PNNL-26869, Rev. 0
RPT-LPIST-002, Rev. 0

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

Gas Generation Testing of Spherical Resorcinol-Formaldehyde (sRF) Resin

HA Colburn
SA Bryan
DM Camaioni
LA Mahoney
SR Adami

January 2018

U.S. DEPARTMENT OF
ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service
5301 Shawnee Rd., Alexandria, VA 22312
ph: (800) 553-NTIS (6847)
email: orders@ntis.gov <http://www.ntis.gov/about/form.aspx>
Online ordering: http://www.ntis.gov

PNNL-26869, Rev. 0
RPT-LPIST-002, Rev. 0

Gas Generation Testing of Spherical Resorcinol-Formaldehyde (sRF) Resin

HA Colburn
SA Bryan
DM Camaioni
LA Mahoney
SR Adami

January 2018

Prepared for
the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

The Direct Feed Low-Activity Waste (DFLAW) process has been proposed to support early production of immobilized low-activity waste (ILAW). In the DFLAW process, Hanford tank waste is sent to the Low-Activity Waste Pretreatment System (LAWPS) for filtration and cesium removal. The resultant treated waste is delivered to the LAW Vitrification Facility at the Hanford Tank Waste Treatment and Immobilization Plant (WTP) for immobilization. The conceptual design and ongoing technology maturation of the LAWPS facility are being conducted by Washington River Protection Solutions, LLC (WRPS), but the DFLAW process also necessitates interfaces between WRPS and Bechtel National, Inc. to deliver the treated LAW from the LAWPS facility to the WTP for vitrification.

This report describes gas generation testing of the spherical resorcinol-formaldehyde (sRF) resin that was conducted to support the technology maturation of the LAWPS facility. The current safety basis for the LAWPS facility is based primarily on two studies that had limited or inconclusive data sets. One of the two studies indicated a 40% increase in hydrogen generation rate of water (as predicted by the Hu model) with sRF resin over water alone, resulting in the assumption derived by WRPS that the maximum hydrogen production in the presence of sRF resin is 1.4 times the Hu model output for water.[1] However, the previous studies did not test the range of conditions (process fluids and temperatures) that are expected in the LAWPS facility. Additionally, the previous studies did not obtain replicate test results or comparable liquid-only control samples. To address the knowledge gaps and address potential gas generation under LAWPS operating conditions, this study was conducted under the following conditions:

- Water alone and in the presence of Na-form sRF resin at 25 °C, 45 °C, and 70 °C
- 5.6M Na nominal feed simulant alone and in the presence of Na-form sRF resin at 25 °C, 45 °C, and 70 °C. An additional condition of the 5.6M Na nominal feed simulant with 1% (w/w) total organic carbon added in the form of Na_3-HEDTA was tested with and without Na-form resin at 70 °C
- 0.45M HNO_3 alone and in the presence of H-form sRF resin at 25 °C, 45 °C, and 70 °C

All of the testing described in this report returned hydrogen generation rates that are within the current safety basis for the facility of 1.4 times the Hu model output for water. One unexpected result of note is the self-heating behavior that was observed in the 45°C and 70°C vessels with resin and 0.45M nitric acid once heated. The vessels continued to increase in temperature, requiring intervention on the part of the analyst to maintain the temperatures at the testing set-points. This behavior was observed in both the thermal and irradiated systems.

---

[1] Yarbrough RJ and WE Bryan. 2014. *Flammable Gas Calculations for the LAWPS Project Vessels*, RPP-CALC-57640 Rev. 1. Washington River Protection Solutions, Richland, WA.

Acknowledgements

The authors would like to thank Pacific Northwest National Laboratory staff members who contributed to the completion of the experimental work and this report. Several staff were instrumental in the fabrication and calibration of the equipment used for the experimental work: Randal Berg, Greg Carter, Jim Hilliard, Gayland Kellison, Gene Gould, Kim Piper and Mark Murphy. Experimental and analysis support staff included Randal Berg, Margaret (Peggy) Smoot, James Peterson, Rich Cox, and Crystal Rutherford. The authors are also grateful for the support of Sandy Fiskum and Amy Rovira for technical review and assistance with the data tables respectively, the editorial review of Matthew Wilburn, and the quality support provided by Bill Dey.

The work discussed in this report was funded by Washington River Protection Solutions, LLC, and many of their staff were also helpful in shaping this document. This work was shaped by a close working relationship with WRPS to deliver the gas generation results that would inform their safety basis.

Acronyms and Abbreviations

% RSD	percent relative standard deviation
ACS	American Chemical Society
ASO	Analytical Support Operations
CD	Critical Decision
DFLAW	Direct Feed Low-Activity Waste
DI	deionized
DOE-ORP	U.S. Department of Energy Office of River Protection
FIO	For Information Only
G-value	a constant in the radiolysis rate equation of gas generation
HEDTA	N-(2-Hydroxyethyl)ethylenediaminetriacetic acid
HEF	High Exposure Facility
HGR	hydrogen generation rate
ILAW	immobilized low-activity waste
LAW	low-activity waste
LAWPS	Low-Activity Waste Pretreatment System
LC-MS	liquid chromatography-mass spectrometry
LFL	lower flammability limit
MCNP	Monte Carlo N-particle transport code
PNNL	Pacific Northwest National Laboratory
QA	quality assurance
R&D	research and development
RPL	Radiochemical Processing Laboratory
sRF	spherical resorcinol-formaldehyde
TIC	total inorganic carbon
TOC	total organic carbon
UFL	upper flammability limit
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WWFTP	WRPS Waste Form Testing Program

Contents

Executive Summary iii
Acknowledgements iv
Acronyms and Abbreviations v
1.0 Introduction 1.1
2.0 Quality Assurance 2.1
3.0 Evaluation of Simulants for Gas Generation Testing 3.1
  3.1 The Hu Model 3.1
    3.1.1 Modeling Assumptions and Conditions 3.2
  3.2 Liquid Compositions Evaluated by the Hu Model 3.3
  3.3 Modeled Hydrogen Generation Rates 3.3
4.0 Experimental 4.1
  4.1 Experimental Conditions and Equipment 4.1
  4.2 Gas Generation System Tests 4.5
    4.2.1 Gas Generation System 1 (Rad System) 4.6
    4.2.2 Gas Generation System 2 (Thermal-only System) 4.8
  4.3 Simulant Preparation and sRF Resin Conditioning 4.11
    4.3.1 Simulant Preparation 4.11
    4.3.2 sRF Resin Handling and Preparation 4.12
    4.3.3 Vessel Loading 4.12
  4.4 Gamma Dose Calibration 4.12
  4.5 Experiment Setup and Execution 4.13
    4.5.1 Gas Sampling 4.14
  4.6 Gas Generation Test Conditions 4.14
    4.6.1 Test 1 – Water with and without Na-form Resin 4.14
    4.6.2 Test 2 – 5.6M Na LAWPS-IST Simulant without Added TOC, with and without Na-Form Resin 4.15
    4.6.3 Test 3 – 0.45M HNO_3 .... 4.17
    4.6.4 Test 4 – Water at 70 °C and Simulant with HEDTA at 70 °C 4.18
    4.6.5 Test 5 – HNO_3 at 70 °C and 5.6M Na Simulant at 70 °C 4.20
  4.7 Data Analysis 4.21
5.0 Gas Generation Testing Experimental Design and Results 5.1
  5.1 Water Results 5.1
  5.2 5.6M Na Nominal Feed Simulant Results 5.6
  5.3 0.45M HNO_3 Results 5.11
  5.4 Summary 5.16
6.0 Post-Irradiation Examination of Resin and Liquids 6.1

6.1 Visual Examination of Resin and Test Liquids 6.1
  6.1.1 Test 1 – Water 6.1
  6.1.2 Test 2 – Simulant 6.3
  6.1.3 Test 3 – 0.45M HNO_3 .... 6.4
  6.1.4 Test 4 – Water, Simulant with TOC, 70 °C 6.6
  6.1.5 Test 5 – 0.45M HNO_3, Simulant, 70 °C 6.10
6.2 Formaldehyde Analysis 6.11
6.3 Total Organic Carbon Analysis 6.12
  6.3.1 Total Organic Carbon Results 6.12
  6.3.2 Carbon Species Analysis by LC-MS 6.12
6.4 Video of Resin Irradiation 6.12
7.0 Gas Generation Results Self-Flammability Evaluation 7.1
7.1 Deionized Water with and without Resin 7.2
7.2 Nominal Target Feed Simulant with and without Resin 7.2
7.3 Nominal Target Feed Simulant Plus HEDTA with and without Resin 7.3
7.4 Nitric Acid with and without Resin 7.3
7.5 Summary 7.4
8.0 Summary 8.1
9.0 References 9.1
Appendix A – Gas Composition Analysis Results A.1
Appendix B – Total Carbon Analysis Results B.1
Appendix C – Gamma Dose Calibration Report C.1

Figures

Figure 1.1. General conceptual schematic of the LAWPS facility unit operations and process streams. 1.1

Figure 3.1. Modeled hydrogen generation rates of simulants and LAWPS process liquids. 3.4

Figure 4.1. Schematic of the gas generation manifold with attached gas generation test vessel. 4.2

Figure 4.2. Photo of the thermal gas generation manifold with attached gas generation test vessels. 4.2

Figure 4.3. Schematic drawing of the “gamma bunker” used for gas generation testing. 4.3

Figure 4.4. Photograph of the gamma bunker payload (left) and close-up photo of the gas generation vessels loaded into the carousel prior to loading into the gamma bunker (right). 4.4

Figure 4.5. Assembled irradiation system with the source in place. 4.5

Figure 4.6. Gas Generation System 1, system test temperature profiles. 4.6

Figure 4.7. Gas Generation System 1, system test pressure profiles. 4.7

Figure 4.8. Gas Generation System 1; gas generation system test – moles calculation for Vessel 1. 4.8

Figure 4.9. Gas Generation System 2, system test temperature profiles. 4.9

Figure 4.10. Gas Generation System 2, system test pressure profiles. 4.10

Figure 4.11. Gas Generation System 2; gas generation system test – moles calculation for Vessel 1. 4.11

Figure 5.1. Radiolytic hydrogen gas generation from sRF resin in contact with water at various temperatures. The data are shown as cumulative moles H_2 produced per kg of water vs. run time. 5.3

Figure 5.2. Thermal hydrogen gas generation from sRF resin in contact with water at various temperatures. The data are shown as cumulative moles H_2 produced per kg of water vs. run time. 5.4

Figure 5.3. G-value measurements for radiolytic hydrogen production ($G(H_2)$-values) for the water + resin experiments conducted at various temperatures. 5.5

Figure 5.4. Radiolytic hydrogen gas generation from 5.6M Na nominal feed simulant at various temperatures with and without resin. The data are shown as cumulative moles H_2 produced per kg of simulant vs. run time. 5.8

Figure 5.5. Thermal hydrogen gas generation from 5.6M Na nominal feed simulant at various temperatures with and without resin. The data are shown as cumulative moles H_2 produced per kg of simulant vs. run time. 5.9

Figure 5.6. G-value measurements for radiolytic hydrogen production ($G(H_2)$-values) for the 5.6M Na nominal feed simulant + resin experiments conducted at various temperatures. 5.10

Figure 5.7. Radiolytic hydrogen gas generation from sRF resin in contact with 0.45M HNO_3 various temperatures. The data are shown as cumulative moles H_2 produced per kg of 0.45M HNO_3 vs. run time. 5.13

Figure 5.8. Thermal hydrogen gas generation from sRF resin in contact with 0.45M HNO_3 at various temperatures. The data are shown as cumulative moles H_2 produced per kg of 0.45M HNO_3 vs. run time. 5.14

Figure 5.9. G-value measurements for radiolytic hydrogen production ($G(H_2)$-values) for the 0.45M HNO_3 + resin experiments conducted at various temperatures. 5.15

Figure 5.10. Comparison of actual results to Hu modeled results. 5.18
Figure 6.1. Test 1, Vessel 1-2 resin appeared to “climb” up and adhere to the vessel walls. 6.1
Figure 6.2. Color difference of resin from the rad system (left) and thermal system (right). 6.2
Figure 6.3. Pink-tinged liquid from Test 1 rad system water/resin after irradiation. 6.2
Figure 6.4. Orange-tinged liquid from Test 1, thermal system water/resin. 6.3
Figure 6.5. Test 2, resin color difference post-test: rad system (left), thermal system (right). 6.3
Figure 6.6. Radiolytic system Vessel 1-4 resin and liquid post-irradiation. 6.4
Figure 6.7. Comparison of Test 3 resin and liquids from the thermal system (left) and rad system (right). 6.5
Figure 6.8. Test 3 rad system Vessel 1-8 post-test. Example of resin climbing the walls. 6.5
Figure 6.9. Rad system Vessel 1-8 post-test. Example of clumped resin. 6.6
Figure 6.10. Test 4 rad system post-test water with resin. 6.7
Figure 6.11. Test 4 thermal system post-test resin with water. 6.7
Figure 6.12. Test 4 thermal system post-test resin and simulant with HEDTA. 6.8
Figure 6.13. Test 4 rad system simulant with HEDTA and resin post-test. 6.8
Figure 6.14. Test 4 rad system simulant with HEDTA (no resin) after irradiation. 6.9
Figure 6.15. Nitric acid after exposure to the thermal vessel at 70 °C (left). Resin after exposure to nitric acid at 70 °C. 6.10
Figure 6.16. Test 5 rad system nitric acid post-test acid only and resin. 6.10
Figure 6.17. Test 5 post-test thermal system simulant and resin. 6.11
Figure 6.18. Test 5 post-test rad system simulant and resin. 6.11
Figure 7.1. Flammability characteristics of gases from Test 1. .... 7.5
Figure 7.2. Flammability characteristics of gases from Test 2. .... 7.6
Figure 7.3. Flammability characteristics of gases from Test 3. .... 7.7
Figure 7.4. Flammability characteristics of gases from Test 4. .... 7.8
Figure 7.5. Flammability characteristics of gases from Test 5. .... 7.9

Tables

Table 3.1. Modeled Simulant Compositions 3.3

Table 4.1. System 1 (w/ radiation) System Test Results 4.8

Table 4.2. System 2 (thermal) System Test Results 4.11

Table 4.3. Gas Generation Test Conditions Matrix 4.14

Table 4.4. Test 1 Experimental Design – Rad System (shaded rows indicate duplicates) 4.15

Table 4.5. Test 1 Experimental Design – Thermal System (shaded rows indicate duplicates) 4.15

Table 4.6. Nominal Composition of the 5.6M Na LAWPS Simulant without Oxalate 4.16

Table 4.7. Test 2 Experimental Design – Rad System (shaded rows indicate duplicates) 4.16

Table 4.8. Test 2 Experimental Design – Thermal System (shaded rows indicate duplicates) 4.17

Table 4.9. Test 3 Experimental Design – Rad System (shaded rows indicate duplicates) 4.18

Table 4.10. Test 3 Experimental Design – Thermal System (shaded rows indicate duplicates) 4.18

Table 4.11. Nominal Composition of the 5.6M Na LAWPS Simulant with 1% (w/w) TOC as Na_3-HEDTA 4.19

Table 4.12. Test 4 Experimental Design – Rad System (shaded rows indicate duplicates) 4.19

Table 4.13. Test 4 Experimental Design – Thermal System (shaded rows indicate duplicates) 4.20

Table 4.14. Test 5 Experimental Design – Rad System (shaded rows indicate duplicates) 4.21

Table 4.15. Test 5 Experimental Design – Thermal System (shaded rows indicate duplicates) 4.21

Table 5.1. Water Testing Average Cumulative $G(H_2)$ Values 5.2

Table 5.2. Simulant Testing Average Cumulative $G(H_2)$ Values 5.7

Table 5.3. 0.45M HNO_3 Testing, Average Cumulative $G(H_2)$ Values 5.12

Table 5.4. Summary of Hydrogen Generation Rates Calculated for a Temperature of 45 °C and 43 kRad/hr Dose Rate (the expected bounding condition during LAWPS use), Using $G(H_2)$-Values Given in Table 5.1, Table 5.2, and Table 5.3 .... 5.17

Table A.1. Percent Composition of Gas Sampled (including argon) – Water-Only Data, 25 °C A.1

Table A.2. Percent Composition of Gas Sampled (including argon) – Water-Only Data, 45 °C A.2

Table A.3. Percent Composition of Gas Sampled (including argon) – Water-Only Data, 70 °C A.3

Table A.4. Percent Composition of Gas Sampled (including argon) - Water Plus Resin Data, 25 °C A.4

Table A.5. Percent Composition of Gas Sampled (including argon) - Water Plus Resin Data, 45 °C A.5

Table A.6. Percent Composition of Gas Sampled (including argon) - Water Plus Resin Data, 70 °C A.6

Table A.7. Percent Composition of Gas Sampled (including argon) – Nitric Acid Only Data, 25 °C A.7

Table A.8. Percent Composition of Gas Sampled (including argon) – Nitric Acid Only Data, 45 °C A.8

Table A.9. Percent Composition of Gas Sampled (including argon) – Nitric Acid Only Data, 70 °C A.9

Table A.10. Percent Composition of Gas Sampled (including argon) – Nitric Acid plus Resin Data, 25 °C A.10

Table A.11. Percent Composition of Gas Sampled (including argon) – Nitric Acid plus Resin Data, 45 °C A.11

Table A.12. Percent Composition of Gas Sampled (including argon) – Nitric Acid plus Resin Data, 70 °C A.12

Table A.13. Percent Composition of Gas Sampled (including argon) – Simulant Only Data, 25 °C..... A.14

Table A.14. Percent Composition of Gas Sampled (including argon) – Simulant Only Data, 45 °C..... A.15

Table A.15. Percent Composition of Gas Sampled (including argon) – Simulant Only Data, 70 °C..... A.16

Table A.16. Percent Composition of Gas Sampled (including argon) – Simulant Plus Resin Data, 25 °C A.17

Table A.17. Percent Composition of Gas Sampled (including argon) – Simulant Plus Resin Data, 45 °C A.18

Table A.18. Percent Composition of Gas Sampled (including argon) – Simulant Plus Resin Data, 70 °C A.19

Table A.19. Percent Composition of Gas Sampled (including argon) – Simulant w/ TOC Data, 70 °C A.20

Table A.20. Percent Composition of Gas Sampled (including argon) – Simulant w/ TOC plus Resin Data, 70 °C........ A.21

Table B.1. Water Data B.1

Table B.2. 0.45M HNO_3 Data........ B.1

Table B.3. 5.6M Na Simulant Data........ B.2

Table B.4. 5.6M Na Simulant with 1%(w/w) Total Organic Carbon Data........ B.2

1.0 Introduction

The primary mission of the U.S. Department of Energy Office of River Protection (DOE-ORP) is to retrieve and process approximately 56 million gallons of radioactive waste from 177 underground tanks located on the Hanford Site. The Hanford waste tanks are currently operated and managed by Washington River Protection Solutions, LLC (WRPS). As part of tank farm operations, WRPS supports DOE-ORP's waste retrieval mission. An important element of the DOE-ORP mission is the construction and operation of the Hanford Tank Waste Treatment and Immobilization Plant (WTP). The WTP is tasked with separating the waste into low-activity waste (LAW) and high-level waste fractions and immobilizing these fractions by vitrification. The primary contractor supporting the construction of the WTP is Bechtel National, Inc.

To support early production of immobilized LAW, the Direct Feed Low-Activity Waste (DFLAW) process has been proposed. In the DFLAW process, supernatant is sent to the Low-Activity Waste Pretreatment System (LAWPS) for filtration and cesium removal. The resultant treated waste is delivered to the WTP LAW Vitrification Facility for immobilization. The conceptual design and ongoing technology maturation of the LAWPS facility are being conducted by WRPS, but the DFLAW process also necessitates interfaces between WRPS and Bechtel National, Inc. to deliver the treated LAW from the LAWPS to the WTP for vitrification.

Before the feed is transferred to the WTP LAW Vitrification Facility, tank supernatant waste will be pretreated in the LAWPS to meet the WTP LAW waste acceptance criteria. The key process operations for treating the waste include solids separation (by crossflow filtration) and cesium removal (by ion exchange). Figure 1.1shows a general schematic of the anticipated process streams and unit operations.

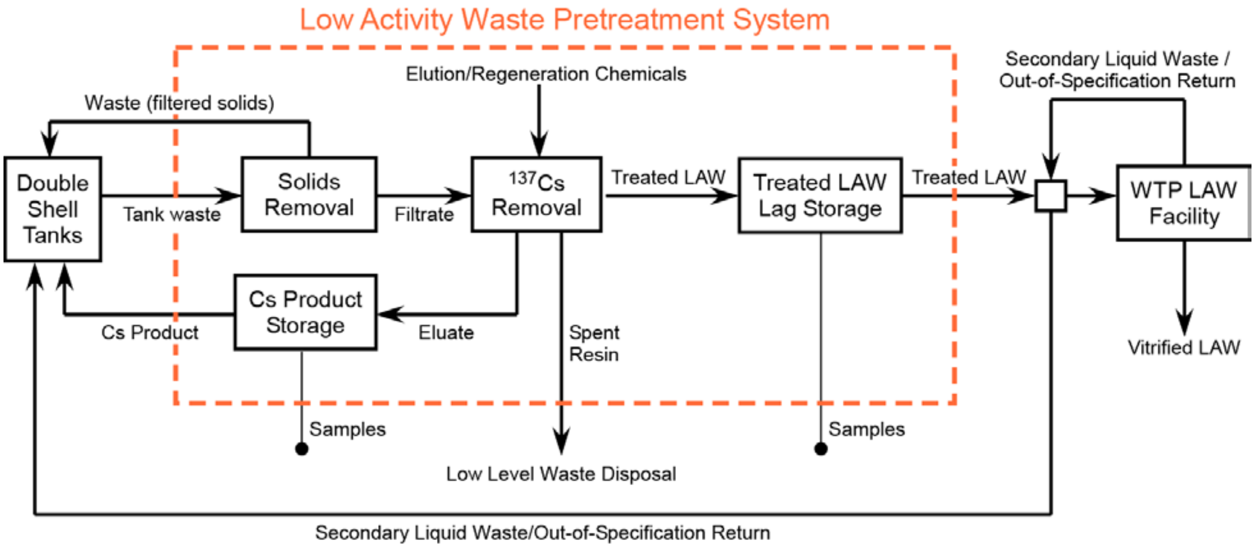

Figure 1.1. General conceptual schematic of the LAWPS facility unit operations and process streams.

To support LAWPS design selections prior to key project milestones (Critical Decisions[1]) and to improve the technology maturation level of the LAWPS, WRPS has planned both an integrated engineering-scale test facility using prototypic equipment and a full-scale test apparatus for the ion exchange columns. To support these larger-scale facilities, WRPS identified five technical tasks in statements of work[2,3,4] to be performed by Pacific Northwest National Laboratory (PNNL). These tasks are distinct from the larger-scale test facilities and are intended to help achieve the following objectives:

- Provide technical information or data that
  - supports refinements or simplifications of larger-scale test facilities; or
  - provides expected performance of unit operations (guiding larger-scale operation or providing scale-up data).
- Support the safety basis of the planned LAWPS facility, specifically regarding hydrogen management.

The five PNNL technical tasks consist of the following focus areas:

1. Development of LAW waste simulants
2. Small-scale crossflow filtration testing with simulants
3. Gas generation measurements in the presence of spherical resorcinol-formaldehyde (sRF) ion exchange resin
4. Gas retention/release dynamics and fluidization of sRF ion exchange resin
5. General technical support to the larger-scale testing

Tasks 1 and 2 are focused on providing technical information to inform the larger-scale test facilities, whereas the Tasks 3 and 4 support the LAWPS facility safety basis. Task 5 directly supports the larger-scale testing. This report details work performed to address Task 3, "Gas generation measurements in the presence of sRF ion exchange resin."

Gas generation during LAWPS operations can come from three main sources: thermal degradation of organic species, radiolytic degradation (both of water and organic species), and corrosion processes. Some of the constituents of tank wastes inhibit both corrosion and radiolytic generation of hydrogen (e.g., NO_2^- and NO_3^-). Currently, the estimation of gas generated in Hanford tank wastes is performed using a model derived empirically from a study using a large number of waste simulants and actual tank wastes (Hu 2004, 2012), typically referred to as the Hu model. Within the gas generation model, the waste constituents that affect the generation rate (either inhibiting or enhancing the rate) include total organic carbon [TOC], $[NO_2^-]$, $[NO_3^-]$, $[Na^+]$, and $[Al^{3+}]$. The effect of sRF resin on this gas generation is not well understood, as the current state of knowledge in gas generation from sRF ion exchange resin in tank waste simulants is derived from two studies (comprised of a sum total of four tests; see Duffey and Walker 2006

---

[1] Critical Decisions (CDs) are defined in DOE O 413.3B, *Program and Project Management for the Acquisition of Capital Assets*, dated 12/20/2016. The relevant CDs being supported as described in the text of this report are CD-2, Approve Performance Baseline, and/or CD-3, Approve Start of Construction/Execution.

[2] Statement of Work, July 29, 2015, Requisition 279909, LAWPS Integrated Support Testing, Rev. 1.

[3] Statement of Work, April 4, 2016, Requisition 279909, LAWPS Integrated Support Testing, Rev. 2.

[4] Statement of Work, August 31, 2016, Requisition 279909, LAWPS Integrated Support Testing, Rev. 3.

and Birdwell et al. 2010). The current safety basis for hydrogen generation is based on the previous testing that was performed, which indicated a 40% increase in hydrogen generation with sRF resin present over that of liquid alone; therefore, the safety basis has been using 1.4 times the Hu model for water as the maximum possible hydrogen production within the facility. The effect of the sRF resin is twofold: first, when it is loaded with radio-cesium, it is a source for radiation, and second, it provides organic material that can be radiolytically and thermally degraded to generate hydrogen. During operations of the ion exchange columns in LAWPS, four separate solutions come in contact with the loaded ion exchange resin: 1) waste feed, 2) dilute sodium hydroxide rinse, 3) water rinse, and 4) 0.45 molar nitric acid elution solution. Of these four, the water rinse step is expected to provide the greatest potential for hydrogen gas generation. The simple solutions of dilute hydroxide and nitric acid should generate hydrogen gas at rates less than or equal to the generation rate in the water rinse, but are expected to have higher hydrogen generation rates than waste feed. As provided for in the gas generation model, Hanford tank wastes have components that can both inhibit and enhance the generation of hydrogen gas. Testing was needed to determine the effect of the sRF resin on gas generation and the applicability of the existing gas generation models.

