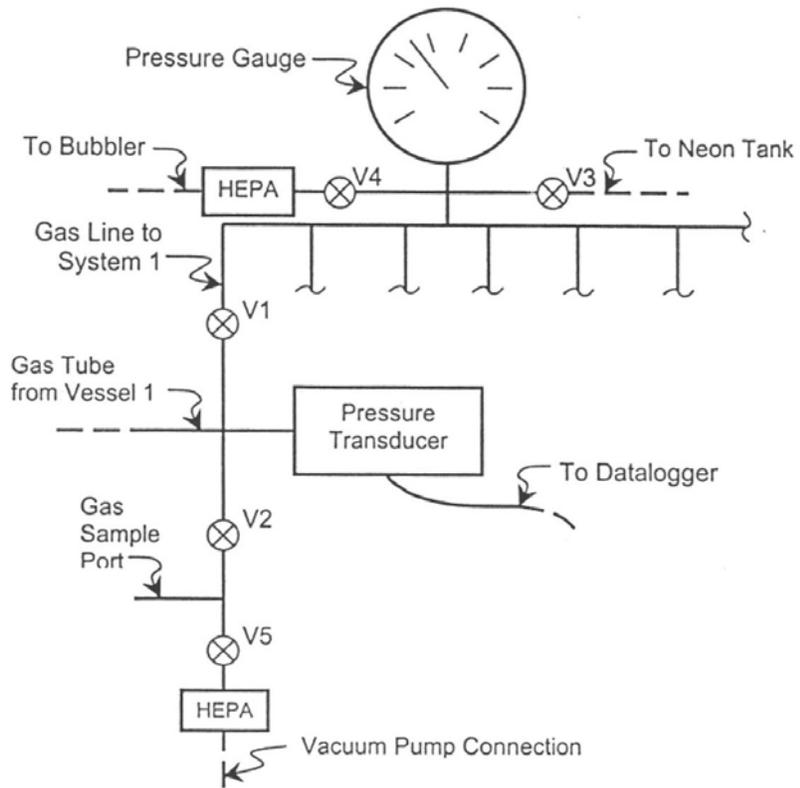


Figure 1. Pressure Manifold System Used in Gas Generation Tests

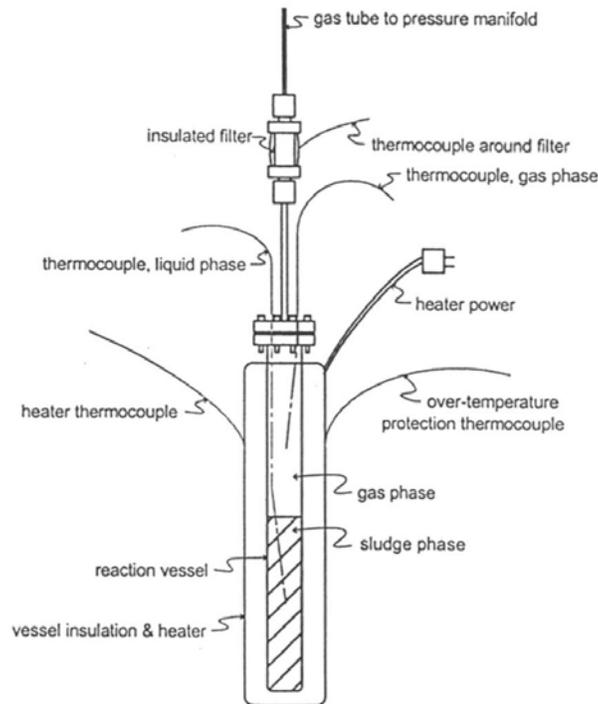


Figure 2. Reaction Vessel Used in Small-Scale Gas Generation Tests

Test Environment

All gas generation testing will be conducted at PNNL's High Level Radiochemistry Facility (325A HLRF) in the RPL facility.

Data Treatment

Gas generation will be studied both in the presence and absence of an external gamma radiation source (^{137}Cs capsule). In both experiments, the rates and composition of gases generated will be measured at three temperatures in duplicate. Separate samples are used for each temperature, and separate samples will be used for the thermal and the radiolytic experiments. Composition of gases generated will be measured by mass spectrometry according to analytical procedure ALO-284, Rev 1.

Experimental Matrix and Data Analysis

The planned test is expected to generate the data indicated in Table 1. The design variables, temperature ($^{\circ}\text{C}$) and 'Rep' (for replicate) are indicated in the first two columns. The gas generation rate for H_2 , N_2 , N_2O , and CH_4 will be calculated from known volume of the reaction vessel and its contained sample, measured temperature and pressure, and from gas samples taken for analysis for specific gases during the experiment. Gas samples will be taken every three weeks for the 60°C reactions, and more often for the higher temperature reactions.

Table 1. Expected Data Matrix from Gas Generation Testing

Temp	Rep	Thermal Gas Gen. Rate (mol/kg/day)						Radiolytic Gas Gen. Rate (mol/kg/day)					
		total	H ₂	N ₂	N ₂ O	NH ₃	CH ₄	total	H ₂	N ₂	N ₂ O	NH ₃	CH ₄
60°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
75°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
90°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
105°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—
120°C	1	—	—	—	—	—	—	—	—	—	—	—	—
	2	—	—	—	—	—	—	—	—	—	—	—	—

The analysis of data will provide an empirical fit describing the relationship between the gas generation rate, the temperature applied to the reaction vessel, and the radiation dose. The analysis will account for variability in the temperature for each vessel and the goodness of fit of the statistical model describing the relationship and experimental variability due to any lack of homogeneity in the material sampled and the conduct of the experimental procedure. Since the reactions at each temperature will be duplicated, it will be possible to separate differences due to temperature from the differences due to random variability in the application of the procedure.

Quality Control

This work will be performed in accordance with the PNNL’s quality assurance plan for its RPP-WTP Project, CHG-QAPjP, Rev. 0, as approved by the RPP-WTP QA organization. The work will be performed in compliance with 10 CFR 830.120, “Quality Assurance Requirements”.

The *Quality Assurance Requirements and Description* (DOE/RW-00333P), the principal quality assurance document for the Civilian Radioactive Waste Management Program, does not apply to activities described in this test plan.

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