Initially, potential simulants were evaluated using the Hu model and the testing conditions were agreed upon in consultation with WRPS. The technical approach to the testing is described in addition to the results of the testing. Water, 5.6M Na nominal feed simulant (Russell et al. 2017), and 0.45M HNO_3 were tested alone and in the presence of sRF simulant at 25 °C, 45 °C, and 70 °C, in duplicate, with and without exposure to radiation. Additionally, the 5.6M Na nominal feed simulant with 1%(w/w) TOC in the form of Na_3-HEDTA (N-(2-Hydroxyethyl)ethylenediaminetriacetic acid) was tested with and without resin at 70 °C in duplicate. In each test, the delivered total dose was approximately 300 MRad (± 10%). This report presents the experimental details as well as the testing results for all of the conditions tested.

2.0 Quality Assurance

This work was conducted with funding from WRPS under contract 36437-187, *"LAWPS Integrated Support Testing," Low-Activity Waste Pretreatment System (LAWPS) Integrated Testing Project*. The work was conducted as part of PNNL project 67535.

All research and development (R&D) work at PNNL is performed in accordance with PNNL's Laboratory-Level Quality Management Program, which is based on a graded application of NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*, to R&D activities. To ensure that all client quality assurance (QA) expectations were addressed, the QA controls of the WRPS Waste Form Testing Program (WWFTP) QA program were also implemented for this work. The WWFTP QA program implements the requirements of NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*, and NQA-1a-2009, *Addenda to ASME NQA-1-2008*, and consists of the WWFTP Quality Assurance Plan (QA-WWFTP-001) and associated QA-NSLW-numbered procedures that provide detailed instructions for implementing NQA-1 requirements for R&D work.

Specific details of this project's approach to assuring quality are contained in the *LAWPS Testing Program Quality Assurance Plan* (67535-QA-001, Rev. 0) and associated implementing procedures. The QA plan describes how the procedures of the WWFTP QA program were used in conducting the work. The work described in this report was assigned the technology level "Applied Research," and was planned, performed, documented, and reported in accordance with procedure QA-NSLW-1102, *Scientific Investigation for Applied Research*. All staff members contributing to the work received proper technical and QA training prior to performing quality-affecting work.

3.0 Evaluation of Simulants for Gas Generation Testing

Prior to conducting gas generation testing, the hydrogen generation rates for various liquids, both LAWPS process liquids and simulated liquid wastes, were modeled. The modeled results were presented to WRPS early in the project to guide the direction of gas generation testing. The modeled results are presented here.

3.1 The Hu Model

LAWPS process liquids and potential tank waste simulants were evaluated for the potential for hydrogen gas production using the Hu model (Hu 2004, 2012). The Hu model is an empirical model that was derived, based on actual hydrogen generation measurements, to describe the hydrogen generation behavior of the Hanford waste tanks.

The model is divided into empirically derived terms that describe the hydrogen generation (HGR) from various waste components as a thermal organic term ($HGR_{THM\ Org}$), a radiolytic organic term ($HGR_{RAD\ Org}$), a radiolytic aqueous term ($HGR_{RAD\ H2O}$), and a corrosion term (HGR_{corr}). For the purposes of the modeling for gas generation testing that was to be conducted with only gamma dose and in stainless steel (e.g., corrosion-free), the terms involving alpha dose and corrosion were assumed to be zero. Therefore, the modeling was conducted using the following equations:

$$HGR = HGR_{THM\ Org} + HGR_{RAD\ Org} + HGR_{RAD\ H_2O}\ ,$$

where

$$HGR_{THM\ Org} = a_{thm} \times \left(r_f \times [\mathrm{TOC}]\right) \times [\mathrm{Al}]^{0.4} \times L_f \times e^{\left(-\frac{E_{thm}}{RT}\right)}\ ,$$

$$HGR_{RAD\ Org} = [G^{\substack{\beta\\\gamma}}_{(H_2)_{ORG}} \times H^{\substack{\beta\\\gamma}}_{load}] \times L_f \times CF_1\ ,$$

and

$$HGR_{RAD\ H_2O} = [G^{\substack{\beta\\\gamma}}_{(H_2)_{H_2O}} \times H^{\substack{\beta\\\gamma}}_{load}] \times L_f \times CF_1\ ,$$

with

$$G^{\beta/\gamma}_{(H_2)_{ORG}} = a_{rad} \times e^{(-\frac{E_{rad}}{RT})} \times \left(r_f \times [\mathrm{TOC}]\right),$$

and

$$G^{\substack{\beta\\\gamma}}_{(H_2)_{H_2O}} = \frac{0.32}{1+2.4[\mathrm{NO_3^-}]+0.62[\mathrm{NO_2^-}]+0.31[\mathrm{Na^+}]_{ex}^2} + \frac{0.13}{1+139[\mathrm{NO_3^-}]+54[\mathrm{NO_2^-}]}\ ,$$

and where

E_{thm} = 89.6 kJ/mol = activation energy for the thermal reaction

$a_{thm} = 4.56\times10^{4}$ mol/kg·s = pre-exponential factor of the thermal rate

E_{rad} = 48.8 kJ/mol = activation energy in organic radiolysis G

$a_{rad} = 1.11\times10^{7}$ molecules H_2/100 eV = pre-exponential term in organic radiolysis G

r_f = 0.6 for double-shell tanks and 0.3 for single-shell tanks = TOC reactivity coefficient

R = 8.314 J/mol·K = gas constant

[TOC] = TOC concentration in the simulated liquid waste (wt%)

[Al] = aluminum ion concentration in simulated liquid waste (wt%)

$[\mathrm{NO_3^-}]$ = nitrate ion concentration in the simulated liquid waste (M)

$[\mathrm{NO_2^-}]$ = nitrite ion concentration in the simulated liquid waste (M)

$[\mathrm{Na^+}]_{ex}$ = concentration of sodium minus nitrate and nitrite concentration in simulated liquid waste (M)

$H_{load}^{\frac{\beta}{\gamma}}$ = total heat load from beta/gamma radiation (W/kg)

L_f = liquid weight fraction

T = temperature (K)

CF_1 = conversion factor from (molecules H_2/100eV)(W/kg) to (mole/kg·s)

3.1.1 Modeling Assumptions and Conditions

As stated previously, in the case of the gas generation experiment specifically, only gamma dose was modeled, so the terms involving alpha dose were zero. Within the LAWPS ion exchange column, the alpha dose rate is anticipated to be negligible after the ultrafiltration. Additionally, the materials of construction of the column should not contribute to hydrogen generation through the effects of corrosion. The modeled conditions were for the gas generation experiment as well as the anticipated operating conditions of the LAWPS facility. To that end, the following conditions were modeled and are reported here: 25 °C operating temperature and 310 kRad/hr dose rate, 45 °C operating temperature and 310 kRad/hr dose rate, and 45 °C operating temperature and 42.6 kRad/hr dose rate (this last dose value is For Information Only [FIO]). The first two conditions listed above covered the original two temperatures and the anticipated dose rate in the gas generation experiment. The final model condition represents the maximum designed operating temperature for the LAWPS facility and the anticipated dose rate (as calculated by PNNL radiological engineers using MicroShield®, assuming a point source from the center of a 42-inch-diameter × 50-inch-high resin column) for the ion exchange resin fully loaded with 106,000 Ci of Cs-137. Note that the dose estimate for the LAWPS facility is an FIO estimate. It should also be noted that for the most part, G-values are not dose rate dependent, and as shown above, hydrogen generation has a linear relationship with dose rate. The TOC reactivity coefficient (r_f) of 0.6 was employed as a 'worst-case' scenario for hydrogen generation by assuming that the TOC present has a high activity for hydrogen generation. The liquid fraction (L_f) of 1.0 was used because the assumption is that all of the gas generation is happening in the liquid phase and the modeling was conducted for liquids only.

3.2 Liquid Compositions Evaluated by the Hu Model

A variety of liquid compositions were modeled using the Hu model to cover a range of sodium, nitrate, nitrite, aluminum, and TOC concentrations. Most of the modeled liquids were tank waste simulants with their compositions taken from Golcar et al. (2000), unless noted. Other liquids were modeled as they are intended for use in the LAWPS process. The bounding case was anticipated to be water, which has a G-value of 0.45, the largest possible G-value for Hu model liquid inputs. Table 3.1 lists the compositions of each of the liquids in terms of their Hu model inputs. Liquid simulants were modeled with and without TOC if their recipes contained TOC. The original intention of this was to select simulants without TOC for testing to allow for the sRF resin to act as the organic in solution and not convolute the effects of added resin with additional TOC.

Table 3.1. Modeled Simulant Compositions

Simulant	[TOC] (wt%)	[NO_2^-]	[NO_3^-]	[Na^+]	[Al^{3+}] (wt%)	Comments
Water	0	0	0	0	0	LAWPS process liquid
Target Feed (5.6M Na simulant)	0	1.02	1.78	5.574	0.350	Initial anticipated concentrations, prior to initial simulant letter report
5.6M Na Simulant with 1% (w/w) TOC as Na_3-HEDTA	1	1.02	1.78	5.887	0.35	Target feed with significant amount of TOC added
Dilute Complex Concentrate Feed AN-102	1.06	0.3	0.9	2.2	0.382	Golcar et al. 2000
AN-107 Simulant	0.976	0.296	2.02	5	0.105	Golcar et al. 2000
A-101	0.158	0.83	0.92	5.01	0.928	Golcar et al. 2000
AN-102 Complex Concentrate	0.976	0.471	1.29	5	0.421	Golcar et al. 2000
AZ-102 Simulant	0	0.43	1.669	4.987	0.943	Golcar et al. 2000
IX Test Feed	0	0.831	2.04	5.012	0.329	Russell et al. 2014
Dilute HNO_3	0	0	0.45	0	0	LAWPS process liquid
Dilute NaOH	0	0	0	2.0	0	LAWPS process liquid (originally modeled as 2M)

3.3 Modeled Hydrogen Generation Rates

Figure 3.1 shows the modeled hydrogen generation rates of the modeled liquids. As expected, according to the Hu model, water has the largest hydrogen generation rate of the liquids that were modeled, with the NaOH resin regeneration liquid and the 0.45M HNO_3 resin cesium elution liquid following closely. The only exception is for a tank waste that is known to have high levels of organic complexant such as AN-102, which, according to Golcar et al. (2000) contains almost 1% (w/w) TOC and has a modeled hydrogen generation rate greater than the nitric acid condition if the TOC is included in the modeling.

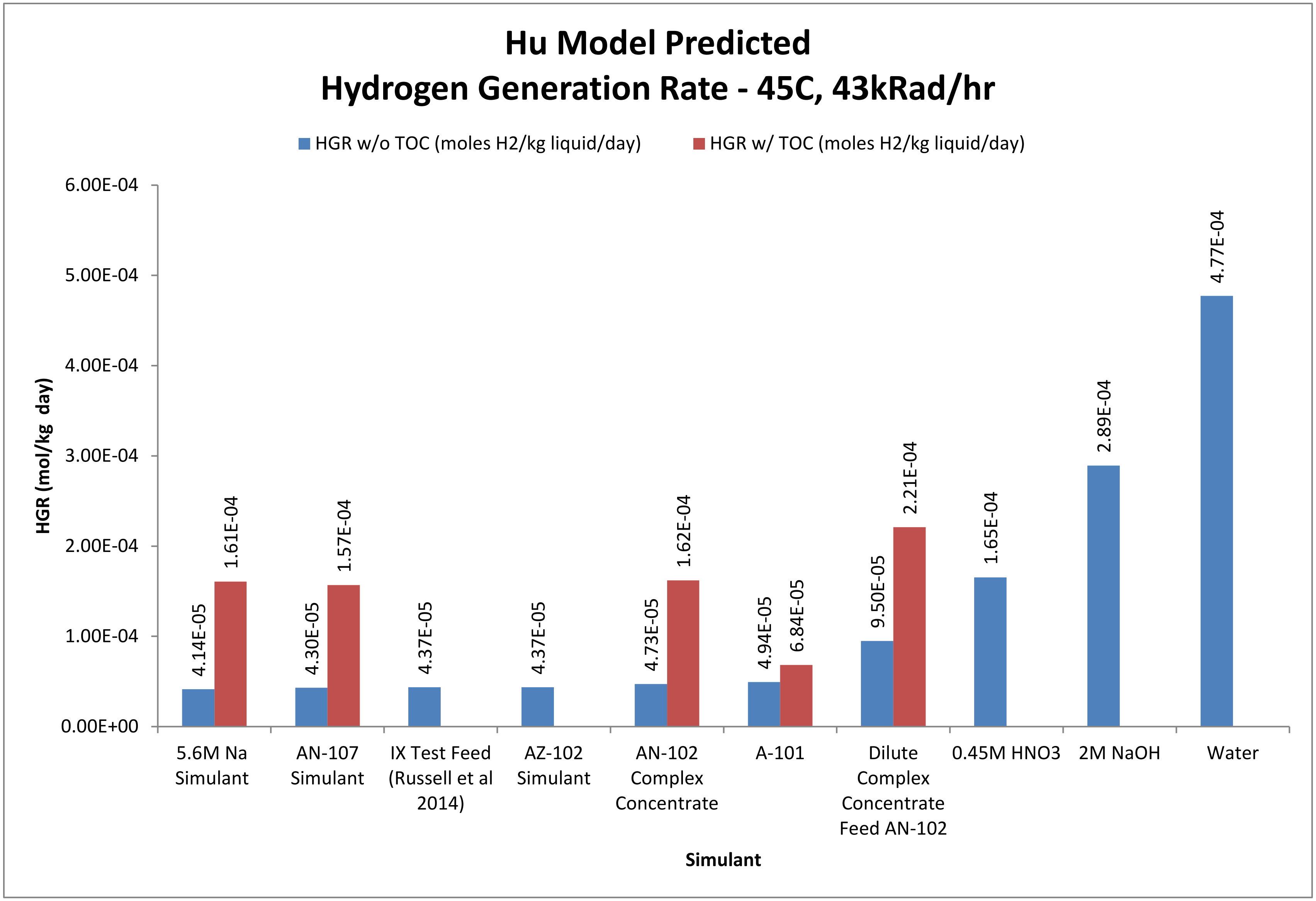

Figure 3.1. Modeled hydrogen generation rates of simulants and LAWPS process liquids.

4.0 Experimental

PNNL has extensive experience measuring the gas generated by actual Hanford tank waste. During the period of 1996-1999, gas generation rates were measured for six Hanford tank waste types, both with and without external radiation exposure (Bryan et al. 1996; King et al. 1997; King and Bryan 1998, 1999). Based on this experience, PNNL reproduced the gas generation apparatus for use in the current sRF resin gas generation testing, described in detail in Section 4.1.

4.1 Experimental Conditions and Equipment

Gas generation experiments were conducted under conditions in which the ideal gas law applies, meaning that at a fixed temperature and volume, if the number of moles of gas increases, then the pressure of the vessel will increase. The gas composition is measured via mass spectrometry, so the number of moles of each gas in each vessel can be calculated if the total number of moles of gas is known.

No air testing was specified. The rationale for excluding oxygen is based on experience with actual waste experiments detailed in Bryan et al (1996). In the sRF resin experiments, the testing was designed to mimic the process conditions for gas generation expected to be seen by the resin in the LAWPS deployment. That is, in a closed column system not actively ventilated with air or other source of oxygen it is unlikely that oxygen (or air) would be in direct contact with the resin bed during use, and considering the low solubility and diffusion of oxygen into the system, this parameter was excluded from testing.

Gas generation measurements were made using reaction vessels and a gas manifold system similar to those used in studies performed on simulated and actual Hanford tank wastes as described by Bryan and Pederson (1994, 1995). As in the past testing, the current gas generation rate measurements are made using reaction vessels and a gas manifold system. Two systems were constructed, one for the irradiated vessels and one for the thermal-only testing. The reaction vessels are connected to the gas manifold using small-diameter stainless steel connecting tubing. Small-diameter tubing was selected to minimize condensate collection in the tubing and to minimize the unheated portion of the system. Little to no condensate was observed in the tubing at the end of testing. Each reaction vessel has its own pressure transducer connected to the vessel’s gas manifold line. The entire surface of the reaction system exposed to the simulant sample is stainless steel, except for a gold-plated copper gasket sealing the flange at the top of the reaction vessel. Figure 4.1 shows a schematic of a reaction vessel with thermocouple placement in relation to the gas manifold system. Figure 4.2 is a photo of thermal gas generation manifold with attached gas generation test vessels, which was built specifically for this testing.

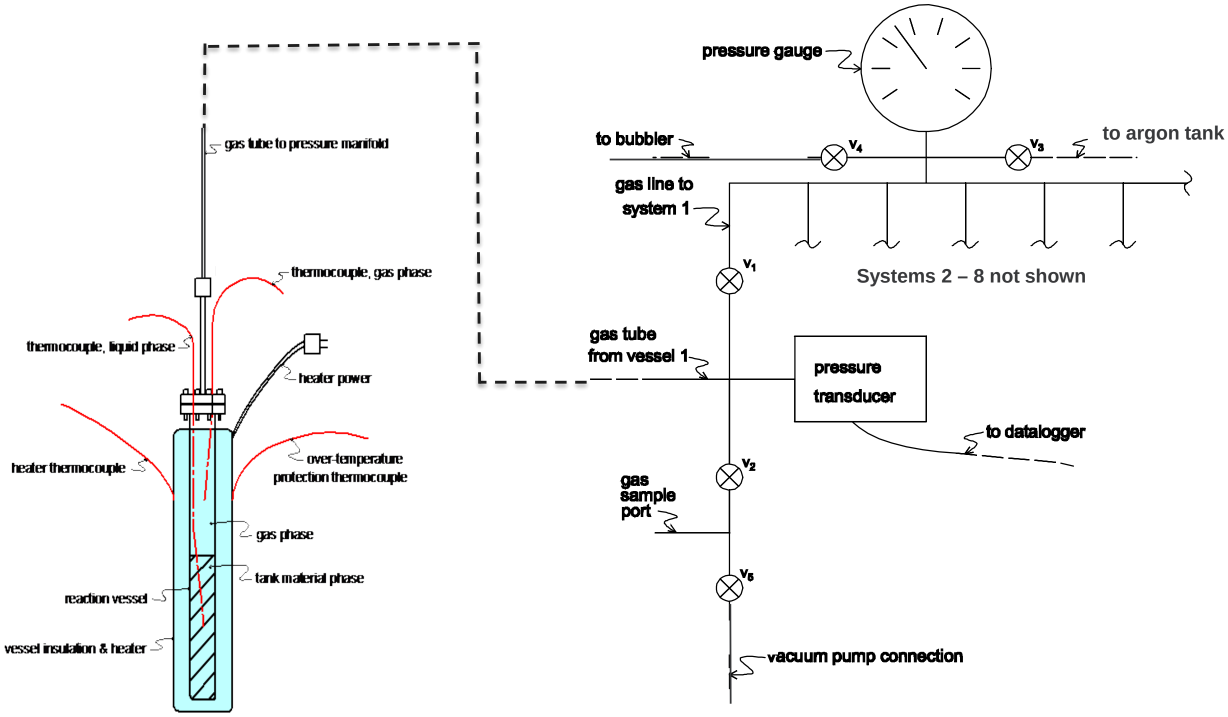

Figure 4.1. Schematic of the gas generation manifold with attached gas generation test vessel.

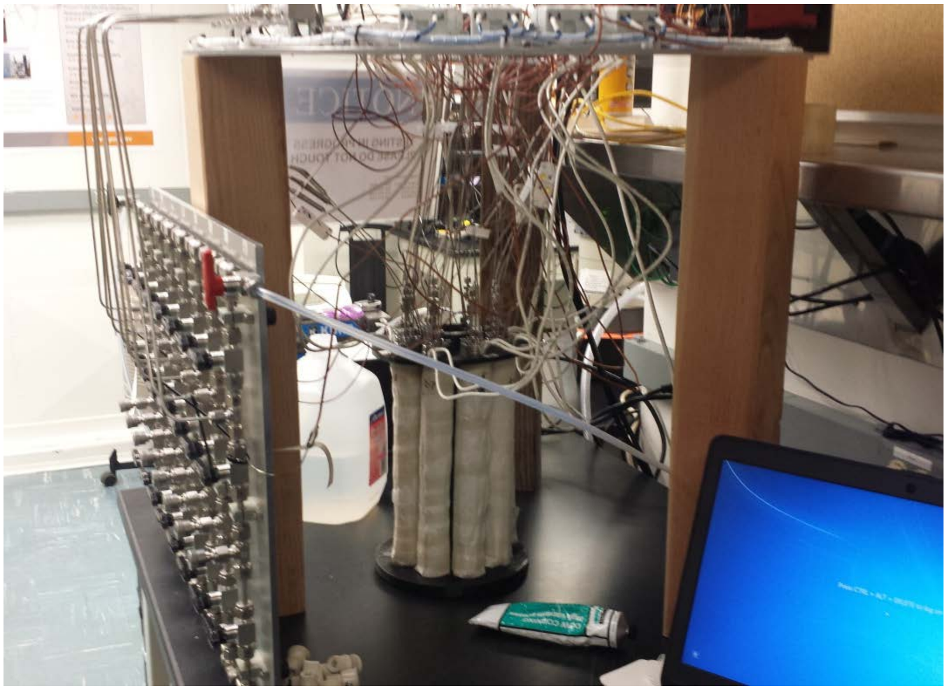

Figure 4.2. Photo of the thermal gas generation manifold with attached gas generation test vessels.

Sample irradiation experiments were performed at the High Exposure Facility (HEF) within the 318 Building at PNNL. Due to the long duration of the irradiation exposures (35 to 40 days), a lead-lined bunker was constructed next to the HEF to house the gas generation experiment payload with the ~1500 Ci Co-60 source centered on the gas generation test vessels. The bunker provides 8 inches of solid poured lead for shielding. Figure 4.3 shows the design drawing of the bunker, including a cut-away showing the sample carousel/source holder and the bunker plug, which is also lead-filled. The cutaway shown at left includes the gas generation vessel carousel that also holds the gamma source in the center, and the bunker plug including compound angle tubes for cable and gas line pass-through. The modeled external dose rate was expected to be < 50 mrem/hr. The actual external dose rates at the surface of the bunker closest to the source were closer to 30 mrem/hr.

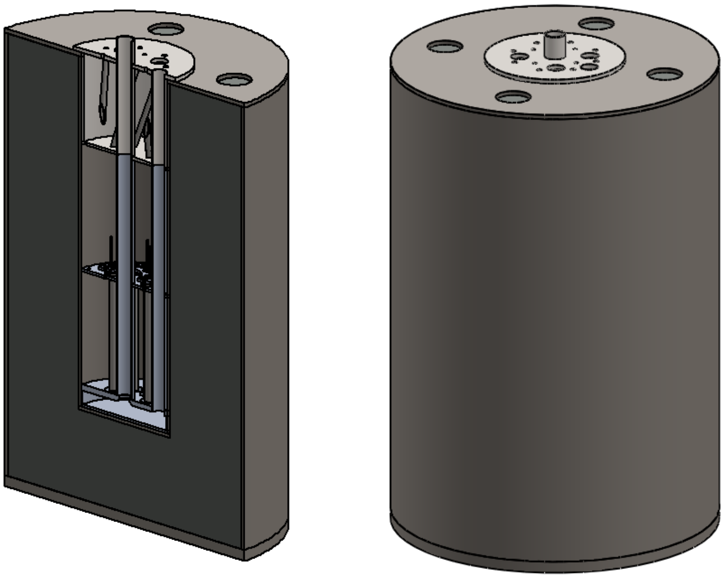

Figure 4.3. Schematic drawing of the “gamma bunker” used for gas generation testing.

The photo on the left in Figure 4.4 is of the radiolytic “gamma bunker” in the background with the bunker payload (carousel attached to the bunker plug and manifold) staged to be transferred into the bunker prior to source transfer. The photo on the right in Figure 4.4 is a close-up view of the gas generation test vessels in the carousel prior to being loaded into the bunker. Figure 4.5 shows a picture of the assembled irradiation system in place for testing after source transfer. In the case of the 25 °C and 45 °C testing, the bunker was actively cooled by flowing dry, compressed air through a freezer (not shown) and into the bunker. In Figure 4.5, the attached gas generation test vessels are within the bunker and are not in view.

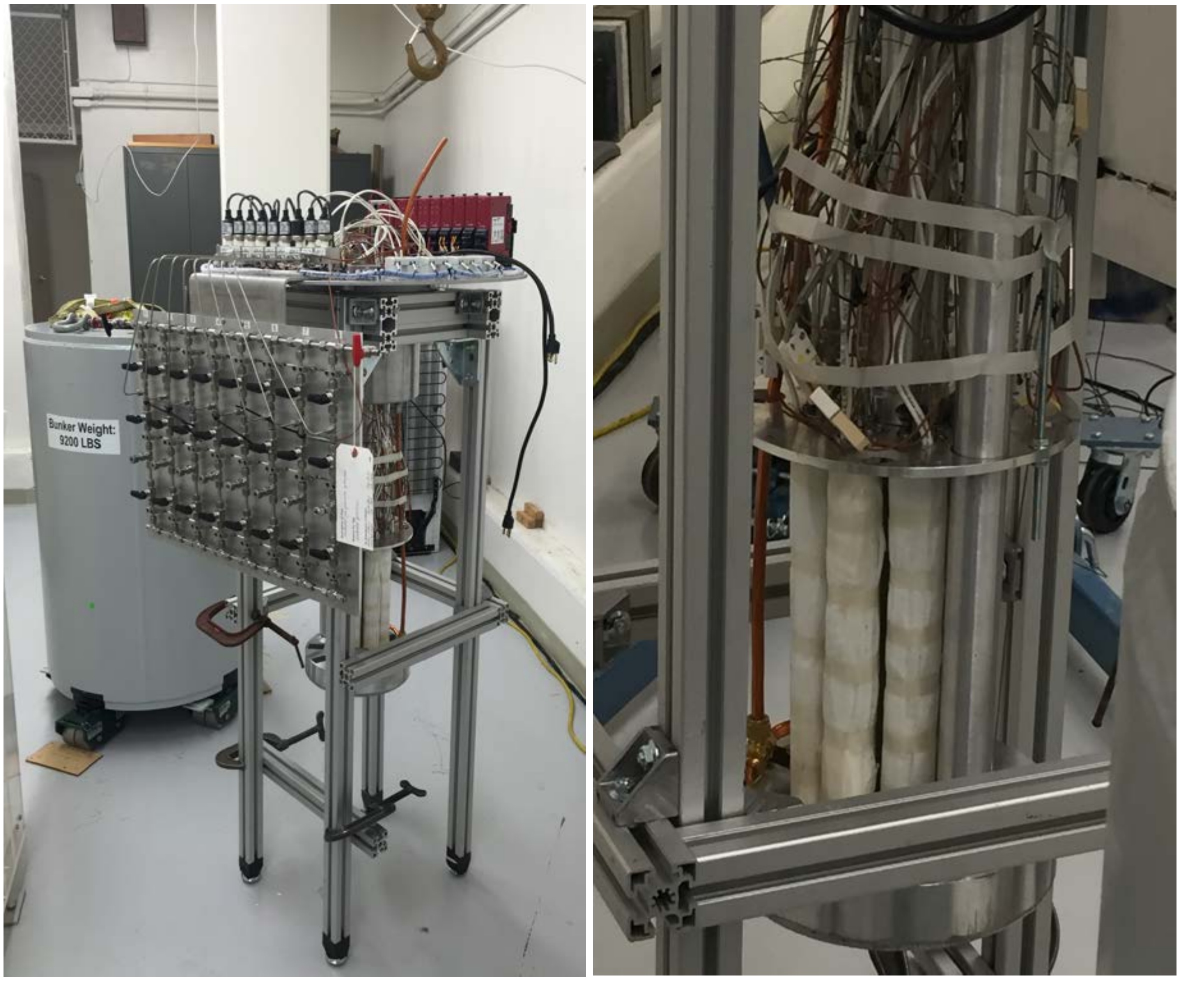

Figure 4.4. Photograph of the gamma bunker payload (left) and close-up photo of the gas generation vessels loaded into the carousel prior to loading into the gamma bunker (right).

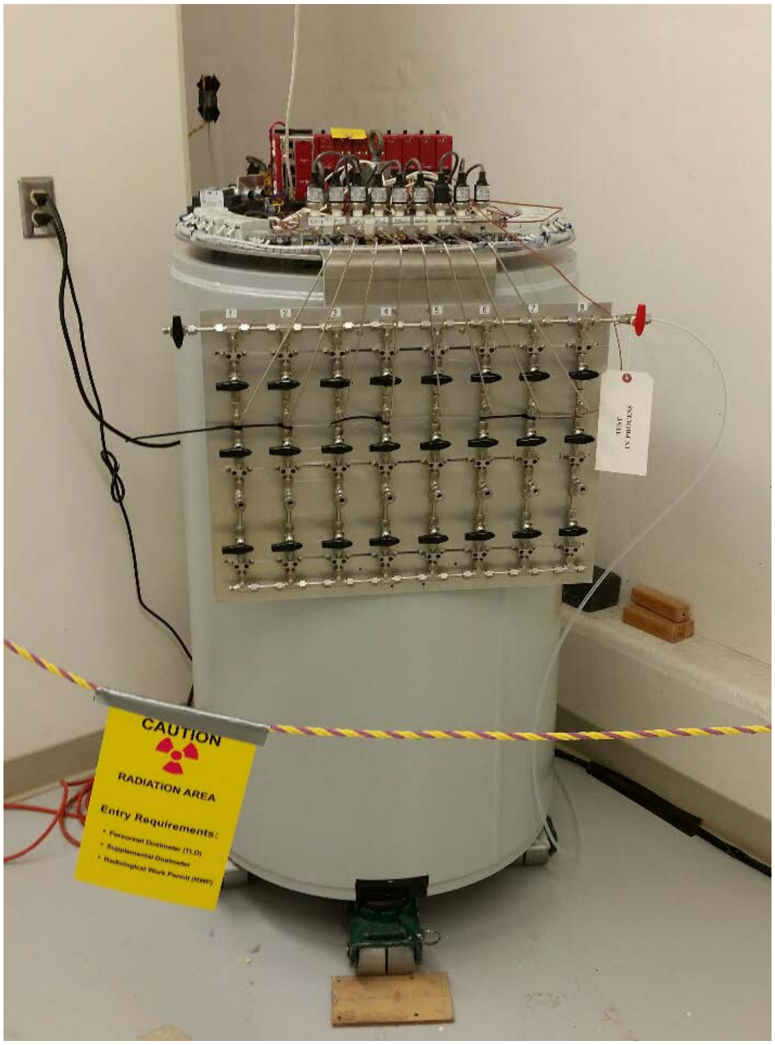

Figure 4.5. Assembled irradiation system with the source in place.

4.2 Gas Generation System Tests

To ensure that the moles of gas could be measured accurately when the reaction vessel temperature was changed, an experiment was conducted in which a known quantity of gas was measured at various reaction vessel temperatures. The reaction vessel temperature was increased from a starting temperature set-point of 25 °C to a set-point of 45 °C and held for approximately an hour, and then was increased to a temperature set-point of 70 °C, where it was held for approximately 20 hours. After the overnight hold, the vessels were cooled to a set-point of 45 °C for approximately an hour and then to a set-point of 25 °C and held for approximately an hour. This temperature range encompassed the expected temperature range for gas generation testing at the beginning of the project. The pressure of each vessel increased as the temperature increased. The number of moles calculated in each vessel remained constant. The results of each system test are described below.

4.2.1 Gas Generation System 1 (Rad System)

Figure 4.6 shows the temperature profiles of the eight vessels in Gas Generation System 1 during the system test. Figure 4.7 shows the pressure profiles of the eight vessels in Gas Generation System 1 during the system test. The corresponding example moles calculation is shown in Figure 4.8 while Table A.1 shows the mean calculated moles for each vessel in System 1 based on the measured temperatures and pressures from the system test. The standard deviation, percent relative standard deviation (% RSD), and % spread in the number of calculated moles are also presented. The % RSD for all vessels is less than 0.3% with a spread in the calculated moles of less than 2% in all vessels.

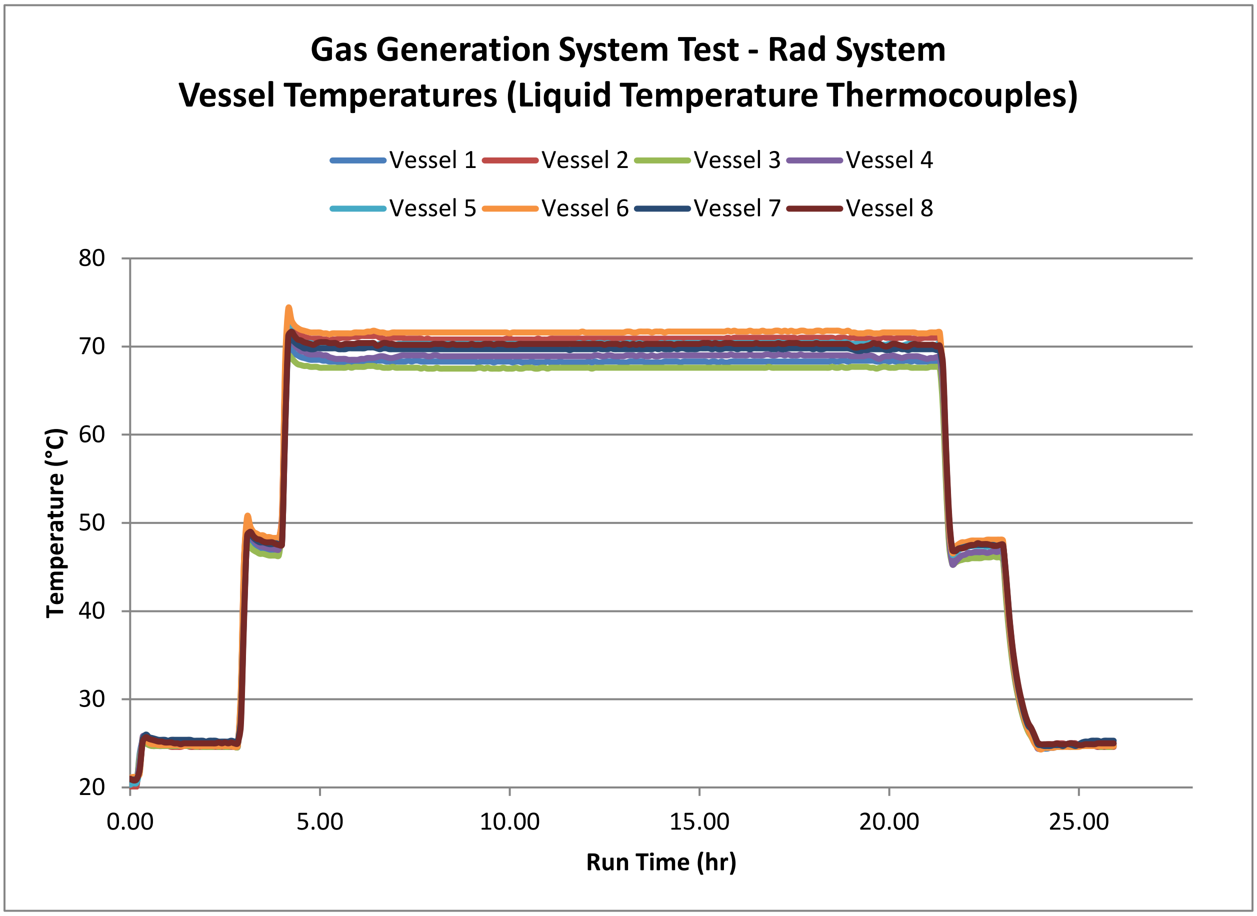

Figure 4.6. Gas Generation System 1, system test temperature profiles.

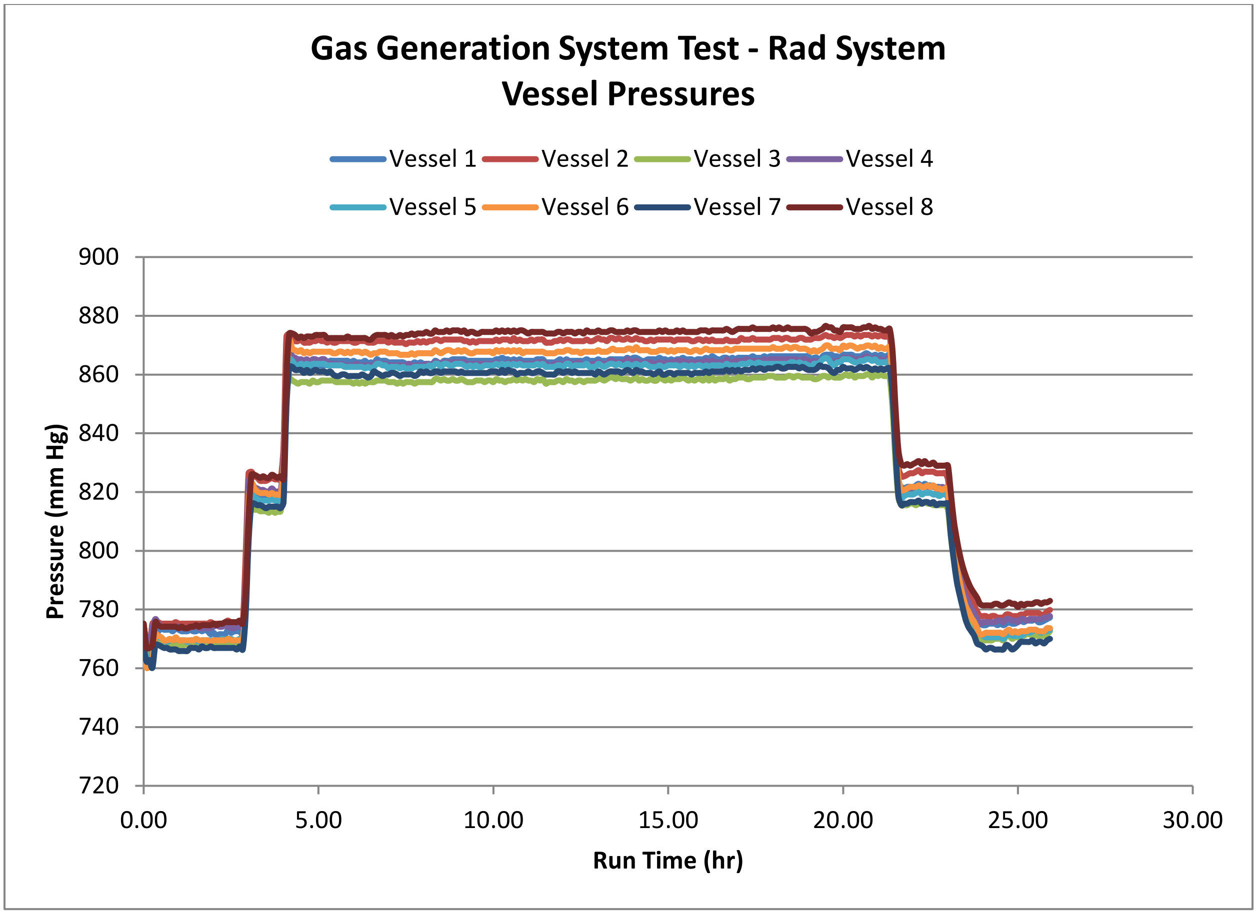

Figure 4.7. Gas Generation System 1, system test pressure profiles.

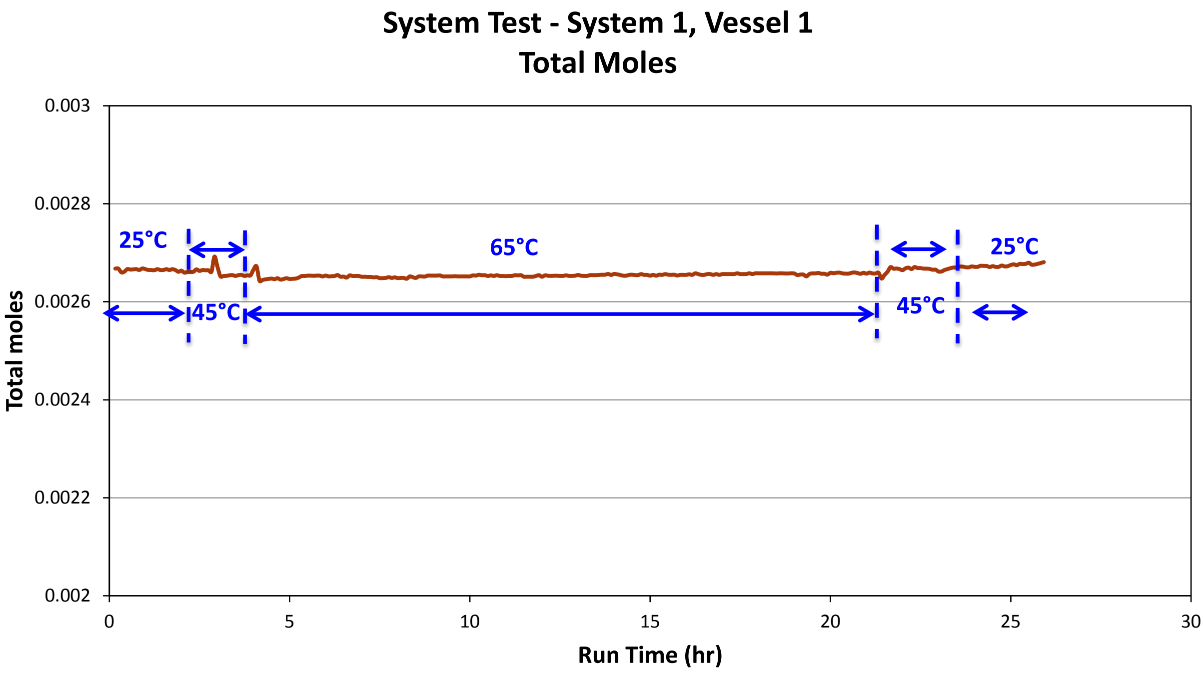

Figure 4.8. Gas Generation System 1; gas generation system test – moles calculation for Vessel 1.

Table 4.1. System 1 (w/ radiation) System Test Results

	Channel 1	Channel 2	Channel 3	Channel 4	Channel 5	Channel 6	Channel 7	Channel 8
Mean	0.002713	0.002701	0.002694	0.00271	0.002687	0.002731	0.002654	0.002725
Std. Dev.	6.21E-06	7.52E-06	4.87E-06	5.96E-06	4.83E-06	6.13E-06	5.13E-06	7.88E-06
% RSD	0.229	0.279	0.181	0.220	0.180	0.224	0.193	0.289
% Spread	1.661	1.961	0.943	1.623	1.467	1.041	1.261	1.276

4.2.2 Gas Generation System 2 (Thermal-only System)

System 2 had temperature and pressure profiles that were very similar to System 1, as can be seen in Figure 4.9 and Figure 4.10, respectively. The corresponding example moles calculation is shown in Figure 4.11 while Table A.1 shows the mean calculated moles for each vessel in System 2 based on the measured temperatures and pressures from the system test. The standard deviation, % RSD, and % spread in the number of calculated moles are also presented. The % RSD for all vessels is less than 0.25% with a spread in the calculated moles of less than 1.3% in all vessels.

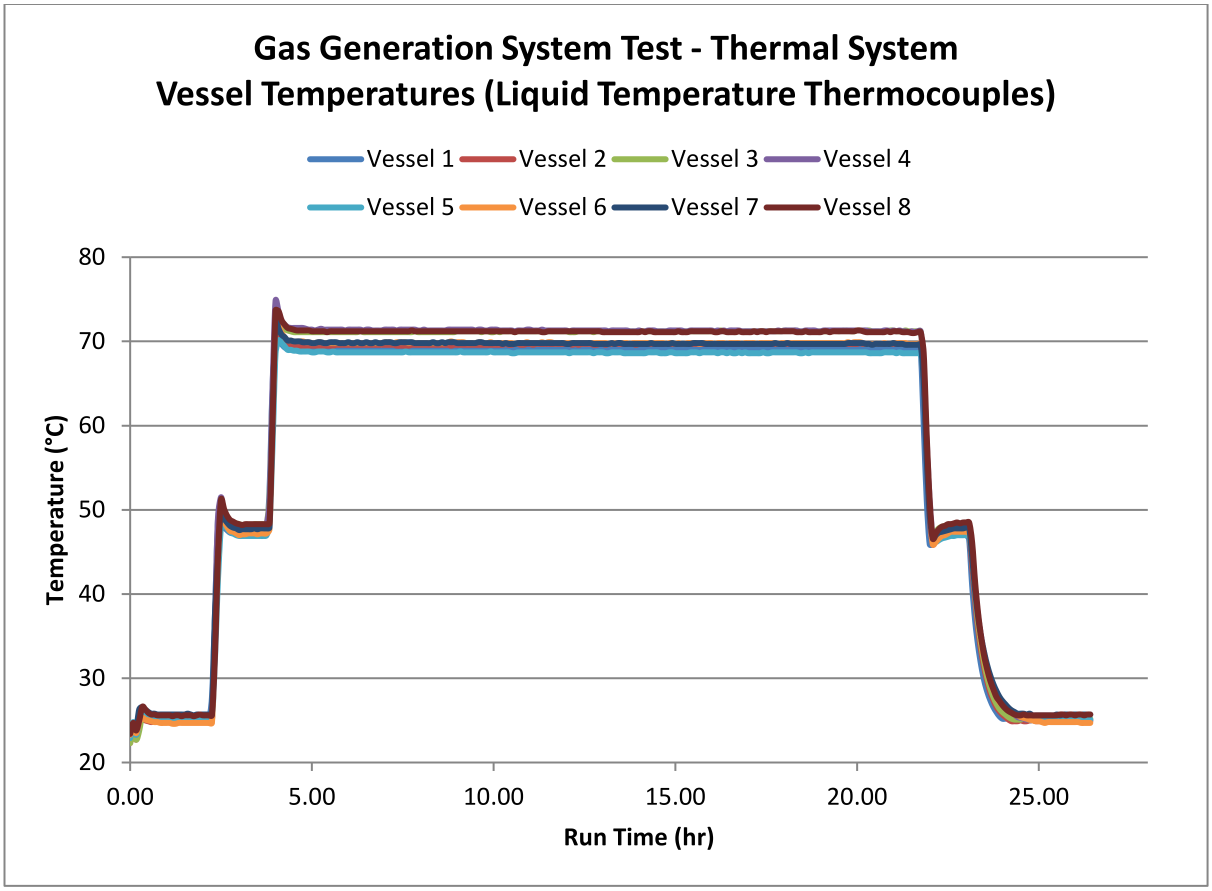

Figure 4.9. Gas Generation System 2, system test temperature profiles.

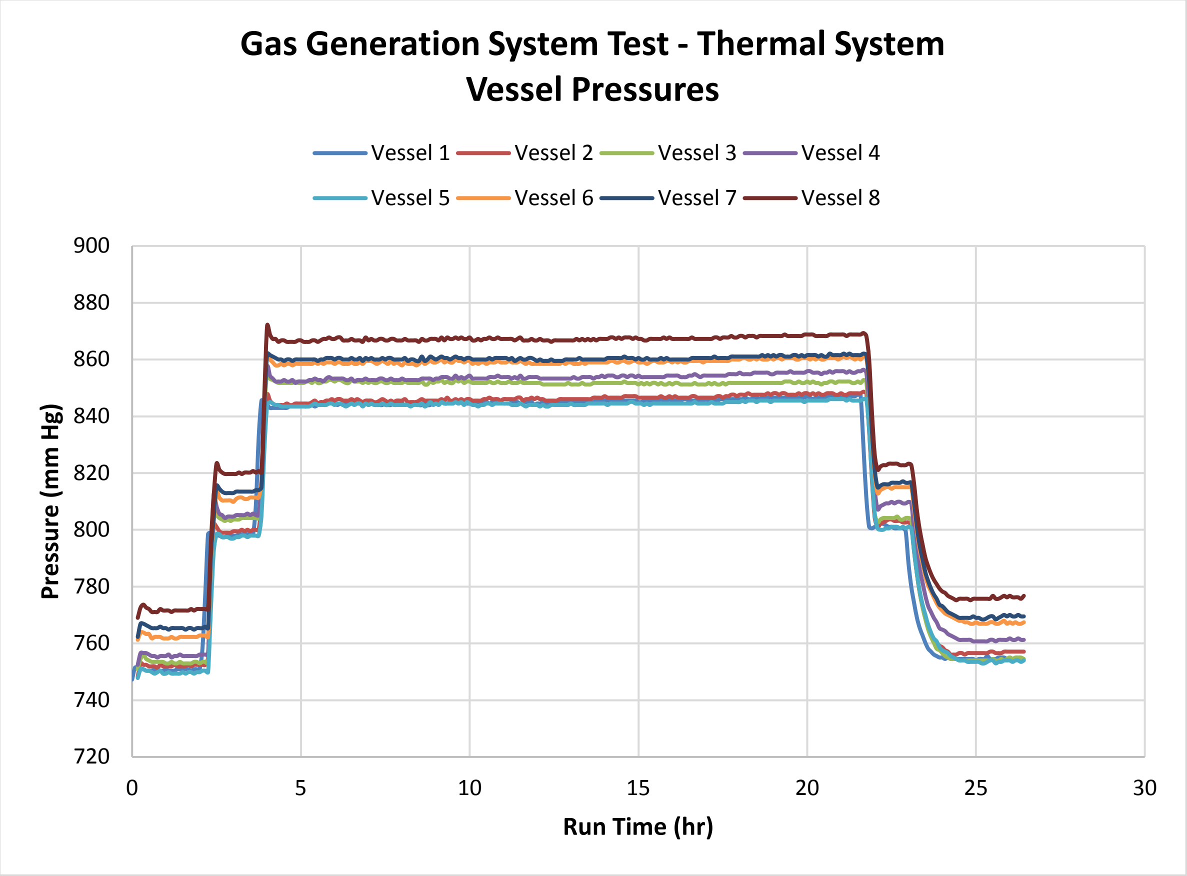

Figure 4.10. Gas Generation System 2, system test pressure profiles.

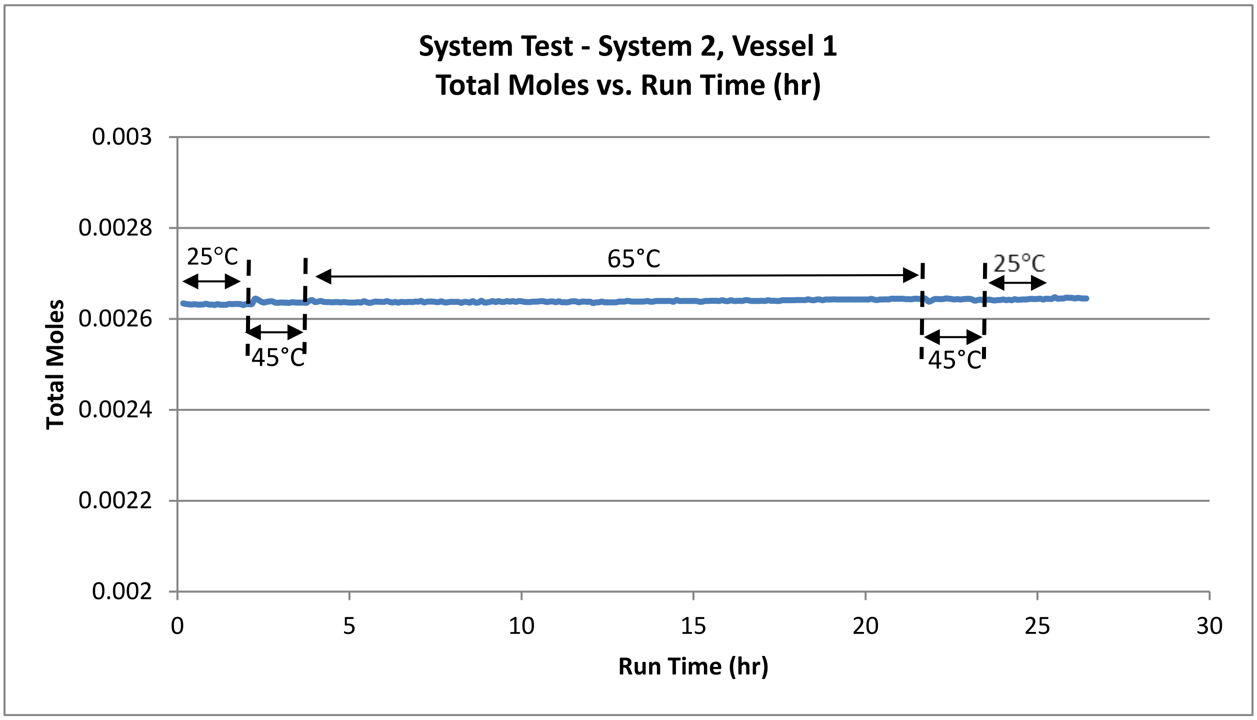

Figure 4.11. Gas Generation System 2; gas generation system test – moles calculation for Vessel 1.

Table 4.2. System 2 (thermal) System Test Results

	Channel 1	Channel 2	Channel 3	Channel 4	Channel 5	Channel 6	Channel 7	Channel 8
Mean	0.002639	0.002632	0.002656	0.002656	0.002662	0.002676	0.002669	0.002691
Std. Dev.	3.49E-06	5.39E-06	4.34E-06	5.98E-06	5.11E-06	5.64E-06	4.9E-06	5.52E-06
% RSD	0.132	0.205	0.163	0.225	0.192	0.211	0.183	0.205
% Spread	0.645	0.860	1.250	1.185	1.109	1.025	0.802	1.278

4.3 Simulant Preparation and sRF Resin Conditioning

4.3.1 Simulant Preparation

Simulant preparation was conducted with American Chemical Society (ACS) reagent grade materials. For the simulants with added NaOH, it was added in the form of a commercially supplied 50% (w/w) solution. The minor constituents in any simulant recipes were added from stock solutions so as not to rely on weighing milligram quantities of minor constituents. All other components were obtained and added directly as salts. The final volume was obtained through the addition of deionized (DI) water. The simulant preparations were filtered prior to loading into the vessels for testing.

4.3.2 sRF Resin Handling and Preparation

The sRF resin production batch 1F-370/1392 was supplied by WRPS and was used for gas generation testing. PNNL's approach to handling the sRF resin is described in the document *PNNL Resin Handling Approach* [1] , issued by the project that conducted the testing described in this report. The process for sampling resin from the original containers is discussed in project document GD-LPIST-001, Rev. 0.0.[2] A sample of the sRF resin batch was collected in sufficient volume to complete all of the gas generation testing. The collected sRF resin-water slurry samples were flushed with argon gas to remove entrained O_2 and then tightly capped. Aliquots from this sample were collected for gas generation testing as needed and the parent sample material was flushed again with argon gas.

Aliquots of the sampled resin were pretreated as outlined in the document *PNNL Resin Handling Approach* and the references therein. Briefly, the resin was conditioned for use by cycling from acid form to base form twice. The resin started out (as supplied by WRPS) in acid form and after rinsing with DI water was converted to base form (or Na-form) with the addition of 1.0M NaOH. After rinsing, the resin was converted back to acid form (H-form) using 0.45M HNO_3. If H-form resin was used, processing was stopped here after rinsing. If Na-form resin was used, the resin was soaked in 1.0M NaOH after rinsing and then rinsed prior to use. In both the Na-form and H-form cases, the final resin was suspended in the test liquid prior to use.

When aliquoting for gas generation testing was needed, a known volume of resin was transferred to the gas generation vessels and excess liquid was decanted to just above the top surface of the resin. An aliquot was sampled for F-factor (water content) analysis to determine the dry mass per unit wet resin volume that was used in calculations. The F-factor was determined by drying the F-factor samples at 45 °C under vacuum until constant mass was achieved.

4.3.3 Vessel Loading

Test vessels were prepared by wrapping heat tape around the exterior with two thermocouples, one for the heater/controller for the vessel and one for over-temperature control.

Vessels were loaded with simulant, water, simulant with resin, or water with resin as specified in the governing test instruction. Prepared vessels were temporarily sparged with argon and capped. After all vessels had been prepared, the vessels were uncapped and installed in the testing apparatus .

4.4 Gamma Dose Calibration

A study and calibration of the gamma dose to the sample vessels was conducted prior to the start of testing. This study included three evaluation methodologies, air-equivalent ionization chamber measurements, radiochromic film irradiations, and MCNP (Monte Carlo N-Particle transport code) modeling. The report of calibration is attached in its entirety as Appendix C of this report. This study was

---

[1] Schonewill PP. 2015. *PNNL Resin Handling Approach*, Rev. 0. September 22, 2015. Pacific Northwest National Laboratory, Richland, WA.

[2] Tran DN. 2015. *Sampling and Handling of Spherical Resorcinol-Formaldehyde Resin from FINNCONT or Smaller Resin Storage Containers*. GD-LPIST-001, Rev. 0.0, Pacific Northwest National Laboratory, Richland, WA.

specific to the source and vessels used in testing to provide an estimate as well as the range of error in the dose received by all of the samples in the radiolytic system.

4.5 Experiment Setup and Execution

The vessels were loaded into the testing apparatus and all electrical and gas line connections made. The apparatus containing all reaction vessels was leak-tested prior to use. For testing, there was one apparatus for the non-rad testing located on the ground floor of the 318 Building, while the apparatus for the rad-exposure testing was located in the basement of the 318 Building.

Prior to the start of the simulant and nitric acid experiments, the vapor pressure of the liquids was determined by connecting vessels with either simulant or nitric acid to the thermal system. The liquid was loaded into the vessels and the vessels refrigerated overnight prior to attaching to the system. After connecting the vessels to the system, they were purged and vented to atmospheric pressure with argon. The system was closed and the heater/controllers turned on starting at a 25 °C set-point. The temperature and pressure were allowed to equilibrate and then the set-point was increased at 10 °C increments to just above the anticipated testing temperature. When the vessels had reached maximum temperature, the heaters were turned off and the vessels were allowed to cool overnight with the data logger turned on. The cool-down temperature and pressure data were used to fit a curve to determine the vapor pressure function for the liquid. This function was used to correct the data for vapor pressure (see Section 4.7).

The rad-exposure apparatus, once connected and leak-checked, was lowered into a lead-shielded bunker. The bunker was then capped and the Co-60 source transferred to the center of the bunker pneumatically and remotely. The transfer of the Co-60 source established time-zero (t_0) for the rad testing, with the thermal testing having a similar start time. During the course of testing, temperatures and pressures were monitored daily during the work week, and gas samples were taken approximately once a week. A more detailed description of how samples were collected is included below. Gas analysis was conducted on the gas mass spectrometer by PNNL’s Analytical Support Operations (ASO) organization in the Radiochemical Processing Laboratory (RPL) building, primarily for hydrogen; however, other gases such as nitrogen, nitrous oxide, methane, and hydrocarbons were also analyzed. Analysis for formaldehyde was performed opportunistically as a For Information Only (FIO) analysis. After each gas sample, the test vessels were back-filled with argon and vented to atmospheric pressure through a bubbler. Based on preliminary results using the Hu model at the anticipated dose rate and conditions of the experiment, testing was expected to generate from 1×10^{-4} mole H_2 per week for the target feed simulant to 7×10^{-4} mole of H_2 per week for water, which established the sampling rate, as these anticipated levels of hydrogen are within the quantitation limits of the gas mass spectrometer.

At the conclusion of the test, the Co-60 source was transferred out of the bunker pneumatically. At that time, it was safe to remove the bunker shielding plug, and the reaction vessel apparatus was removed for preparation for the next test.

A formaldehyde test kit was used to determine the approximate level of formaldehyde in the liquid phase before beginning and at the conclusion of each test. These opportunistic data were not obtained in accordance with the formal controls defined by the project’s QA program and are therefore provided for information only.

At the end of each test, liquid samples were collected and held for total inorganic carbon (TIC)/TOC analyses. It should be noted that the TIC/TOC data were not used for any additional modeling.

4.5.1 Gas Sampling

A sampling event started with connecting 75 mL valved sampling bulbs to the gas sampling ports on the manifold. The bulb volumes were chosen to be larger than the system volume, and were almost double the combined volume of the vessel, gas lines, and manifold. The bulbs were previously evacuated by the mass spectrometry lab to below 1×10^{-6} Torr. After the bulbs were connected to the manifold, valve 5 (refer to Figure 4.1) was opened for each line, and the vacuum turned on. The manifold was evacuated for approximately one hour prior to starting sampling. Gas samples were collected by closing valve 5, opening valve 2 and the valve on the sample bulb, and allowing the system to come to equilibrium. Then valve 2 was closed, the sample bulb valve was closed, and the bulb was removed from the manifold. The process was repeated for each vessel. After sampling, the vessels were backfilled with argon and vented through a bubbler to atmospheric pressure.

4.6 Gas Generation Test Conditions

Table 4.3 summarizes the temperatures and liquids tested in each of the five tests. Further detail on each of the tests is outlined below.

Table 4.3. Gas Generation Test Conditions Matrix

Simulant and Simulant + sRF Resin	25 °C	45 °C	70 °C
Laboratory-grade DI Water	Test 1	Test 1	Test 4
Nominal 5.6M Na Simulant (oxalate omitted)	Test 2	Test 2	Test 5
0.45M HNO_3	Test 3	Test 3	Test 5
Nominal 5.6M Na Simulant with 1% (w/w) TOC as HEDTA	Not tested	Not tested	Test 4

4.6.1 Test 1 – Water with and without Na-form Resin

Test 1 was started on January 28, 2016, and ran until March 4, 2016, for an accumulated time of almost 859 hours on the rad system and 834 hours on the thermal system. The water-only vessels contained approximately 30 mL of 18 MΩ DI water. The resin/water vessels contained 30 mL of settled sodium-form (Na-form) resin with enough water to fill just to the top of the resin bed. The dry resin mass used was approximately 9.5 g. Refer to Table 4.4 and Table 4.5 for the experimental design. The exact mass of material added to each vessel is listed in Table 4.4 and Table 4.5. Each condition was tested at 25 °C and 45 °C in duplicate both with and without radiation. The average gamma dose rate for the experiment was 353.7 kRad/hr, with a total delivered dose for the radiolytic test of 304 MRad.

Four gas samplings took place over the course of the experiment, on February 8, 16, and 24, and March 4, 2016. The gas samples were delivered to the gas mass spectrometry laboratory in the PNNL RPL building for analysis. After the final gas sampling, the source was removed from the gamma bunker, and a fresh argon gas atmosphere was introduced to each vessel.

The vessels were removed from both systems on March 7, 2016, and were transferred to RPL for unloading and examination of the vessel contents. The vessels were unloaded on March 14, 2016. The resin was transferred to glass jars and put under fresh argon-purged DI water for storage. An aliquot of the liquid was tested for formaldehyde content using the EMD Millipore Formaldehyde Test Kit (part number 110036) and the remainder was transferred to vials for storage.

Table 4.4. Test 1 Experimental Design – Rad System (shaded rows indicate duplicates)

Vessel #	System 1 (Rad System) - Gamma Experiments	Mass Water (g)	Dry Resin Mass (g)
1-1	Water only, 25 °C, rep #1	29.81	--
1-2	Water + resin, 25 °C, rep #1	32.69	9.46
1-3	Water only, 45 °C, rep #1	30.06	--
1-4	Water + resin, 45 °C, rep #1	26.90	9.52
1-5	Water only, 25 °C, rep #2	30.29	--
1-6	Water + resin, 25 °C, rep #2	26.96	9.49
1-7	Water only, 45 °C, rep #2	30.26	--
1-8	Water + resin, 45 °C, rep #2	26.31	9.46

Table 4.5. Test 1 Experimental Design – Thermal System (shaded rows indicate duplicates)

Vessel #	System 2 (Thermal System) - Thermal-only Experiments	Mass Water (g)	Dry Resin Mass (g)
2-1	Water only, 25 °C, rep #1	30.28	--
2-2	Water + resin, 25 °C, rep #1	30.39	9.46
2-3	Water only, 45 °C, rep #1	31.65	--
2-4	Water + resin, 45 °C, rep #1	29.21	9.46
2-5	Water only, 25 °C, rep #2	31.14	--
2-6	Water + resin, 25 °C, rep #2	33.72	9.55
2-7	Water only, 45 °C, rep #2	30.44	--
2-8	Water + resin, 45 °C, rep #2	31.57	9.49

4.6.2 Test 2 – 5.6M Na LAWPS-IST Simulant without Added TOC, with and without Na-Form Resin

Test 2 tested the gas generation of the 5.6M Na LAWPS simulant (see Russell et al. 2017 for additional information) with and without resin. The simulant was prepared without the sodium oxalate, and the nominal composition is listed in Table 4.6. Test 2 was started on March 10, 2016, and ran until April 15, 2016, for a total of almost 860 hours on the rad system and almost 863 hours on the thermal system. The simulant-only vessels contained approximately 30 mL of 5.6M Na LAWPS simulant. The resin/simulant vessels contained 30 mL of settled sodium-form (Na-form) resin with enough simulant to fill just to the top of the resin bed. The dry resin mass used was approximately 9.4 g. Refer to Table 4.7 and Table 4.8 for the experimental design. The exact mass of material added to each vessel is listed in Table 4.7 and Table 4.8. Each condition was tested at 25 °C and 45 °C in duplicate both with and without radiation. The average gamma dose rate for the experiment was 348 kRad/hr, with a total delivered dose for the radiolytic test of 300 MRad.

Table 4.6. Nominal Composition of the 5.6M Na LAWPS Simulant without Oxalate

Dissolved Species	Concentration (M)
Al	1.66×10^{-1}
Cs	1.04×10^{-4}
Nitrate	1.78×10^{0}
Nitrite	1.02×10^{0}
Phosphate	4.32×10^{-2}
Sulfate	6.61×10^{-2}
Inorganic C	4.67×10^{-1}
Chloride	1.22×10^{-1}
Free Hydroxide	1.41×10^{0}
Potassium	1.22×10^{-1}
Sodium	5.57×10^{0}

Four gas samplings took place over the course of the experiment, on March 17 and 24 and April 5 and 15, 2016. The gas samples were delivered to the gas mass spectrometry laboratory in the PNNL RPL building for analysis. After the final gas sampling, the source was removed from the gamma bunker, and a fresh argon gas atmosphere was introduced to each vessel.

The vessels were removed from both systems on April 18, 2016, and were transferred to RPL for unloading and examination of the vessel contents. The vessels were unloaded on April 19, 2016. The resin was transferred to glass jars and put under fresh argon-purged DI water for storage. An aliquot of the liquid was tested for formaldehyde content using the EMD Millipore Formaldehyde Test Kit (part number 110036) and the remainder was transferred to vials for storage.

Table 4.7. Test 2 Experimental Design – Rad System (shaded rows indicate duplicates)

Vessel #	System 1 (Rad System) - Gamma Experiments	Mass Simulant (g)	Dry Resin Mass (g)
1-1	Simulant only, 25 °C, rep #1	37.53	--
1-2	Simulant + resin, 25 °C, rep #1	29.34	9.42
1-3	Simulant only, 45 °C, rep #1	37.99	--
1-4	Simulant + resin, 45 °C, rep #1	31.42	9.42
1-5	Simulant only, 25 °C, rep #2	37.94	--
1-6	Simulant + resin, 25 °C, rep #2	29.84	9.55
1-7	Simulant only, 45 °C, rep #2	37.81	--
1-8	Simulant + resin, 45 °C, rep #2	28.71	9.45

Table 4.8. Test 2 Experimental Design – Thermal System (shaded rows indicate duplicates)

Vessel #	System 2 (Thermal System) - Thermal-only Experiments	Mass Simulant (g)	Dry Resin Mass (g)
2-1	Simulant only, 25 °C, rep #1	37.85	--
2-2	Simulant + resin, 25 °C, rep #1	32.73	9.55
2-3	Simulant only, 45 °C, rep #1	38.05	--
2-4	Simulant + resin, 45 °C, rep #1	30.74	9.45
2-5	Simulant only, 25 °C, rep #2	38.05	--
2-6	Simulant + resin, 25 °C, rep #2	30.00	9.39
2-7	Simulant only, 45 °C, rep #2	37.76	--
2-8	Simulant + resin, 45 °C, rep #2	29.43	9.39

4.6.3 Test 3 – 0.45M HNO_3

Test 3 was started on May 2, 2016, and ran until June 8, 2016, for a total of 884 hours on the rad system and 882 hours on the thermal system. The liquid-only vessels contained approximately 30 mL of 0.45M HNO_3. The resin/liquid vessels contained 30 mL of settled hydrogen-form (H-form) resin with enough liquid to fill just to the top of the resin bed. The dry resin mass used was approximately 9.0 g. Refer to Table 4.9 and Table 4.10 for the experimental design. The exact mass of material added to each vessel is listed in Table 4.9 and Table 4.10. Each condition was tested at 25 °C and 45 °C in duplicate both with and without radiation. The average gamma dose rate for the experiment was 341.7 kRad/hr, with a total delivered dose for the radiolytic test of 302 MRad.

Five gas samplings took place over the course of the experiment, on May 10, 18, and 25, and June 1 and 8, 2016. The gas samples were delivered to the gas mass spectrometry laboratory in the PNNL RPL building for analysis. After the final gas sampling, the source was removed from the gamma bunker, and a fresh argon gas atmosphere was introduced to each vessel.

The vessels were removed from both systems on June 8, 2016, and were transferred to RPL for unloading and examination of the vessel contents. The vessels were unloaded on June 14 and 15, 2016. The resin was transferred to glass jars and put under fresh argon-purged DI water for storage. An aliquot of the liquid was tested for formaldehyde content using the EMD Millipore Formaldehyde Test Kit (part number 110036) and the remainder was transferred to vials for storage.

Table 4.9. Test 3 Experimental Design – Rad System (shaded rows indicate duplicates)

Vessel #	System 1 (Rad System) - Gamma Experiments	Mass HNO_3 (g)	Dry Resin Mass (g)
1-1	HNO_3 only, 25 °C, rep #1	30.15	--
1-2	HNO_3 + resin, 25 °C, rep #1	26.80	8.96
1-3	HNO_3 only, 45 °C, rep #1	30.17	--
1-4	HNO_3 + resin, 45 °C, rep #1	26.68	8.96
1-5	HNO_3 only, 25 °C, rep #2	30.22	--
1-6	HNO_3 + resin, 25 °C, rep #2	29.83	8.96
1-7	HNO_3 only, 45 °C, rep #2	30.11	--
1-8	HNO_3 + resin, 45 °C, rep #2	28.55	8.96

Table 4.10. Test 3 Experimental Design – Thermal System (shaded rows indicate duplicates)

Vessel #	System 2 (Thermal System) - Thermal-only Experiments	Mass Water (g)	Dry Resin Mass (g)
2-1	HNO_3 only, 25 °C, rep #1	30.07	--
2-2	HNO_3 + resin, 25 °C, rep #1	27.40	8.96
2-3	HNO_3 only, 45 °C, rep #1	30.07	--
2-4	HNO_3 + resin, 45 °C, rep #1	29.87	8.96
2-5	HNO_3only, 25 °C, rep #2	30.37	--
2-6	HNO_3+ resin, 25 °C, rep #2	25.90	8.96
2-7	HNO_3 only, 45 °C, rep #2	30.10	--
2-8	HNO_3+ resin, 45 °C, rep #2	26.98	8.96

4.6.4 Test 4 – Water at 70 °C and Simulant with HEDTA at 70 °C

Test 4 tested the gas generation of water and the 5.6M Na LAWPS simulant with 1% (w/w) TOC in the form of Na_3-HEDTA at 70 °C with and without resin. The 1% (w/w) TOC was added to the simulant prepared for Test 2. The nominal composition is listed in Table 4.11. Test 4 was started on September 21, 2016, and ran until October 31, 2016, for a total of 956 hours on the rad system and 957 hours on the thermal system. The simulant-only vessels contained approximately 30 mL of 5.6M Na LAWPS simulant. The resin/simulant vessels contained 30 mL of settled sodium-form (Na-form) resin with enough simulant to fill just to the top of the resin bed. The dry resin mass used was approximately 8.5 g. Refer to Table 4.12 and Table 4.13 for the experimental design. The exact mass of material added to each vessel is listed in Table 4.12 and Table 4.13. Each condition was tested at 70 °C in duplicate both with and without radiation. The average gamma dose rate for the experiment was 324.6 kRad/hr, with a total delivered dose for the radiolytic test of 310 MRad.

Table 4.11. Nominal Composition of the 5.6M Na LAWPS Simulant with 1% (w/w) TOC as Na_3-HEDTA

Dissolved Species	Concentration (M)
Al	1.66×10^{-1}
Cs	1.04×10^{-4}
Nitrate	1.78×10^{0}
Nitrite	1.02×10^{0}
Phosphate	4.32×10^{-2}
Sulfate	6.61×10^{-2}
Inorganic C	4.67×10^{-1}
Organic C	1.04×10^{0}
Chloride	1.22×10^{-1}
Free hydroxide	1.41×10^{0}
Potassium	1.22×10^{-1}
Sodium	5.89×10^{0}

Six gas samplings took place over the course of the experiment, on September 28 and October 5, 12, 19, 25, and 31, 2016. The gas samples were delivered to the gas mass spectrometry laboratory in the PNNL RPL building for analysis. After the final gas sampling, the source was removed from the gamma bunker, and a fresh argon gas atmosphere was introduced to each vessel.

The vessels were removed from both systems on October 31, 2016, and were transferred to RPL for unloading and examination of the vessel contents. The vessels were unloaded on November 8 and 9, 2016. The resin was transferred to glass jars and put under fresh argon-purged DI water for storage. An aliquot of the liquid was tested for formaldehyde content using the EMD Millipore Formaldehyde Test Kit (part number 110036) and the remainder was transferred to vials for storage.

Table 4.12. Test 4 Experimental Design – Rad System (shaded rows indicate duplicates)

Vessel #	System 1 (Rad System) - Gamma Experiments	Mass Simulant (g)	Dry Resin Mass (g)
1-1	Water only, 70 °C, rep #1	29.88	--
1-2	Water + resin, 70 °C, rep #1	32.35	8.58
1-3	Water only, 70 °C, rep #2	29.81	--
1-4	Water + resin, 70 °C, rep #2	30.25	8.58
1-5	Simulant only, 70 °C, rep #1	37.99	--
1-6	Simulant + resin, 70 °C, rep #1	34.37	8.58
1-7	Simulant only, 70 °C, rep #2	37.73	--
1-8	Simulant + resin, 70 °C, rep #2	30.98	8.58

Table 4.13. Test 4 Experimental Design – Thermal System (shaded rows indicate duplicates)

Vessel #	System 2 (Thermal System) - Thermal-only Experiments	Mass Simulant (g)	Dry Resin Mass (g)
2-1	Water only, 70 °C, rep #1	30.07	--
2-2	Water + resin, 70 °C, rep #1	31.77	8.58
2-3	Simulant only, 70 °C, rep #1	38.02	--
2-4	Simulant + resin, 70 °C, rep #1	30.65	8.58
2-5	Water only, 70 °C, rep #2	30.16	--
2-6	Water + resin, 70 °C, rep #2	34.32	8.58
2-7	Simulant only, 70 °C, rep #2	38.10	--
2-8	Simulant + resin, 70 °C, rep #2	30.47	8.58

4.6.5 Test 5 – HNO_3 at 70 °C and 5.6M Na Simulant at 70 °C

Test 5 tested the gas generation of 0.45M HNO_3 and the 5.6M Na LAWPS simulant at 70 °C with and without resin. The nominal simulant composition is listed in Table 4.6. Test 5 was started on November 10, 2016, and ran until December 20, 2016, for a total of almost 960 hours on the rad system and 960 hours on the thermal system. The HNO_3 and simulant-only vessels contained approximately 30 mL of liquid. The resin/HNO_3 vessels contained 30 mL of settled hydrogen-form (H-form) resin with enough HNO_3 to fill just to the top of the resin bed. The resin/simulant vessels contained 30 mL of settled sodium-form (Na-form) resin with enough simulant to fill just to the top of the resin bed. The dry resin mass used was approximately 8.6 g. Refer to Table 4.14 and Table 4.15 for the experimental design. The exact mass of material added to each vessel is listed in Table 4.14 and Table 4.15. Each condition was tested at 70 °C in duplicate both with and without radiation. The average gamma dose rate for the experiment was 318.7 kRad/hr, with a total delivered dose for the radiolytic test of 306 MRad.

Five full-system gas samplings took place over the course of the experiment, on November 18 and 26 and December 4, 12, and 20, 2016. Due to potential generation of self-flammable gases, the HNO_3/resin vessels were sampled more frequently, with additional samples collected on November 12 (both rad and thermal systems), 14 (both systems), 16 (rad system only), 20 (rad system only), 22 (rad system only), 24 (rad system only), and 30, 2016 (rad system only). The gas samples were delivered to the gas mass spectrometry laboratory in the PNNL RPL building for analysis. After the final gas sampling, the source was removed from the gamma bunker, and a fresh argon gas atmosphere was introduced to each vessel.

The vessels were removed from both systems on December 20, 2016, and were transferred to RPL for unloading and examination of the vessel contents. The vessels were unloaded on December 20 and 21, 2016. The resin was transferred to glass jars and put under fresh argon-purged DI water for storage. An aliquot of the liquid was tested for formaldehyde content using the EMD Millipore Formaldehyde Test Kit (part number 110036) and the remainder was transferred to vials for storage.

Table 4.14. Test 5 Experimental Design – Rad System (shaded rows indicate duplicates)

Vessel #	System 1 (Rad System) - Gamma Experiments	Mass Simulant (g)	Dry Resin Mass (g)
1-1	HNO_3 only, 70 °C, rep #1	30.33	--
1-2	HNO_3 + resin, 70 °C, rep #1	26.57	8.89
1-3	Simulant only, 70 °C, rep #1	37.43	--
1-4	Simulant + resin, 70 °C, rep #1	34.51	8.69
1-5	HNO_3 only, 70 °C, rep #2	30.31	--
1-6	HNO_3 + resin, 70 °C, rep #2	26.34	8.89
1-7	Simulant only, 70 °C, rep #2	38.03	--
1-8	Simulant + resin, 70 °C, rep #2	32.42	8.69

Table 4.15. Test 5 Experimental Design – Thermal System (shaded rows indicate duplicates)

Vessel #	System 2 (Thermal System) - Thermal-only Experiments	Mass Simulant (g)	Dry Resin Mass (g)
2-1	HNO_3 only, 70 °C, rep #1	30.11	--
2-2	HNO_3 + resin, 70 °C, rep #1	26.82	8.89
2-3	Simulant only, 70 °C, rep #1	37.55	--
2-4	Simulant + resin, 70 °C, rep #1	34.83	8.69
2-5	HNO_3 only, 70 °C, rep #2	30.32	--
2-6	HNO_3 + resin, 70 °C, rep #2	26.40	8.89
2-7	Simulant only, 70 °C, rep #2	37.40	--
2-8	Simulant + resin, 70 °C, rep #2	32.34	8.69

4.7 Data Analysis

Following the analysis approach set forth in previous work by Bryan et al. (1996), the temperatures, pressure, and gas analysis data were analyzed to determine the gas generation rates of the simulants with and without sRF resin. Briefly, the ideal gas law is used to determine the moles of gas present in each system, based on the known system volume and temperature and pressure measurements. The moles calculation is broken up into different portions of the system with the temperature measurements of each portion where the portions are: 1. the manifold to the pressure transducer, 2. the pressure transducer to the top of the vessel, and 3. the vessel headspace. In general, the vessel headspace volume is approximately 90% of the total system volume. In order to accurately determine the number of moles of dry gas generated, the vapor pressure of the liquids was determined and subtracted from the pressure measurement prior to the moles calculation. Gas mass spectrometry was used to determine the composition (mole %) of hydrogen as well as other gases generated. Combining the total moles measurement with the mole % composition, the moles of hydrogen and other gases were determined. With the known dose rate applied to the system, the hydrogen generation rate (moles H_2 per kg of liquid per day) was determined. The precision of measurement was determined by comparison of experimental duplicates.

The G-value of hydrogen generated within the experiment can be calculated by the following equation, from the moles of hydrogen formed and the calculated absorbed dose. The assumption was made that gas generation is overwhelmingly within the liquid phase, and therefore the absorbed dose used for purposes of G-value calculation is the dose absorbed by the liquid phase alone. G-values for other gas components can also be determined in a similar way.

$$G(H_2) = \frac{no. of\ H_2\ molecules\ formed}{100\ eV\ absorbed\ dose}$$

5.0 Gas Generation Testing Experimental Design and Results

A total of five gas generation tests were conducted. In the first three tests, a single liquid was tested with and without resin at 25 °C and 45 °C in duplicate, with and without radiation, for a total of 16 vessels tested. A design change to the Low-Activity Waste Pretreatment System necessitated testing of the three liquids at 70 °C, leading to the conditions tested in the fourth and fifth tests. Because space allowed, a fourth liquid was also tested at 70 °C: the nominal feed simulant with the addition of 1% (w/w) TOC in the form of Na_3-HEDTA. Prior to initiation of testing at 70 °C, system modifications were made in the form of the installation of pressure relief valves. All five tests delivered 300 MRad (± 10%) of gamma radiation to the System 1 vessels. The System 2 tests were conducted for approximately the same periods of time as the corresponding System 1 tests. The test results are summarized below.

Gas composition measurements based on mass spectral results for each gas sampling event are given in Appendix A. Based on these measurements, the total moles of hydrogen at each gas sampling event were calculated using system volume, temperature, pressure, and vapor pressure. Hydrogen gas generation from sRF resin in contact with water is described in Section 5.1; in contact with 5.6M Na nominal feed simulant is described in Section 5.2; and in contact with 0.45M HNO_3 is discussed in Section 5.3.

5.1 Water Results

Hydrogen gas generation from sRF resin in contact with water at various temperatures is shown in Figure 5.1 and Figure 5.2 for the "thermal + irradiation" and "thermal only" experiments, respectively. By subtracting the "thermal only" from the "thermal + irradiation" data, it is possible to differentiate the effect of added gamma dose on the gas generation within this system. The amount of gas produced based on gamma radiolysis is then used to estimate the G-value for hydrogen generated, as described in Section 4.0. Note that the thermal-only experiment is shown on the same scale as the irradiated experiment; the hydrogen generation was zero or near zero in all cases.

Table 5.1 and Figure 5.3 shows the $G(H_2)$-value for the water + resin experiments conducted in Test 1. Table 5.1 shows the cumulative $G(H_2)$-values over time for the test while Figure 5.3 shows the average $G(H_2)$-values for the experiment. The water-only $G(H_2)$-values were much lower, in the range of less than 0.04 at 25 °C and less than 0.004 at 45 °C, while the water + resin experiment returned $G(H_2)$-values less than the expected value for water-only from the Hu model (0.45). The water + resin $G(H_2)$-values seem to decrease with increasing temperature, but when examining the average $G(H_2)$-values, the averages are all within the error bars (one standard deviation) of one another, so the observed trend is not statistically significant.

The prompt radiolytic hydrogen generation describes the initial production of molecular hydrogen in an open system under radiolytic conditions. Most experiments to determine the prompt hydrogen value of water or other aqueous species add a reductant such as bromide to preserve the molecular hydrogen from attack by hydroxyl radicals. The water-only values do not match the prompt hydrogen value of 0.45 likely because the experiment was performed in a closed system with laboratory grade deionized water in the absence of reductant species. The values obtained were found to reasonably match literature values for a pure water experiment in a closed system (Pastina and Laverne 2001) as well as the rate constant information in the literature (Buxton et al. 1988).

Table 5.1. Water Testing Average Cumulative G(H_2) Values

25 °C		25 °C w/ resin		45 °C		45 °C w/ resin		70 °C		70 °C w/ resin	
Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)
259.00	0.0034	259.00	0.2780	259.00	0.0043	259.00	0.3394	165.08	0.008	165.08	0.282
450.42	0.0194	450.42	0.3769	450.42	0.0025	450.42	0.2951	333.25	0.028	333.25	0.297
642.42	0.0314	642.42	0.3914	642.42	0.0025	642.42	0.3751	500.75	0.046	500.75	0.302
858.50	0.0226	858.50	0.4258	858.50	0.0018	858.50	0.3598	668.83	0.065	668.83	0.301
								813.17	0.079	813.17	0.308
								956.25	0.088	956.25	0.314

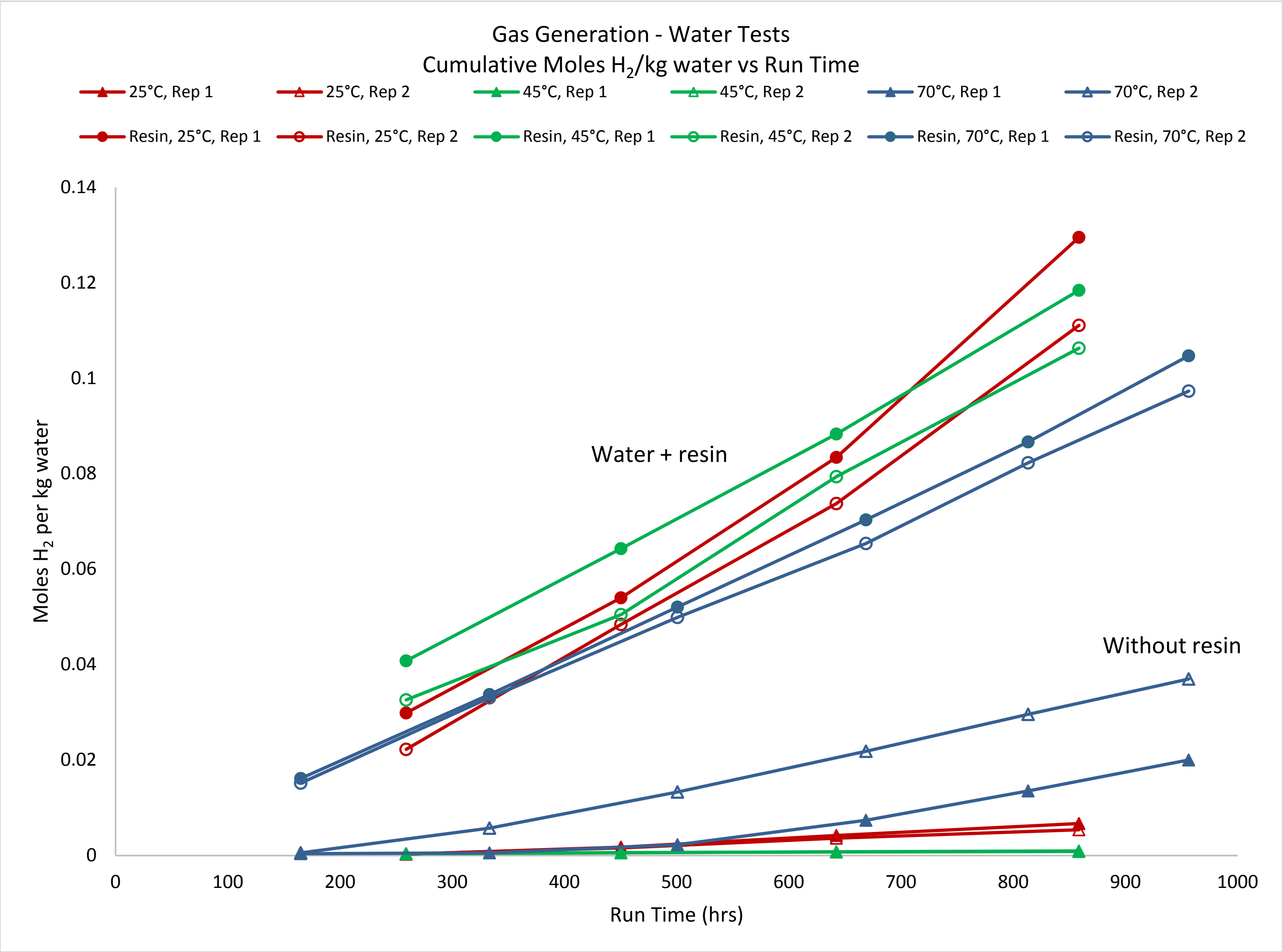

Figure 5.1. Radiolytic hydrogen gas generation from sRF resin in contact with water at various temperatures. The data are shown as cumulative moles H_2 produced per kg of water vs. run time.

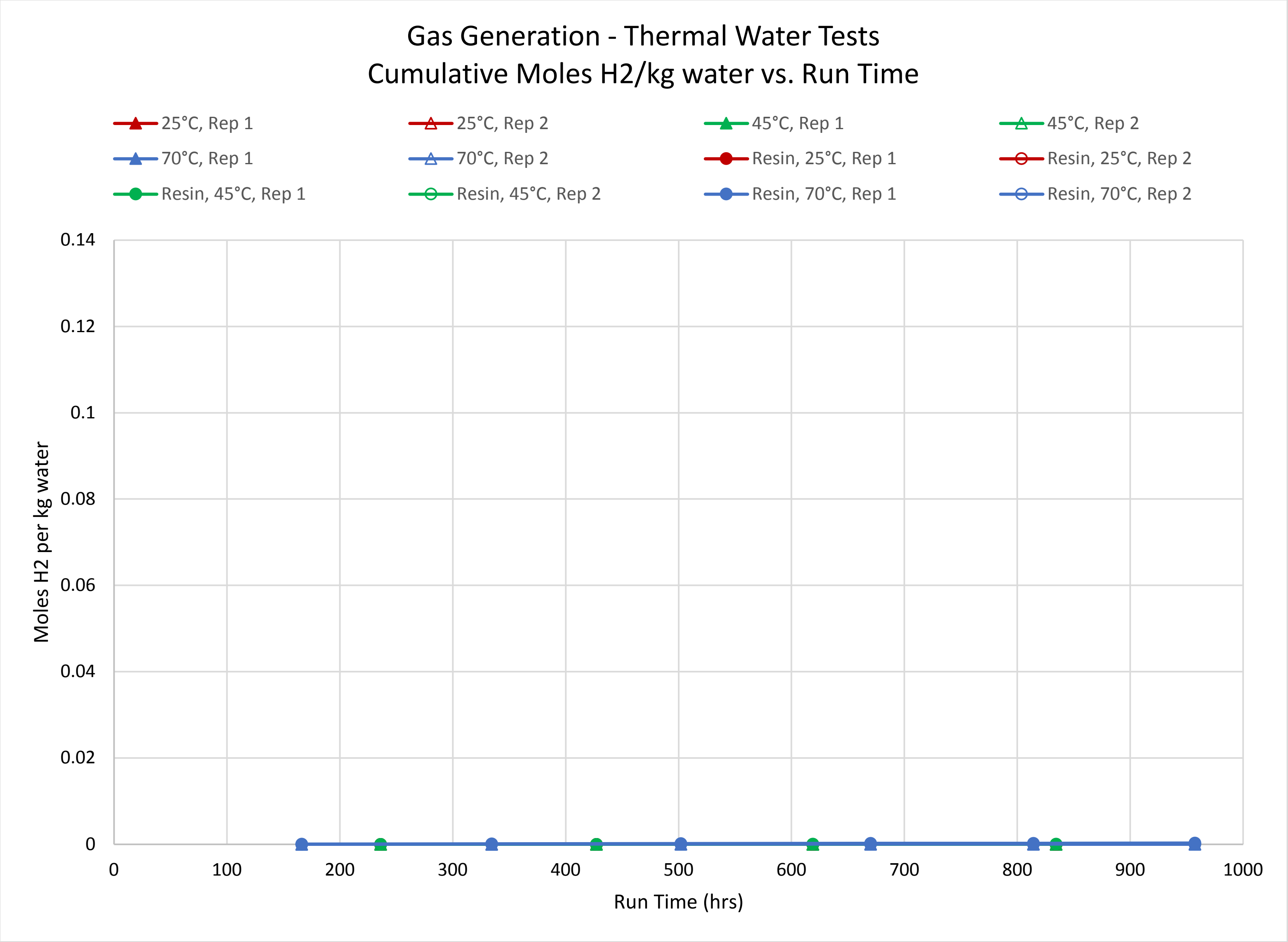

Figure 5.2. Thermal hydrogen gas generation from sRF resin in contact with water at various temperatures. The data are shown as cumulative moles H_2 produced per kg of water vs. run time.

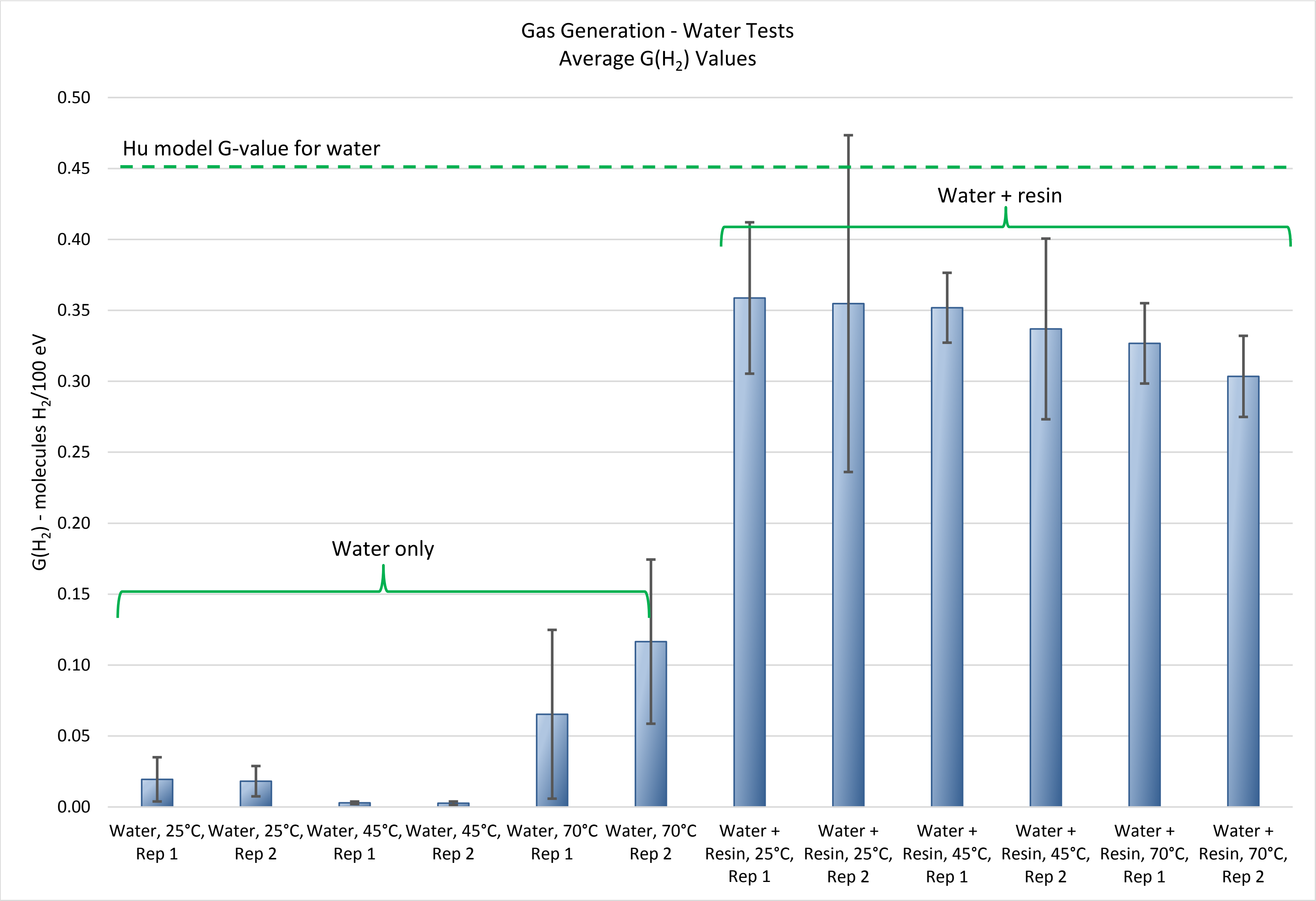

Figure 5.3. G-value measurements for radiolytic hydrogen production (G(H_2)-values) for the water + resin experiments conducted at various temperatures.

5.2 5.6M Na Nominal Feed Simulant Results

Figure 5.4 shows the hydrogen gas generation from 5.6M Na nominal feed simulant at various temperatures with and without resin for the “thermal + irradiation” treatment. In this figure, it can be seen that the hydrogen generation with resin is consistently higher for all temperatures than the simulant without resin present. For comparison purposes, also shown in Figure 5.4 is the hydrogen generation measured for the water system in contact with sRF resin; the hydrogen generation from the 5.6M Na nominal feed simulant is significantly smaller than for the water system with sRF resin. Figure 5.5 shows the hydrogen gas generation from 5.6M Na nominal feed simulant at various temperatures with and without resin for the “thermal only” treatment. By subtracting the “thermal only” from the “thermal + irradiation” data, it is possible to differentiate the effect of added gamma dose on the gas generation within this system. The amount of gas produced based on gamma radiolysis is then used to estimate the G-value for hydrogen generated, as described in Section 4.0.

Table 5.2 and Figure 5.6 show the $G(H_2)$-values for the 5.6M Na nominal feed simulant and the simulant with resin experiments. Table 5.2 shows the cumulative $G(H_2)$-values for the test over time while Figure 5.6 shows the average $G(H_2)$-value for the experiment. The simulant-only $G(H_2)$-values were approximately 0.05 for the 25 °C, 45 °C, and 70 °C conditions, which is slightly above the predicted $G(H_2)$-value of 0.039 based on the Hu model. The simulant + resin experiment $G(H_2)$-values range between 0.08 and 0.12, with no apparent temperature dependence for the range of measurement (25 °C to 70 °C). Note that over time the incremental observed G(H2) values increase and exceed the Hu model value. This is likely due to oxidative degradation of the resin and further scavenging of hydroxyl radicals by the resin to produce hydrogen.

Two experiments were conducted to test the effect of added TOC to the 5.6M Na nominal feed simulant at 70 °C. The first test included added TOC without sRF resin, the second condition tested added TOC with added sRF resin. As can be seen in Figure 5.6, the experimental condition with TOC and with sRF resin ($G(H_2)$ range 0.11 to 0.14) was significantly higher than the condition of added TOC without sRF resin ($G(H_2)$ range 0.07 to 0.08). The Hu model $G(H_2)$ prediction for the 5.6M Na nominal feed simulant with added TOC (without sRF resin) is 0.15. It is evident that the addition of sRF resin has a significantly greater effect on increasing the $G(H_2)$ value than the addition of TOC only.

Table 5.2. Simulant Testing Average Cumulative G(H_2) Values

25 °C		25 °C w/ resin		45 °C		45 °C w/ resin		70 °C		70 °C w/ resin		70 °C TOC		70 °C TOC w/ Resin	
Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)	Run Time (hr)	G(H_2)
161.50	0.03651	161.50	0.02269	161.50	0.04086	161.50	0.01948	193.33	0.0490	193.33	0.1039	165.08	0.072	165.08	0.113
330.42	0.04454	330.42	0.08130	330.42	0.04834	330.42	0.12845	385.67	0.0489	385.67	0.1032	333.25	0.075	333.25	0.118
617.83	0.04504	617.83	0.12052	617.83	0.04832	617.83	0.10003	579.33	0.0493	579.33	0.1037	500.75	0.076	500.75	0.128
859.75	0.04200	859.75	0.11423	859.75	0.04651	859.75	0.10947	768.50	0.0487	768.50	0.1041	668.83	0.075	668.83	0.131
								959.42	0.0485	959.42	0.1049	813.17	0.074	813.17	0.134
												956.25	0.073	956.25	0.137

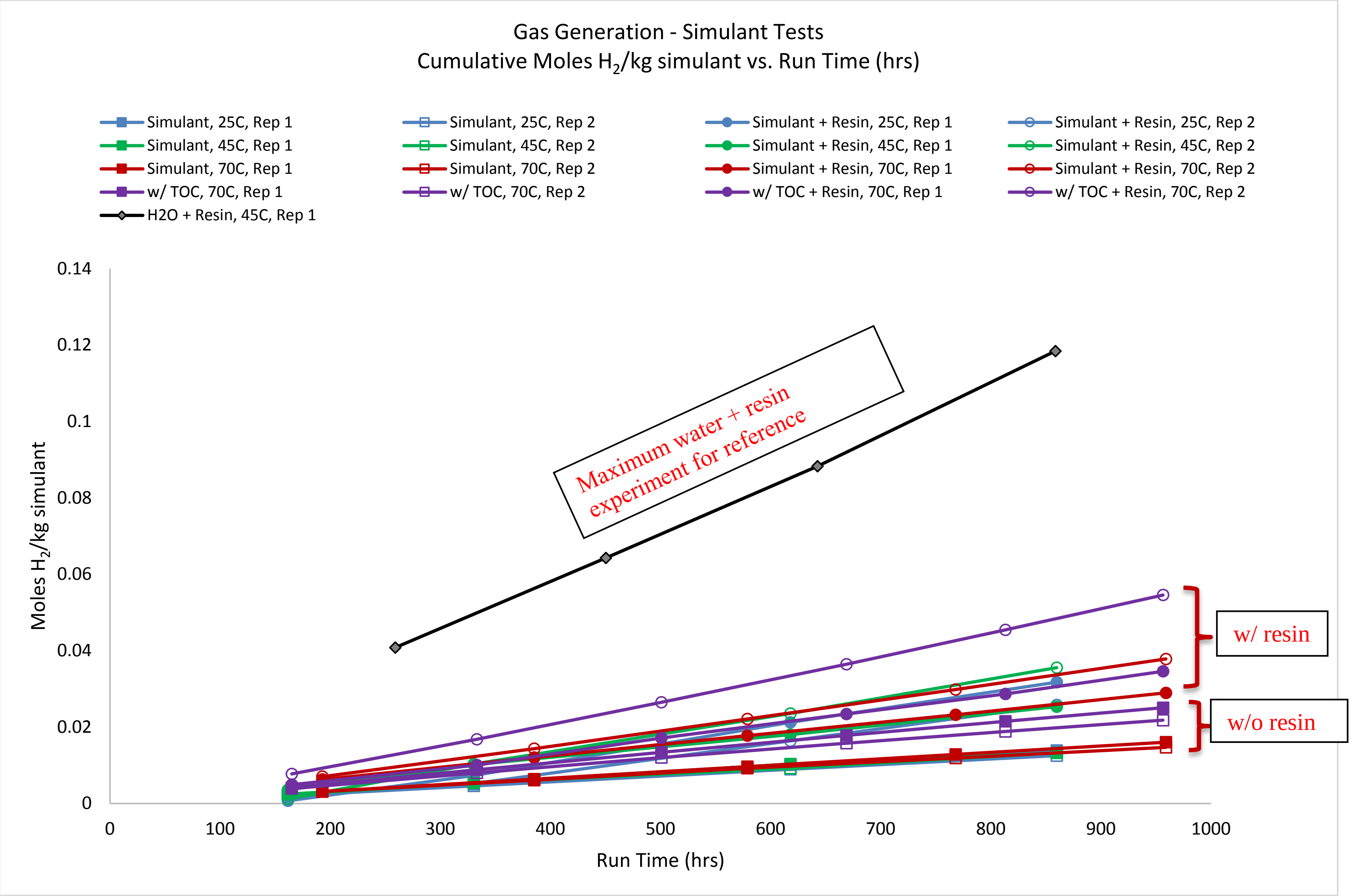

Figure 5.4. Radiolytic hydrogen gas generation from 5.6M Na nominal feed simulant at various temperatures with and without resin. The data are shown as cumulative moles H_2 produced per kg of simulant vs. run time.

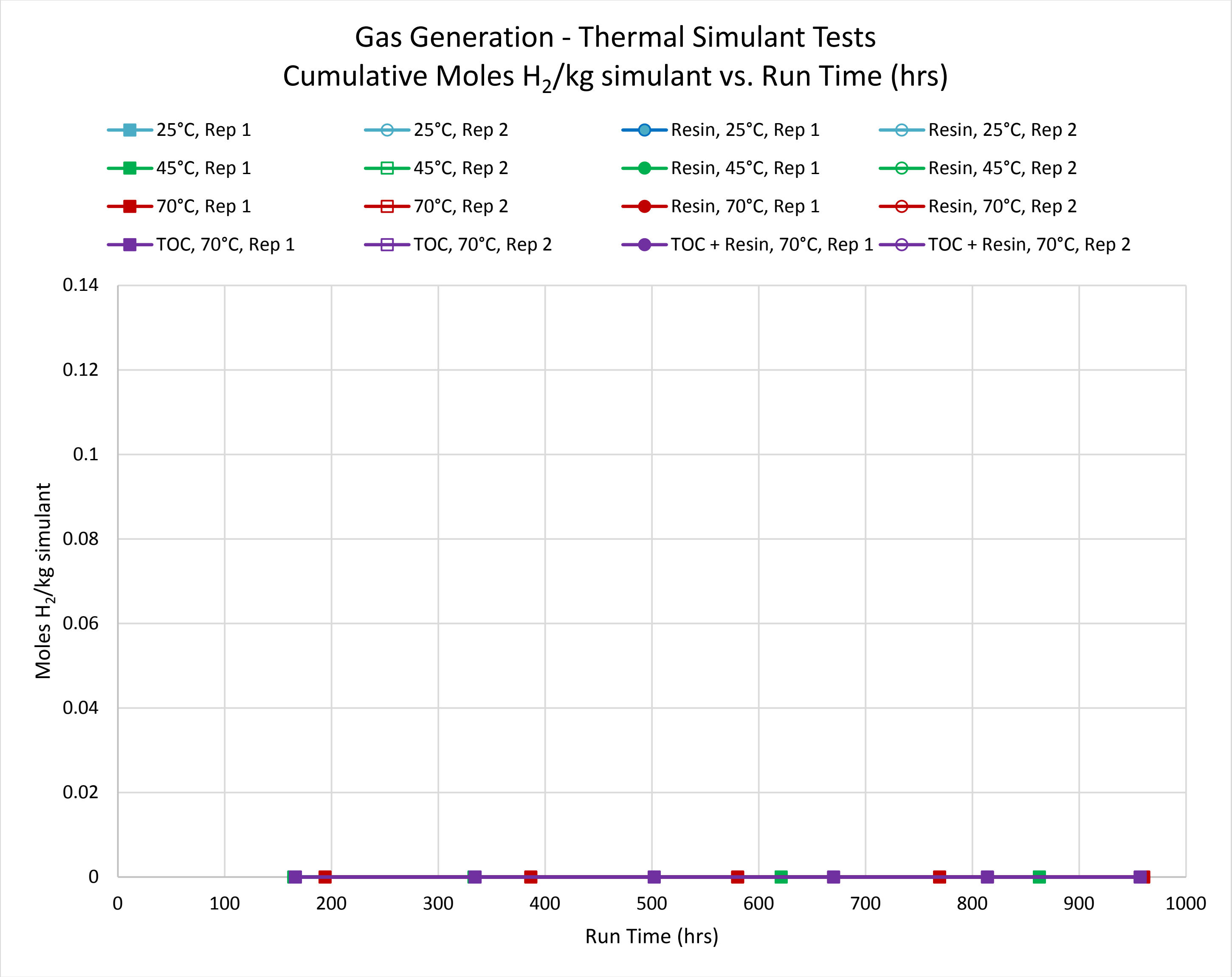

Figure 5.5. Thermal hydrogen gas generation from 5.6M Na nominal feed simulant at various temperatures with and without resin. The data are shown as cumulative moles H_2 produced per kg of simulant vs. run time.

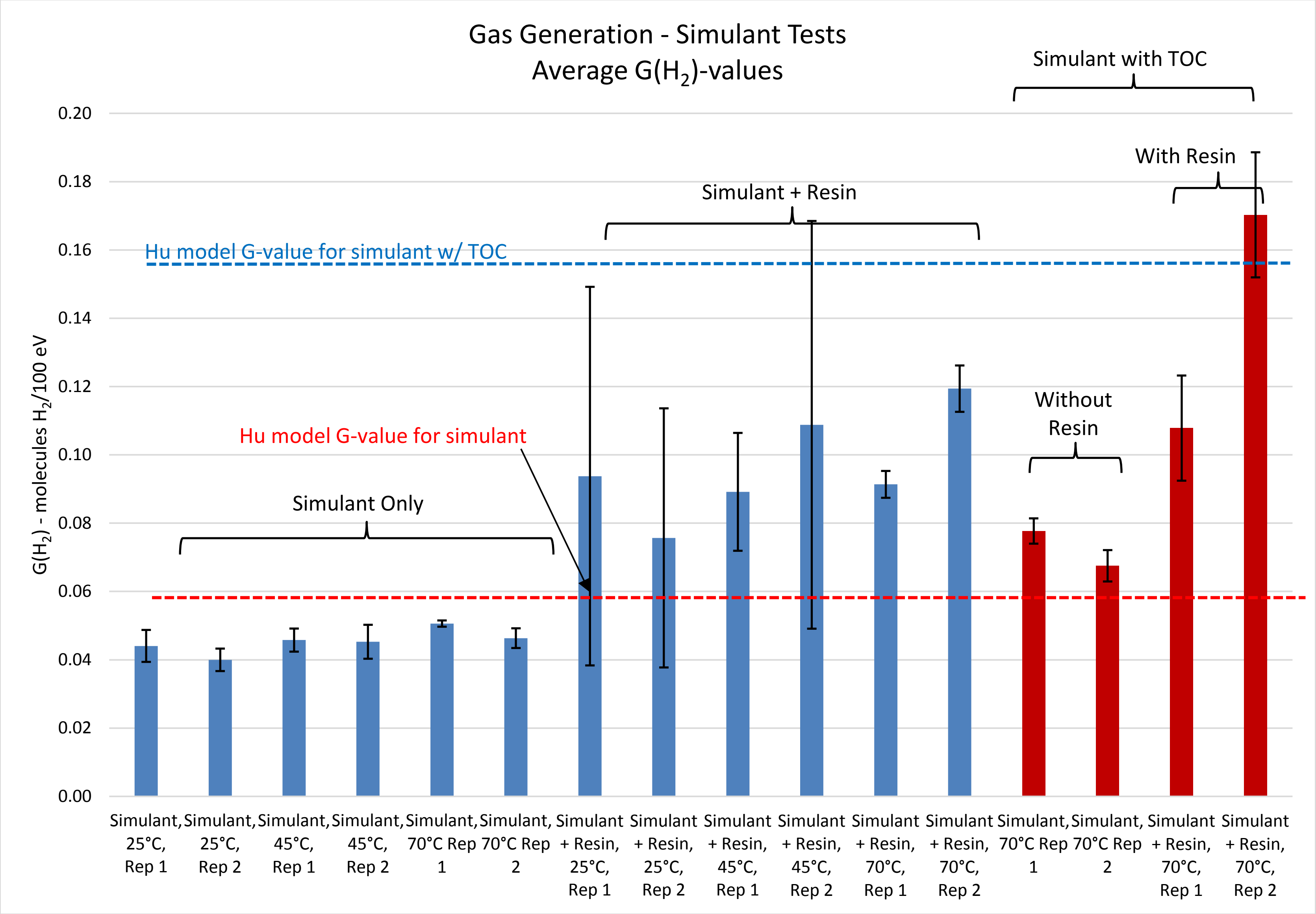

Figure 5.6. G-value measurements for radiolytic hydrogen production (G(H_2)-values) for the 5.6M Na nominal feed simulant + resin experiments conducted at various temperatures.

5.3 0.45M HNO_3 Results

Figure 5.7 shows hydrogen gas generation from 0.45M HNO_3 at various temperatures with and without resin for the “thermal + irradiation” treatment. In this figure, it can be seen that the hydrogen generation with resin (filled circles) is consistently higher for all temperatures than the nitric acid without resin present (open circles). For comparison purposes, also shown in Figure 5.7 is the hydrogen generation measured for the water system in contact with sRF resin; the hydrogen generation from the 0.45M HNO_3 (with or without sRF resin) is significantly smaller than for the water system with sRF resin. Figure 5.8 shows the hydrogen gas generation from 0.45M HNO_3 at various temperatures with and without resin for the “thermal only” treatment. The gas generation for the “thermal only” treatment was observed to be zero for all temperatures and time-points as compared to the gas generation from the “thermal + irradiation” treatment. By subtracting the “thermal only” from the “thermal + irradiation” data, it is possible to differentiate the effect of added gamma dose on the gas generation within this system. The amount of gas produced based on gamma radiolysis is then used to estimate the G-value for hydrogen generated, as described in Section 4.0.

Table 5.3 and Figure 5.9 show the $G(H_2)$-values for the 0.45M HNO_3 with and without resin experiments for measurements under various temperatures. Table 5.3 shows the cumulative $G(H_2)$-values for the test over time while Figure 5.9 shows the average $G(H_2)$-value for the experiment. The nitric acid-only $G(H_2)$-values ranged between approximately 0.075 and 0.10 for the 25 °C, 45 °C, and 70 °C conditions which is less than the literature values as reported by Mahlman (Mahlman 1961). As with the water, there is a discrepancy between the observed nitric acid G-values and the literature values, which is also due to the fact that the experiment was conducted in a closed vessel system without the addition of an impurity to prevent the recombination of molecular hydrogen with hydroxyl radicals, similar to the case with the water observations. The 0.45M HNO_3 + resin experiment $G(H_2)$-values range between 0.08 and 0.19, with the 25 °C measurement having the smallest $G(H_2)$-values and 45 °C having the largest. With experimental scatter between replicates, there was no apparent temperature dependence for the range of measurement (25 °C to 70 °C).

Self-heating behavior was observed when testing the nitric acid with resin at elevated temperatures (45 °C and 70 °C). This behavior was observed in both the irradiated and thermal-only experiments. Once the vessels were heated to temperature using the heater-controllers, the vessels appeared to continue heating, necessitating intervention on the part of the analyst to maintain vessel temperature.

Table 5.3. 0.45M HNO_3 Testing, Average Cumulative $G(H_2)$ Values

25 °C		25 °C w/ resin		45 °C		45 °C w/ resin		70 °C		70 °C w/ resin	
Run Time (hr)	$G(H_2)$	Run Time (hr)	$G(H_2)$	Run Time (hr)	$G(H_2)$	Run Time (hr)	$G(H_2)$	Run Time (hr)	$G(H_2)$	Run Time (hr)	$G(H_2)$
188.00	0.0822	188.00	0.0973	188.00	0.0791	188.00	0.0916	193.33	0.0761	50.83	0.1170
383.58	0.0906	383.58	0.0765	383.58	0.0845	383.58	0.1073	385.67	0.0814	97.25	0.1116
548.08	0.0927	548.08	0.0875	548.08	0.0864	548.08	0.1285	579.33	0.0827	144.00	0.1215
718.92	0.0939	718.92	0.1072	718.92	0.0885	718.92	0.1633	768.50	0.0831	193.33	0.1206
884.25	0.0969	884.25	0.1286	884.25	0.0904	884.25	0.1859	959.42	0.0832	241.92	0.1208
										288.17	0.1215
										337.00	0.1271
										385.67	0.1319
										480.58	0.1351
										579.33	0.1359
										768.50	0.1387
										959.42	0.1394

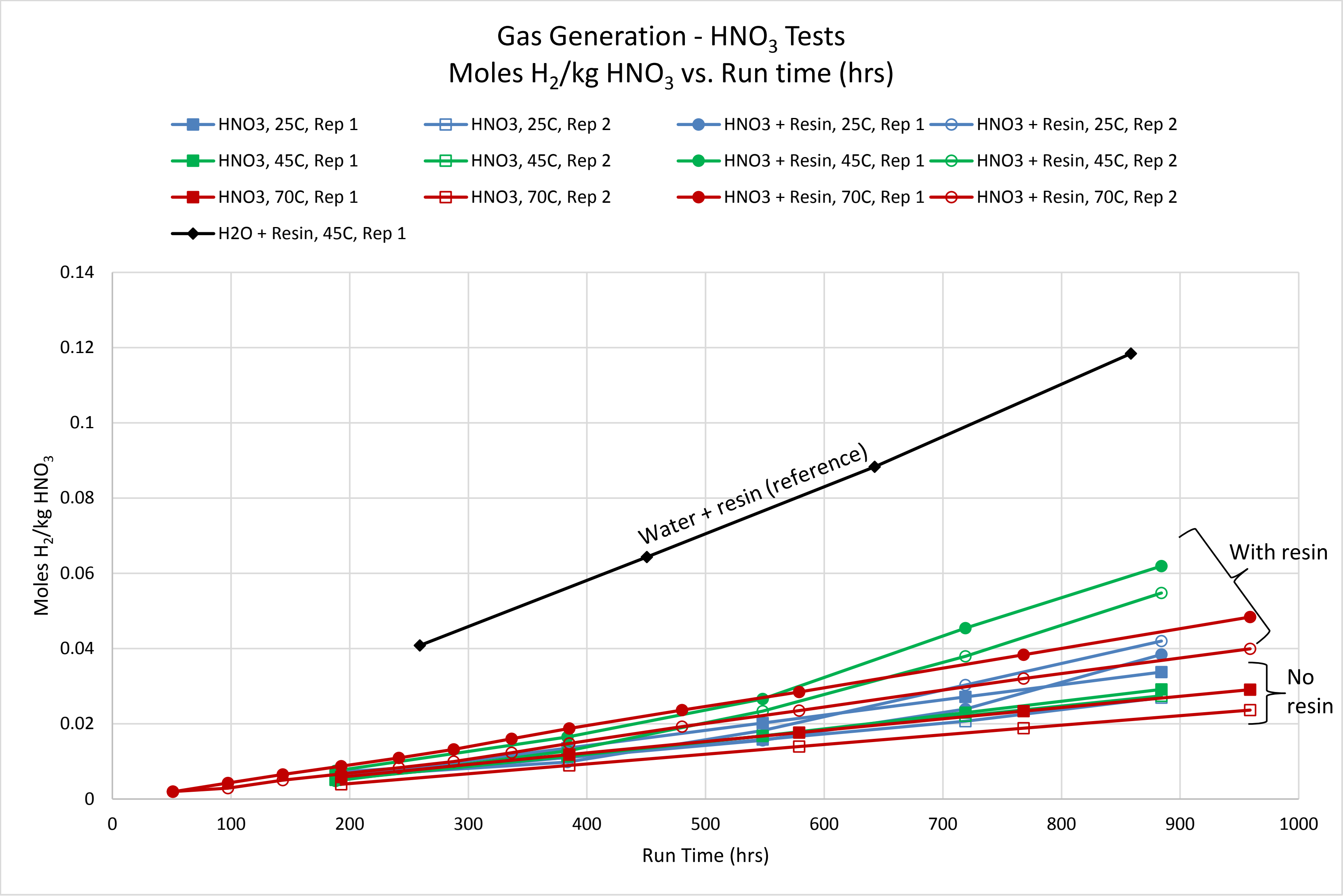

Figure 5.7. Radiolytic hydrogen gas generation from sRF resin in contact with 0.45M HNO_3 various temperatures. The data are shown as cumulative moles H_2 produced per kg of 0.45M HNO_3 vs. run time.

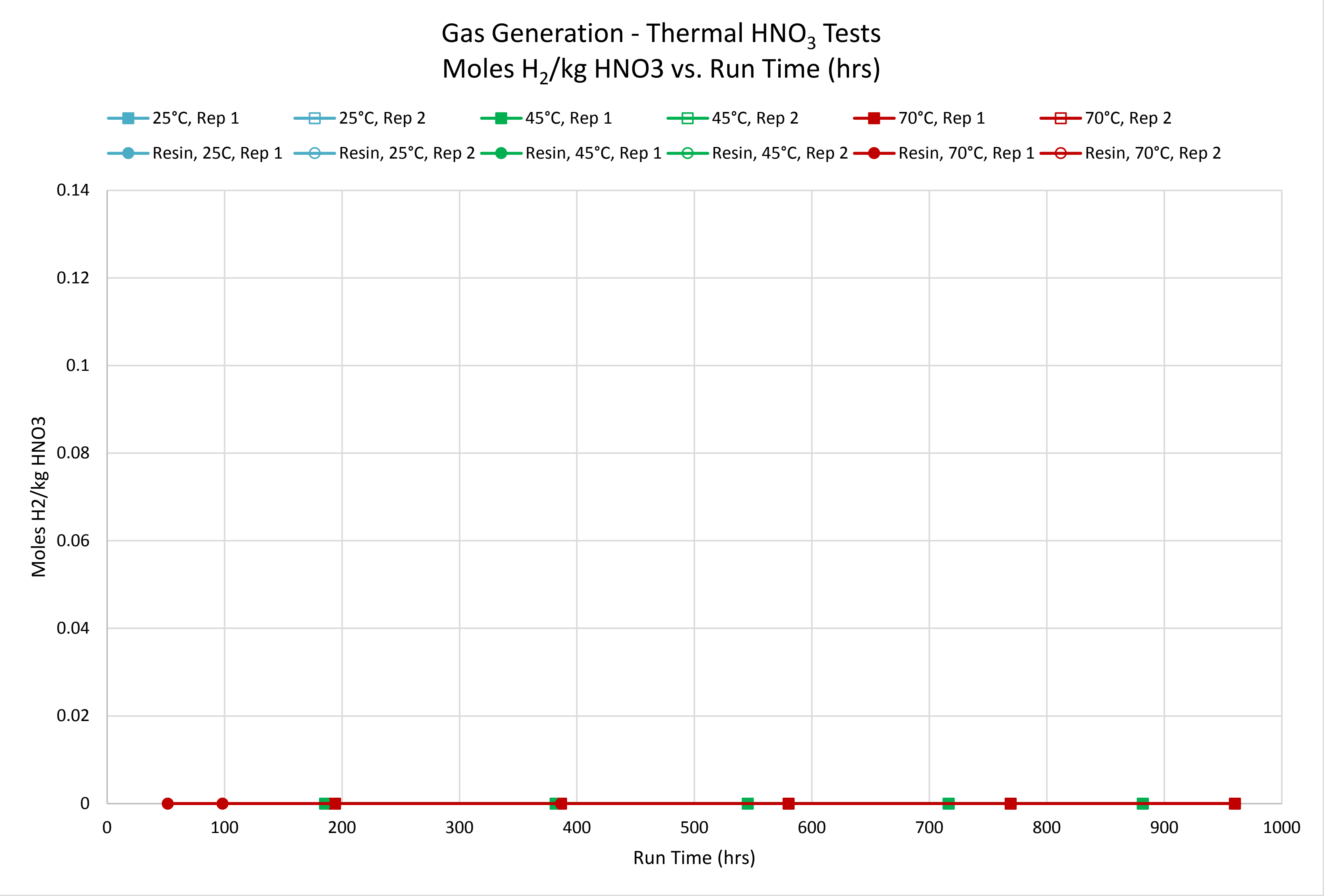

Figure 5.8. Thermal hydrogen gas generation from sRF resin in contact with 0.45M HNO_3 at various temperatures. The data are shown as cumulative moles H_2 produced per kg of 0.45M HNO_3 vs. run time.

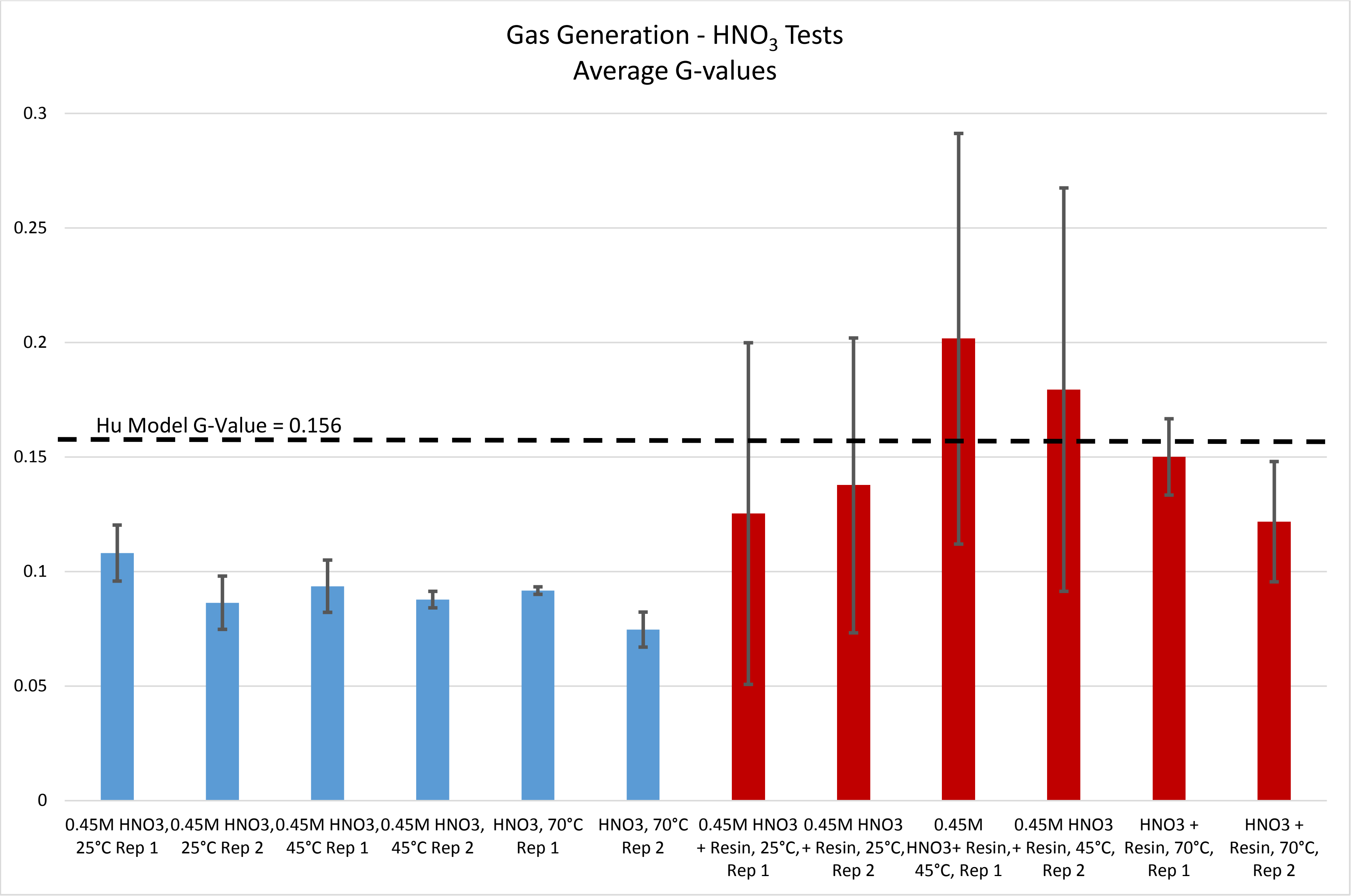

Figure 5.9. G-value measurements for radiolytic hydrogen production (G(H_2)-values) for the 0.45M HNO_3 + resin experiments conducted at various temperatures.

5.4 Summary

Table 5.1, Table 5.2, and Table 5.3 summarize the $G(H_2)$-value results of the hydrogen gas generation rate measurements taken with solution composition of 5.6M Na nominal feed simulant, 0.45M HNO_3, and water, with and without contact with sRF resin, at various temperatures. Using these $G(H_2)$-values, the hydrogen generation rates were calculated for a temperature of 45 °C and 43 kRad/hr dose rate (the expected bounding condition during LAWPS use). These calculated hydrogen generation rate values are listed in Table 5.4 and displayed in Figure 5.10 and compared with the Hu model calculation for solution compositions similar to those used in actual solution measurements.

The Hu model predictions are also shown as the black line in Figure 5.10. The Hu model predictions are plotted as a 1:1 parity plot for the conditions of 5.6M Na nominal feed simulant, 0.45M HNO_3, and water for the temperature and dose rate expected as a bounding condition during LAWPS use, i.e., 45 °C and 42.6 kRad/hr, respectively. Also shown on this plot is the Hu model 1:1.4 line, which represents the assumed “bounding” case for estimating the “worst case” hydrogen gas generation. The black dotted line across the top of the plot is the intersection of the Hu model 1:1.4 line at the value calculated for water. Under the conditions 45 °C and 42.6 kRad/hr, this value is 6.8×10^{-4} mol/kg/day for hydrogen production, and is considered the “bounding” value.

In all cases, the measured hydrogen production rate is lower than the Hu model “bounding” value (6.8×10^{-4} mol/kg/day) for all solution compositions, with and without sRF resin, and with and without added TOC, at various temperatures studied. Except for the 5.6M Na nominal feed simulant with sRF resin, all generation rate measurements are lower than the Hu model 1:1.4 line.

Table 5.4. Summary of Hydrogen Generation Rates Calculated for a Temperature of 45 °C and 43 kRad/hr Dose Rate (the expected bounding condition during LAWPS use), Using G(H_2)-Values Given in Table 5.1, Table 5.2, and Table 5.3.

Observed Condition	Measured G(H_2)-Value (molecules H_2/100 eV absorbed dose)	Modeled Hydrogen Generation Rate at 45 °C, 43 kRad/hour (moles H_2/kg liquid/day)
Water, 25 °C	0.0226	2.40E-05
Water, 45 °C	0.0018	1.91E-06
Water, 70 °C	0.0880	9.33E-05
Water + Resin, 25 °C	0.4258	4.52E-04
Water + Resin, 45 °C	0.3598	3.82E-04
Water + Resin, 70 °C	0.3140	3.33E-04
Simulant, 25 °C	0.0420	4.45E-05
Simulant, 45 °C	0.0465	4.93E-05
Simulant 70 °C	0.0485	5.14E-05
Simulant + Resin, 25 °C	0.1142	1.21E-04
Simulant + Resin, 45 °C	0.1095	1.16E-04
Simulant + Resin, 70 °C	0.1049	1.11E-04
Simulant with TOC, 70 °C	0.0730	7.74E-05
Simulant with TOC + Resin, 70 °C	0.1370	1.45E-04
HNO_3, 25 °C	0.0969	1.03E-04
HNO_3, 45 °C	0.0904	9.59E-05
HNO_3, 70 °C	0.0832	8.82E-05
HNO_3 + Resin, 25 °C	0.1286	1.36E-04
HNO_3 + Resin, 45 °C	0.1859	1.97E-04
HNO_3 + Resin, 70 °C	0.1394	1.48E-04

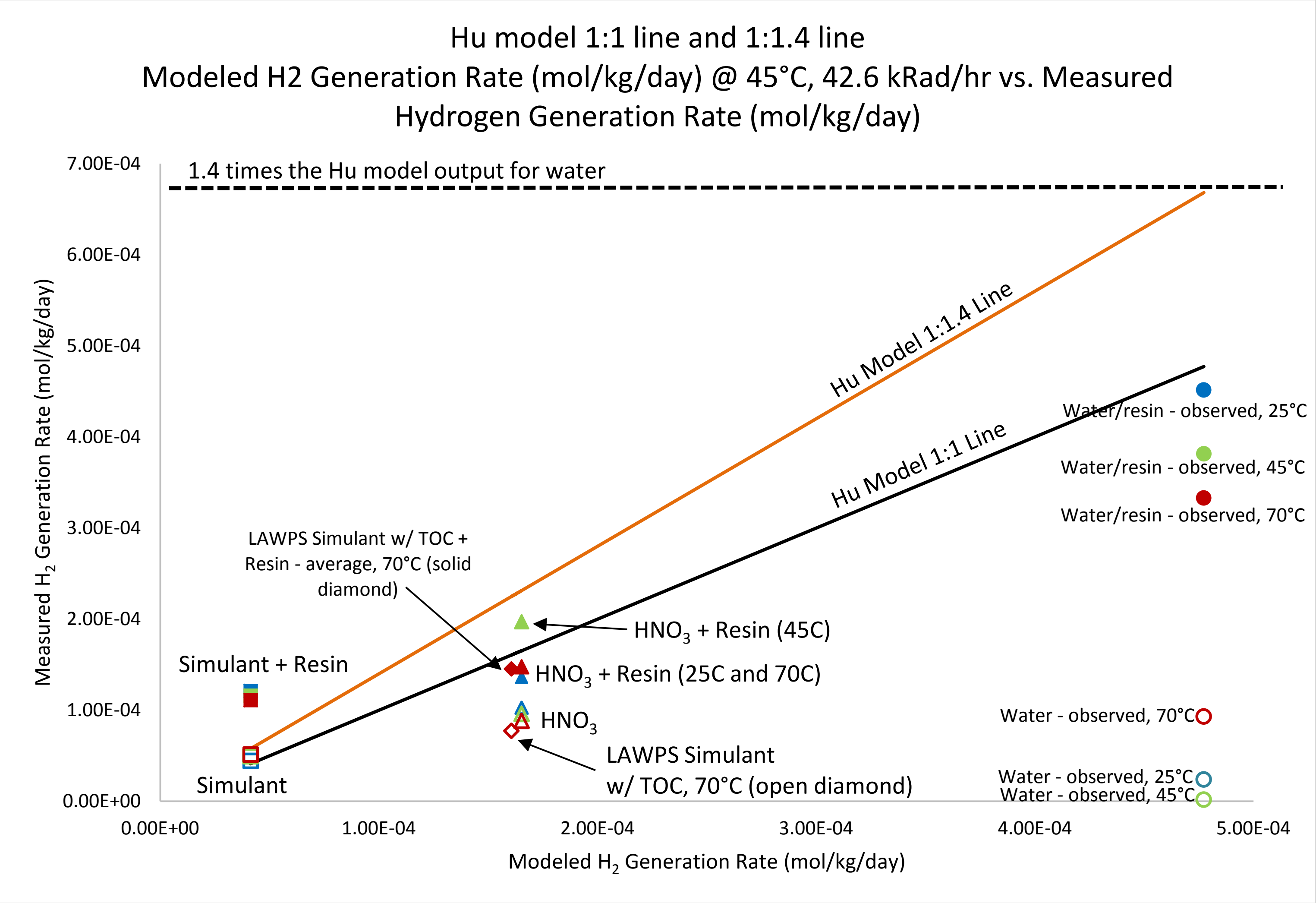

Figure 5.10. Comparison of actual results to Hu modeled results. The 1:1 model line is shown in black, the 1:1.4 model line is shown in orange. Experimental results with resin are shown in the symbols where blue is 25 °C, green is 45 °C, and red is 70 °C. Open symbols are liquid only, filled symbols are liquid plus resin. Water results are shown in the circles, HNO_3 results are shown in triangles, simulant without TOC in squares, and simulant with TOC in diamonds.

6.0 Post-Irradiation Examination of Resin and Liquids

As described in Section 4.0, the resin and liquids were examined and retained after testing. The resin and liquids were visually examined and the resin-contacted liquids were tested for the presence of formaldehyde. A subset of the liquids was submitted for TIC/TOC analysis. An additional study was conducted to see if gas generation of resin could be visualized under dose.

6.1 Visual Examination of Resin and Test Liquids

6.1.1 Test 1 – Water

Following the final sampling and shutdown of the test, the vessels were removed from both systems and their contents emptied and examined. Vessel 1-2 from the radiolytic system had resin adhering to the walls of the vessel almost all the way to the top, as shown in Figure 6.1. This was the only vessel in which this was observed in Test 1. The resin from the radiolytic system for this experiment was darker in color than the resin from the thermal system, as shown in Figure 6.2. In addition, the liquids appeared to take on color, with the liquid from the radiolytic system having a slight pink color (Figure 6.3) while the liquid from the thermal system had a slight orange color (Figure 6.4).

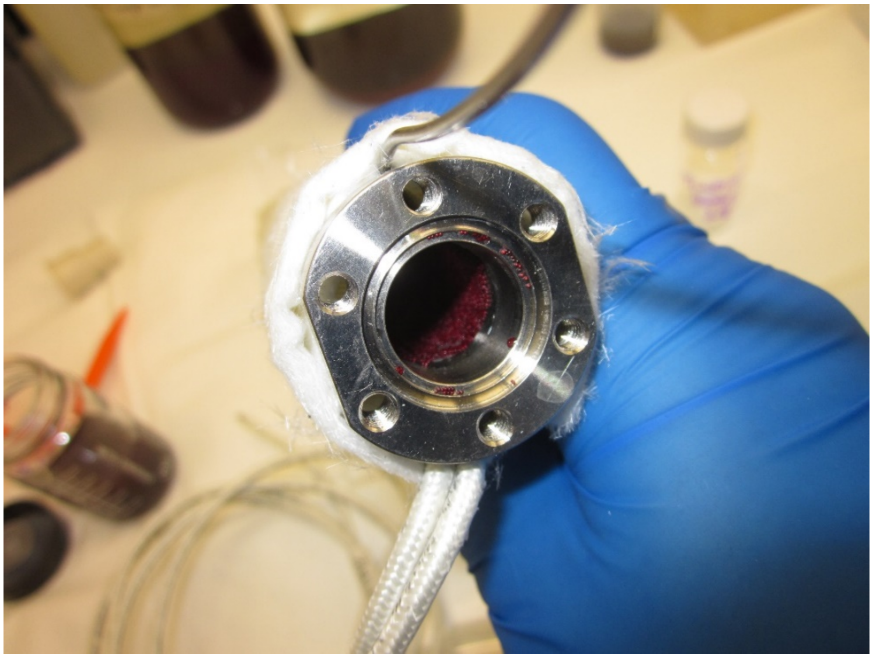

Figure 6.1. Test 1, Vessel 1-2 resin appeared to “climb” up and adhere to the vessel walls.

Figure 6.2. Color difference of resin from the rad system (left) and thermal system (right).

Figure 6.3. Pink-tinged liquid from Test 1 rad system water/resin after irradiation.

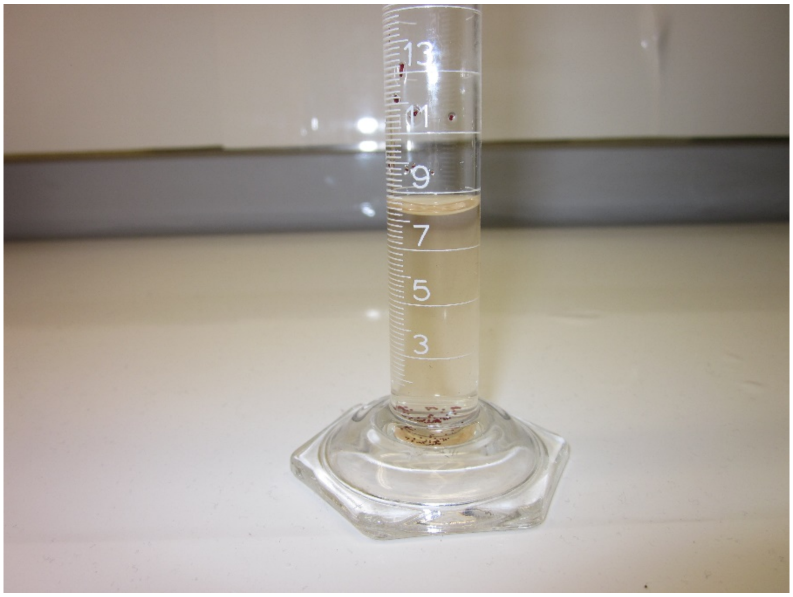

Figure 6.4. Orange-tinged liquid from Test 1, thermal system water/resin.

6.1.2 Test 2 – Simulant

Following the final sampling and shutdown of the test, the vessels were removed from both systems and their contents emptied and examined. The resin from the radiolytic system for this experiment was darker in color than the resin from the thermal system, as shown in Figure 6.5. Figure 6.5 also shows the bright yellow color of the fresh DI water that was added to the resin. Fresh DI water was added to the resin to retain it under liquid while the test liquid was retained separately for analysis. The liquids from the radiolytic system were bright orange-yellow, as shown in Figure 6.6.

Figure 6.5. Test 2, resin color difference post-test: rad system (left), thermal system (right).

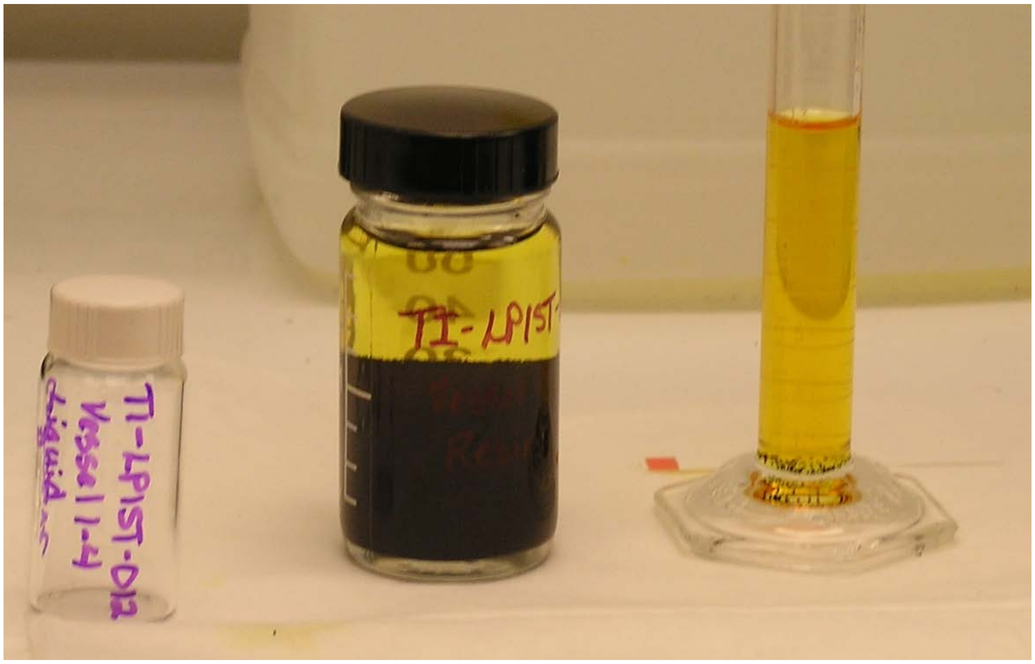

Figure 6.6. Radiolytic system Vessel 1-4 resin and liquid post-irradiation.

6.1.3 Test 3 – 0.45M HNO_3

Figure 6.7 shows a side-by-side comparison of the hydrogen form (H-form) resin used in the nitric acid testing at 25 °C. Notice that the rad system resin appears to be much darker than the thermal system resin. The resin in the 45 °C rad system vessels appears to climb the vessel walls; see Figure 6.8. The resin upon removal had visible clumps that required mechanical removal; see Figure 6.9. When re-suspended in fresh DI water, the clumps fell apart. Resin clumping may have potential implications for resin removal from the columns.

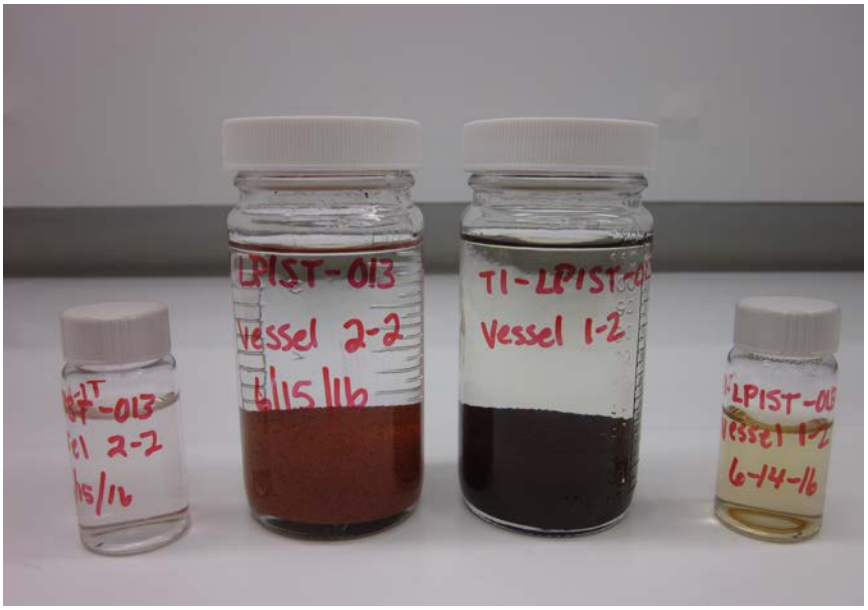

Figure 6.7. Comparison of Test 3 resin and liquids from the thermal system (left) and rad system (right).

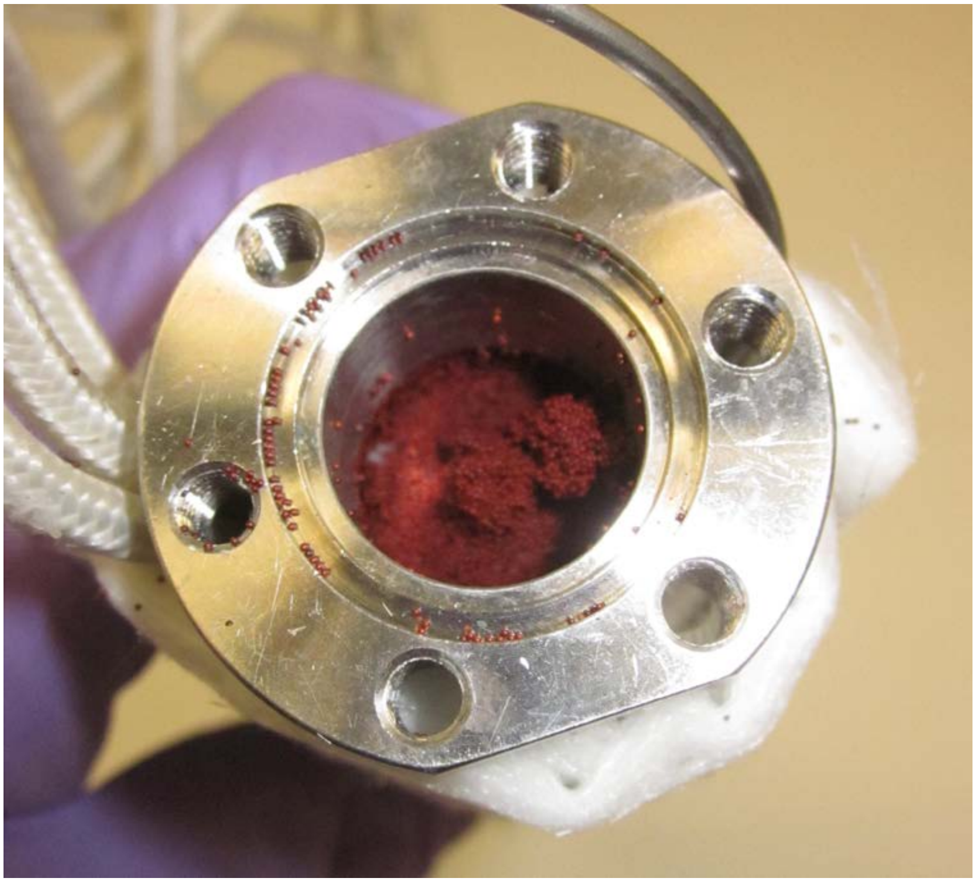

Figure 6.8. Test 3 rad system Vessel 1-8 post-test. Example of resin climbing the walls.

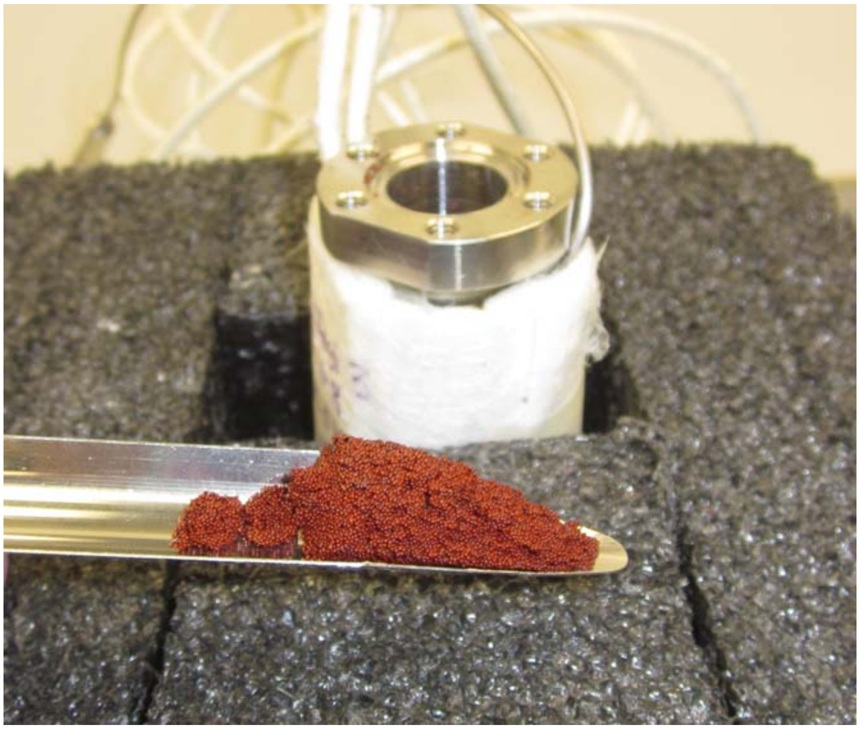

Figure 6.9. Rad system Vessel 1-8 post-test. Example of clumped resin.

6.1.4 Test 4 – Water, Simulant with TOC, 70 °C

Figure 6.10 shows the post-test rad system water with resin, which was very similar to the post-test thermal system water with resin shown in Figure 6.11. No resin clumping was observed; however, both systems had very dark resin after testing. Figure 6.12 shows the thermal system simulant and resin. Note the greater discoloration than the water alone. The pre-test simulant was nearly colorless. The coloration of the liquid is assumed to be from the resin at the elevated temperature. Figure 6.13 shows the resin and simulant from the rad system after irradiation. There is a deep discoloration from the combination of the simulant, temperature, and resin when exposed to gamma dose. Figure 6.14 shows the change in simulant coloration after irradiation without resin exposure.

Figure 6.10. Test 4 rad system post-test water with resin.

Figure 6.11. Test 4 thermal system post-test resin with water.

Figure 6.12. Test 4 thermal system post-test resin and simulant with HEDTA.

Figure 6.13. Test 4 rad system simulant with HEDTA and resin post-test.

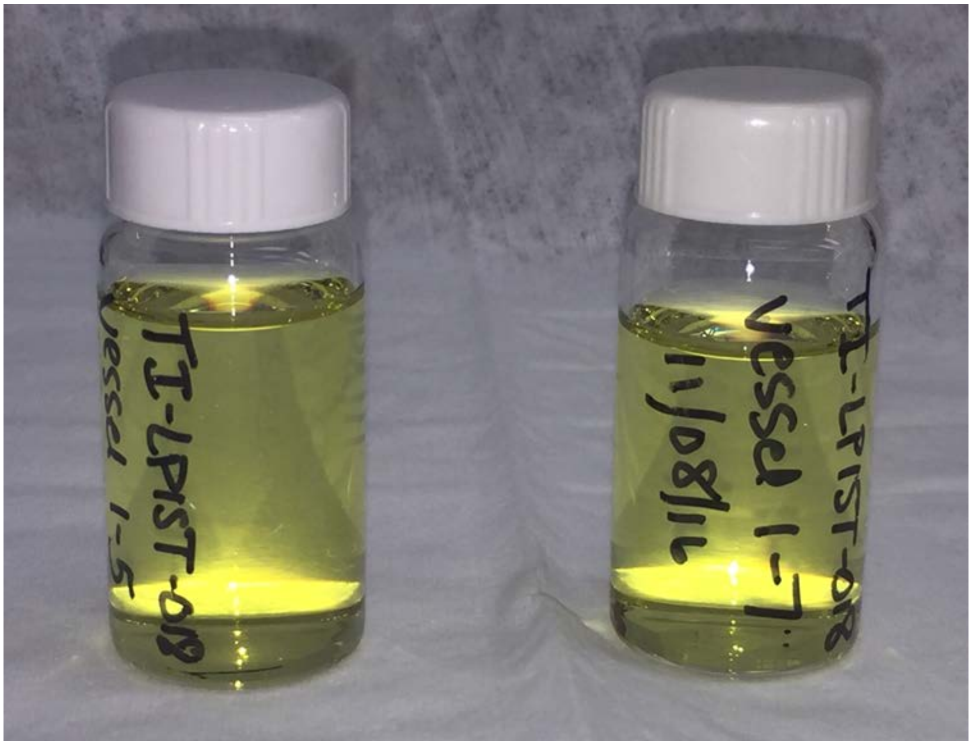

Figure 6.14. Test 4 rad system simulant with HEDTA (no resin) after irradiation.

6.1.5 Test 5 – 0.45M HNO_3, Simulant, 70 °C

Figure 6.15 and Figure 6.16 show the post-test nitric acid and the resin exposed to nitric acid. Figure 6.15 shows the materials removed from the thermal system and Figure 6.16 shows the materials from the rad system. Note that the thermal vessel nitric acid appears to be blue; this was not observed in the rad system liquid. Figure 6.17 and Figure 6.18 show the post-test simulant and the resin exposed to simulant. Figure 6.17 shows the materials removed from the thermal system and Figure 6.18 shows the materials from the rad system.

Figure 6.15. Nitric acid after exposure to the thermal vessel at 70 °C (left). Resin after exposure to nitric acid at 70 °C.

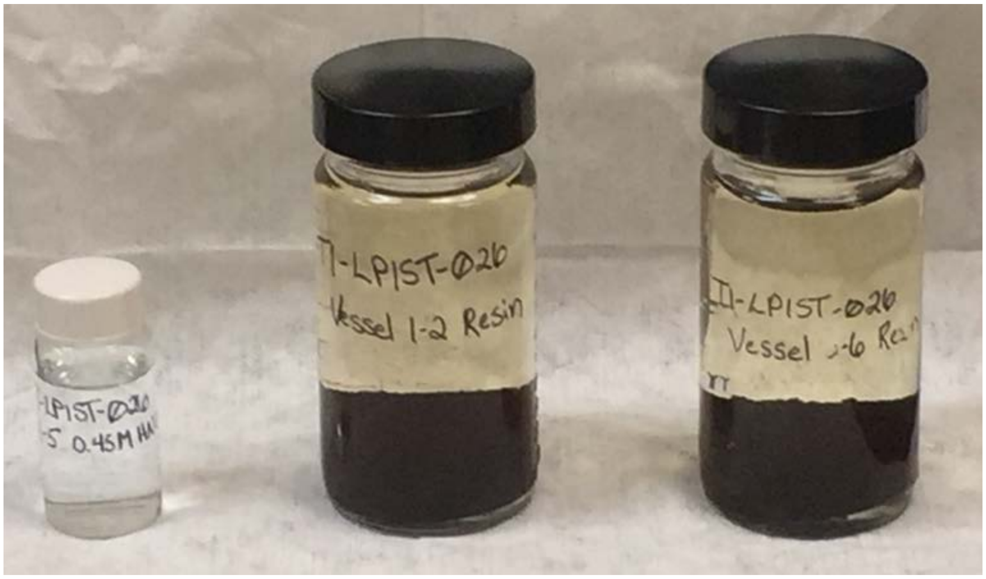

Figure 6.16. Test 5 rad system nitric acid post-test acid only and resin.

Figure 6.17. Test 5 post-test thermal system simulant and resin.

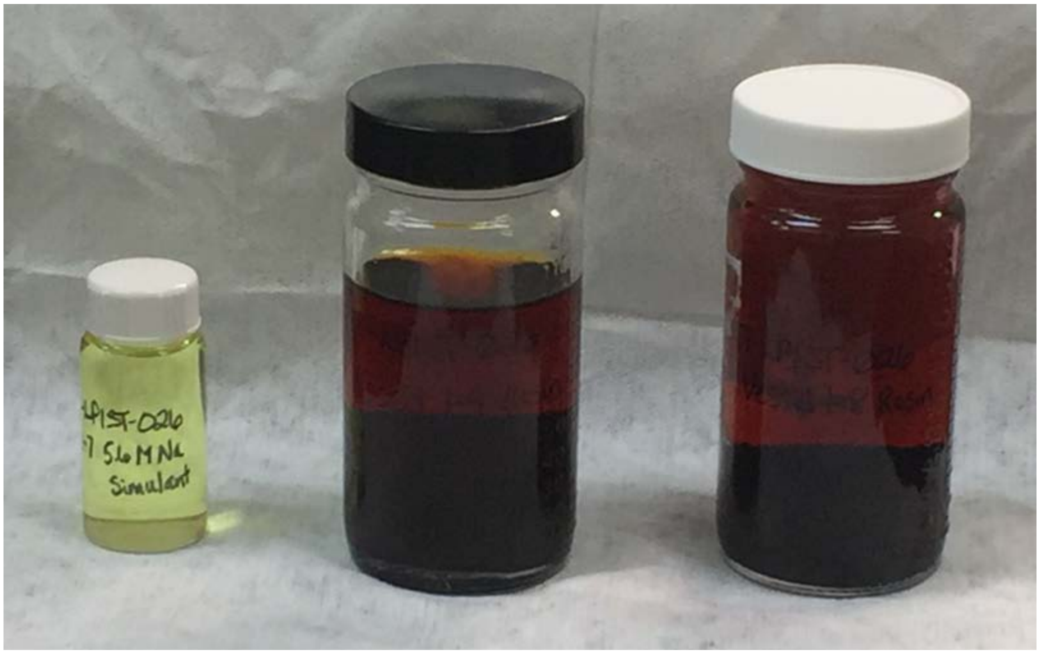

Figure 6.18. Test 5 post-test rad system simulant and resin.

6.2 Formaldehyde Analysis

All of the liquids that were in contact with resin were tested for formaldehyde content using the EMD Millipore Formaldehyde Test Kit (part number 110036) as an FIO analysis. No formaldehyde was observed above the detection limit of the kit in any of the resin-contacted liquids from the gas generation testing. Additionally, the mass spectrometry laboratory was used to look for the presence of formaldehyde as an opportunistic FIO analysis in the gas samples. No formaldehyde was observed in the gas samples.

6.3 Total Organic Carbon Analysis

6.3.1 Total Organic Carbon Results

Samples of the liquids from the thermal and rad systems were submitted to ASO for TOC analysis. The analysis provided both a total inorganic carbon (TIC) in addition to a TOC analysis. Samples of liquid not contacted with resin were also submitted as control samples. The samples were analyzed by ASO in two batches with the water samples analyzed before the acid and caustic simulant samples. The TOC analysis data are provided in Appendix B of this report.

In general, the samples in contact with resin contained greater amounts of TIC and TOC than the liquid alone. The samples exposed to radiation showed a greater amount of TIC than TOC while the opposite was the case in the thermal samples.

The liquids without resin contained both TIC and TOC. All of the reported analytical results were blank-subtracted with the measurement blank result. The deionized water source used for reagent preparation was analyzed and was found to contain carbon, accounting for roughly half of the carbon in the liquids. Other possible sources of carbon in those liquids could be residual organic material on the gas generation test vessels or the vials used for storage of the liquids after testing.

6.3.2 Carbon Species Analysis by LC-MS

The water samples contacted with resin as well as a couple of the water-only liquids were analyzed by electrospray liquid chromatography-mass spectrometry (LC-MS) to get a feel for the types of organic carbon species that may be present in the liquid after contact with resin. In general, the same trend was observed, with more species observed in the thermal system samples than the rad system. In the thermal system samples, several peaks that resembled a polymer chain were observed; however, the unit mass was not an obvious monomer of the sRF polymer and it remains unidentified.

6.4 Video of Resin Irradiation

A 36-mm-diameter by 55-mm-high column of sodium form resin with a 60-mm-high water headspace above the resin was prepared. The resin was exposed to 41 kRad/hr of Co-60 gamma irradiation in the PNNL HEF while a video feed was collected. The total irradiation period was 2 hours, and no signs of gas generation were observed and the video collection was aborted.

7.0 Gas Generation Results Self-Flammability Evaluation

As discussed by Mahoney (2015), some tank wastes generate gases that are self-flammable—i.e., they contain proportions of fuel (primarily hydrogen, H_2), oxidant (nitrous oxide, N_2O), and inertant (nitrogen, N_2) that could allow the generated gas to be ignited even in the absence of air. Because of this possibility, and the possible safety significance of self-flammable gases in the LAWPS resin beds, the gases generated during the tests reported in this document were evaluated for self-flammability.

The basis of calculations was the same set of raw composition data used in determining the hydrogen generation rates. The compositions from pairs of replicates were averaged. The next step of analysis was to account for the effects of two non-generated gases that were present in test gas samples: argon (Ar) purge gas and air that leaked into the test vessels in quantities that most often were insignificant but sometimes were substantial. The Ar was completely removed from the composition and N_2 and O_2 were removed in the proportions found in air (approximately 0.79 moles N_2 to 0.21 moles O_2).

If it was assumed that all the nitrogen measured in the sample gas came from air (N_2 tracer for air), the generated-gas composition was calculated to be

$$[\mathrm{N_2}]_{generated} = [\mathrm{Ar}]_{generated} = 0$$

$$[\mathrm{O_2}]_{generated} = \frac{[\mathrm{O_2}]_{measured} - (21/79)[\mathrm{N_2}]_{measured}}{1 - [\mathrm{N_2}]_{measured} - (21/79)[\mathrm{N_2}]_{measured} - [\mathrm{Ar}]}$$

$$[\mathrm{X}]_{generated} = \frac{[\mathrm{X}]_{measured}}{1 - [\mathrm{N_2}]_{measured} - (21/79)[\mathrm{N_2}]_{measured} - [\mathrm{Ar}]}$$

where X is any gas other than N_2, O_2, or Ar, and the concentrations in brackets are mole fractions of generated or measured gas.

If it was assumed that all the oxygen measured in the sample gas came from air (O_2 tracer for air), the generated-gas composition was calculated to be

$$[\mathrm{O_2}]_{generated} = [\mathrm{Ar}]_{generated} = 0$$

$$[\mathrm{N_2}]_{generated} = \frac{[\mathrm{N_2}]_{measured} - (79/21)[\mathrm{O_2}]_{measured}}{1 - (79/21)[\mathrm{O_2}]_{measured} - [\mathrm{O_2}]_{measured} - [\mathrm{Ar}]}$$

$$[\mathrm{X}]_{generated} = \frac{[\mathrm{X}]_{measured}}{1 - (79/21)[\mathrm{O_2}]_{measured} - [\mathrm{O_2}]_{measured} - [\mathrm{Ar}]}$$

The choice between O_2 or N_2 tracer was made according to the criterion of giving physically reasonable compositions: no mole fractions that were negative or exceeded unity. In many cases, the two tracers were nearly equivalent.

It is recognized that using O_2 and N_2 as air tracers creates some ambiguity, since both of these gases can be involved in the reactions that generate gas. Oxygen can be the limiting gas (O_2 tracer), either because of N_2 generation or because of air in-leakage followed by O_2 consumption. Similarly, nitrogen can be the limiting gas (N_2 tracer), either because of O_2 generation or because of air in-leakage followed by N_2 consumption (although this last possibility is chemically unlikely).

Figure 7.1, Figure 7.2, Figure 7.3, Figure 7.4, and Figure 7.5 (located at the end of this section) show the calculated generated-gas compositions for Tests 1, 2, 3, 4, and 5, respectively. The plots are of the same type used by Mahoney (2015). The y-axis is mole percent fuel; only hydrogen is considered as fuel, since methane and other hydrocarbons were present only in trace quantities. The x-axis is mole percent total inertant: the sum of N_2, carbon dioxide (CO_2), and, in one set of samples, nitric oxide (NO). Flammable conditions exist only in the roughly triangular region between the upper sloping part of the curve (the upper flammability limit [UFL]) and the lower, nearly horizontal part (the lower flammability limit [LFL]). Above the envelope, there is too little oxidant to allow combustion; below the envelope, there is too little fuel.

Note three assumptions in these calculations. First, the literature data that supplied the flammability envelope used only N_2 as an inertant. It is assumed that the other gases that do not participate in H_2/oxidant combustion have the same inerting effect as N_2. This is an approximation. Second, N_2O and O_2 are treated as equivalent oxidants, which is a close approximation for hydrogen combustion. Third, the data are on a dry basis; the separate inerting effect of water vapor is not included. Mahoney (2015) provides further discussion of some of these assumptions.

The self-flammability of generated gases will be discussed on a simulant-by-simulant basis rather than a test-by-test basis, since some simulants were tested at one temperature in some tests and at other temperatures in other tests. Only the tests with radiation present are included.

7.1 Deionized Water with and without Resin

Figure 7.1 shows the self-flammability potential of gases generated by irradiation of water and water/resin at 25 °C and 45 °C, while Figure 7.4 continues to 70 °C. For water/resin, all of the generated gases are above the UFL (fuel-rich), the only significant oxidant is oxygen, and the main generated inertant is nitrogen, although some carbon dioxide is also generated.

For water alone, the generated gases sometimes are self-flammable owing to a higher oxygen fraction than in water/resin and a low fraction of nitrogen and carbon dioxide. It is hard to understand reason for the presence of these latter gases, since they have no obvious sources. Given their low concentration in many of the samples, they may come from noise in the composition measurement or in the air-removal calculations. As can be seen in Figure 7.1 and Figure 7.4, the molar ratio of hydrogen to oxygen is near the stoichiometric value, 2:1.

7.2 Nominal Target Feed Simulant with and without Resin

The nominal target feed simulant used in Test 2 and Test 5 had a sodium (Na) concentration of about 5.6 M and contained no reactive carbon. The self-flammability potential of gases generated by irradiation of simulant and simulant/resin is shown in Figure 7.2 (25 °C and 45 °C) and Figure 7.5 (70 °C). At the lower temperatures, the generated gases from simulant/resin are above the UFL, the only significant oxidant is oxygen (often not present at all), and the only significant inertant is nitrogen, whose mole fraction increases from early to late samples. Only traces of carbon dioxide are present. At 70 °C, as shown in Figure 7.5, the gases remain above the UFL. At this temperature, carbon dioxide is present in later samples in more than trace quantities, but nitrogen is still the predominant inertant.

The gases from simulant alone consistently contain no nitrogen or nitrous oxide, and only traces of carbon dioxide. The oxygen fraction increases with temperature. At 25 °C the gases are barely above the UFL, at 45 °C they are in the center of the envelope, and at 70 °C they are still within the envelope but near the LFL.

7.3 Nominal Target Feed Simulant Plus HEDTA with and without Resin

The 5.6 M Na feed simulant discussed above was tested at 70 °C after adding a low concentration of the reactive carbon compound HEDTA. For brevity, this form of the simulant is referred to as simulant+C in the present discussion. The self-flammability potential of gases generated by irradiation of simulant+C and simulant+C/resin is shown in Figure 7.4 (Test 4).

Most of the gases generated by simulant+C/resin at 70 °C are above the UFL, though closer to it than for plain (no HEDTA) simulant/resin at 70 °C (Figure 7.5). One sample (the second one taken) was only slightly above the UFL, and another (the first) was within the envelope. Over time, the fraction of inertant increased and the mixture became more fuel-rich. Nitrous oxide was the only oxidant and oxygen was absent, the opposite of the situation for plain simulant/resin, and nitrogen was the only inertant.

The simulant+C without resin consistently produced self-flammable gases at 70 °C. The types of gases and the way they changed over time were similar to those for simulant+C/resin, but the inertant (nitrogen) fraction was consistently lower.

7.4 Nitric Acid with and without Resin

Dilute nitric acid (0.45 M HNO_3) was also tested with and without resin at 25 °C, 45 °C, and 70 °C in Tests 3 and 5. The self-flammability potential of gases generated by irradiation of simulant and simulant/resin is shown in Figure 7.3 (25 °C and 45 °C) and Figure 7.5 (70 °C).

At 25 °C and 45 °C, the gas generated from HNO_3/resin was within the flammability envelope at 188 hr, on or not far above the UFL at 383 hr, and definitely above the UFL at later times. Nitrous oxide was the only oxidant, while both nitrogen and carbon dioxide were significant inertants, with carbon dioxide being predominant. The fuel fraction increased over the course of the test, while the oxidant decreased and the inertant peaked and then decreased. At 70 °C, fuel and inertant concentrations were high enough to keep the generated gas almost outside the flammability envelope, although one sample is on the UFL. This was the only test where nitric oxide appeared as a significant fraction of the gas, more than 6 mol% at the beginning of the test, dropping to zero by the end.

The gas generated from HNO_3 alone was consistently self-flammable. The oxidant was oxygen and the inertants were at trace levels in the gas. The molar ratio of hydrogen to oxygen is near the stoichiometric value. The data point that has considerably lower H_2 than the others was affected by a large air in-leakage in one of the replicates. It would have grouped with them if the air-affected data had been excluded.

7.5 Summary

For all four of the simulants tested in this study, the presence of resin led to the production of gases that were less self-flammable than the gases from simulant alone. Although self-flammability was decreased by the presence of resin, the flammability of the resin-affected gas in externally introduced air would be higher in those cases where the fuel content is increased by resin. A brief summary of the effect of sRF resin on self-flammability is as follows:

- Water: The effect of resin, at all tested temperatures, was to make the gases higher in fuel and lower in oxidant.
- Plain feed simulant (no HEDTA): The presence of resin led to gases that contained more fuel and more inertant (and therefore less oxidant) than for the simulant alone, an effect that became more pronounced as temperature increased from 25 °C to 70 °C.
- Feed simulant plus HEDTA: At 70 °C, the only temperature tested, the effect of resin was to increase the fuel and inertant fractions.
- Nitric acid: The effect of resin, at all tested temperatures, was to decrease the fuel fraction and increase the inertant fraction.

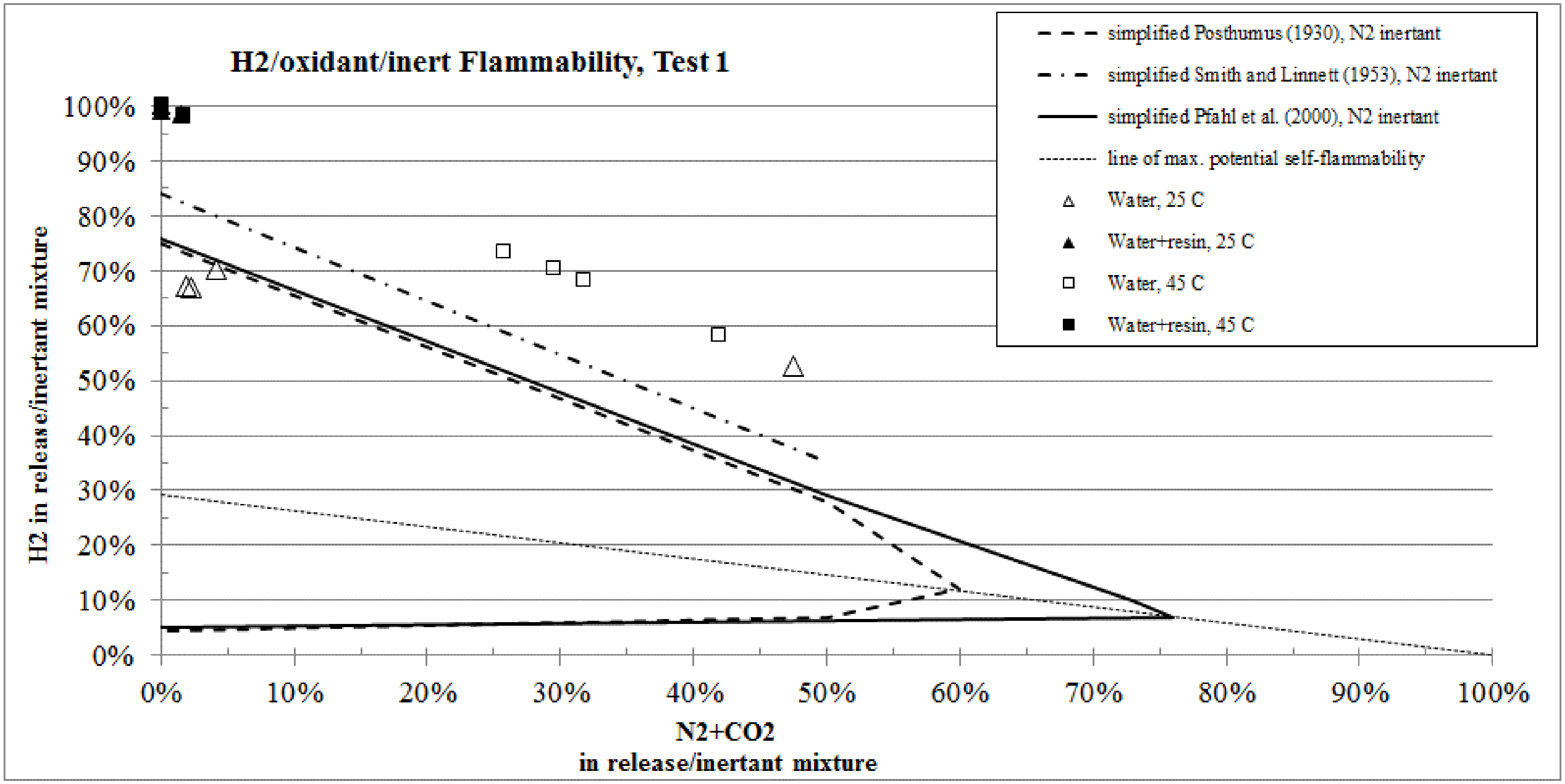

Figure 7.1. Flammability characteristics of gases from Test 1.

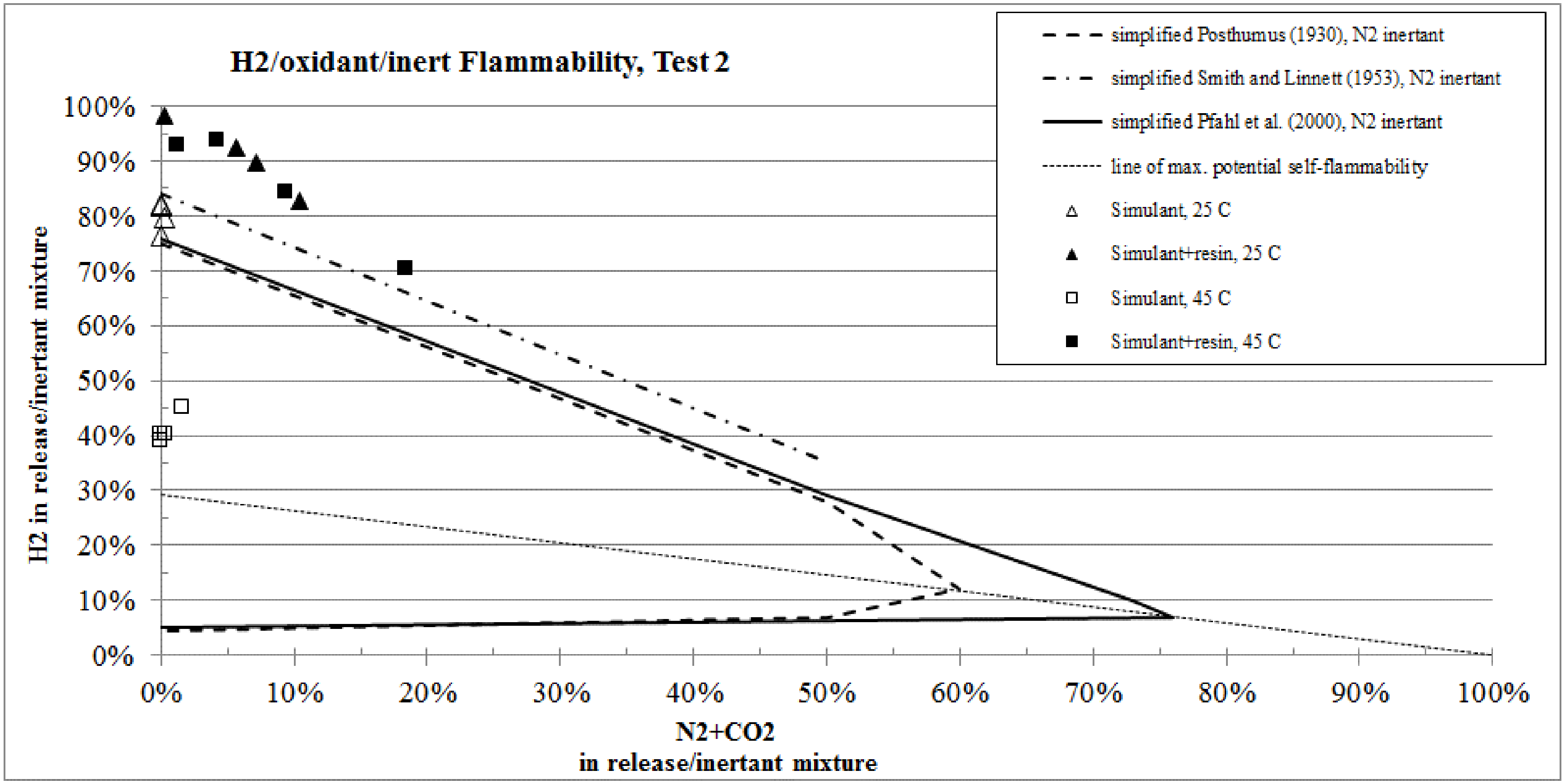

Figure 7.2. Flammability characteristics of gases from Test 2.

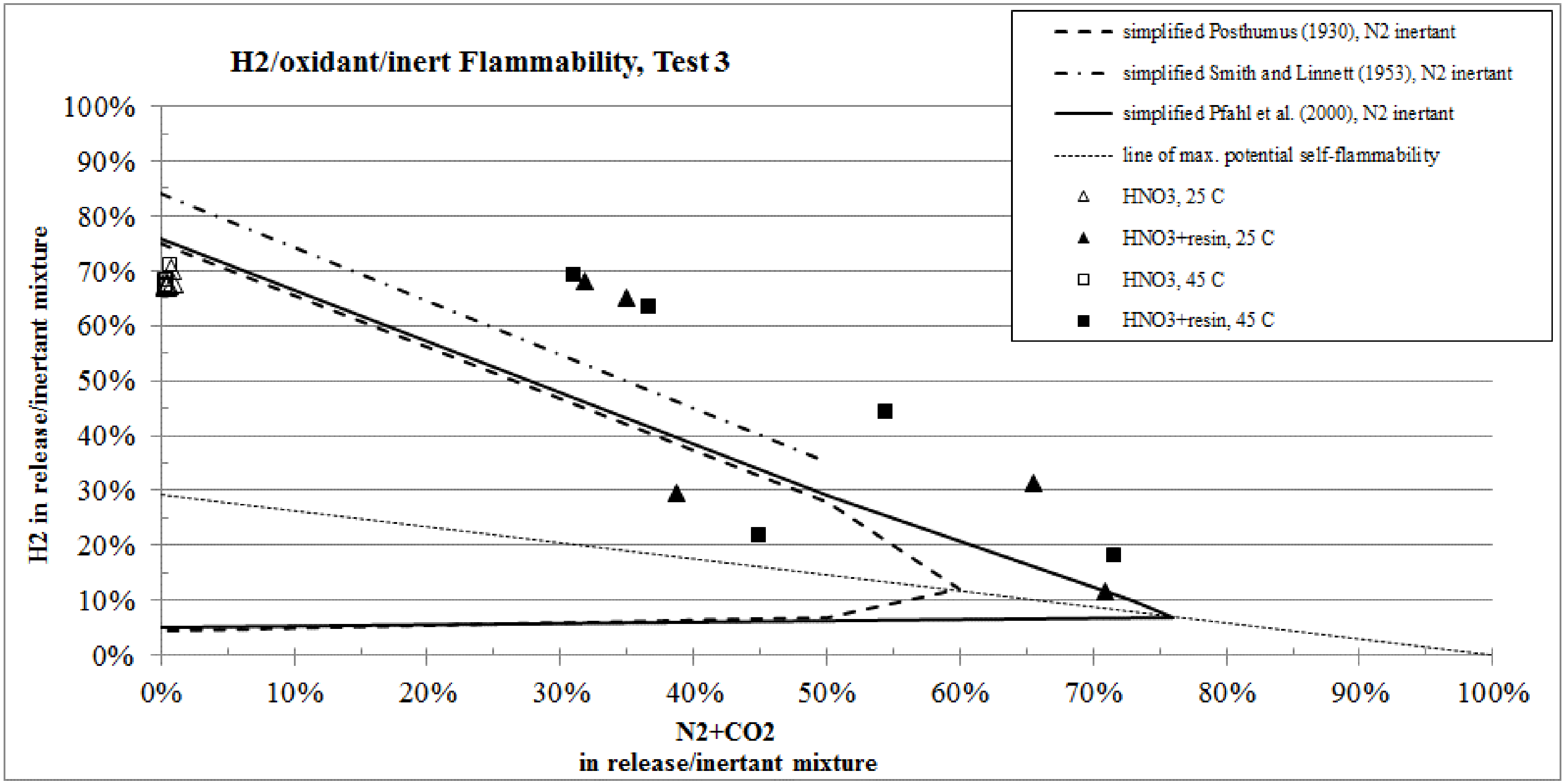

Figure 7.3. Flammability characteristics of gases from Test 3.

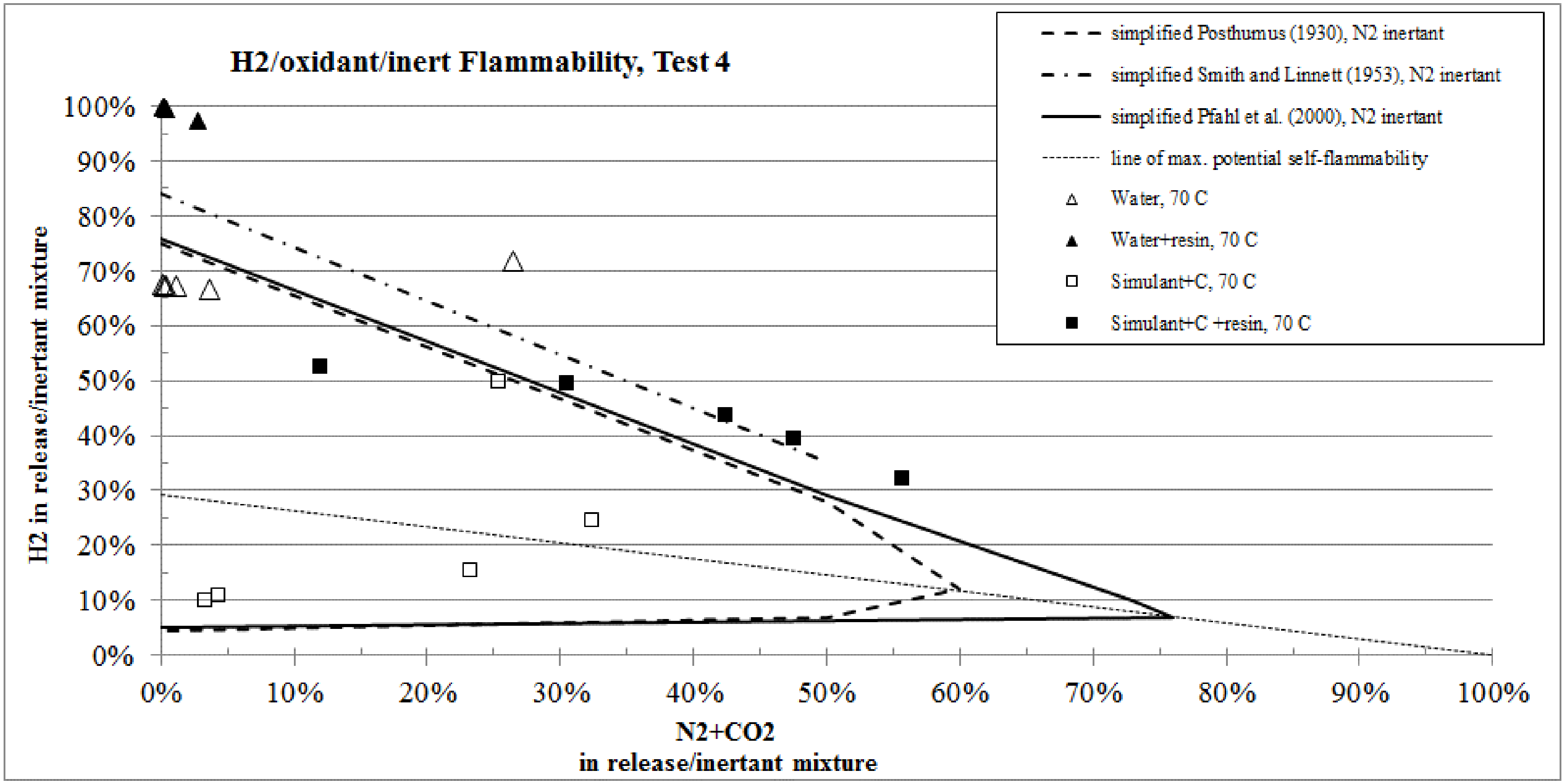

Figure 7.4. Flammability characteristics of gases from Test 4.

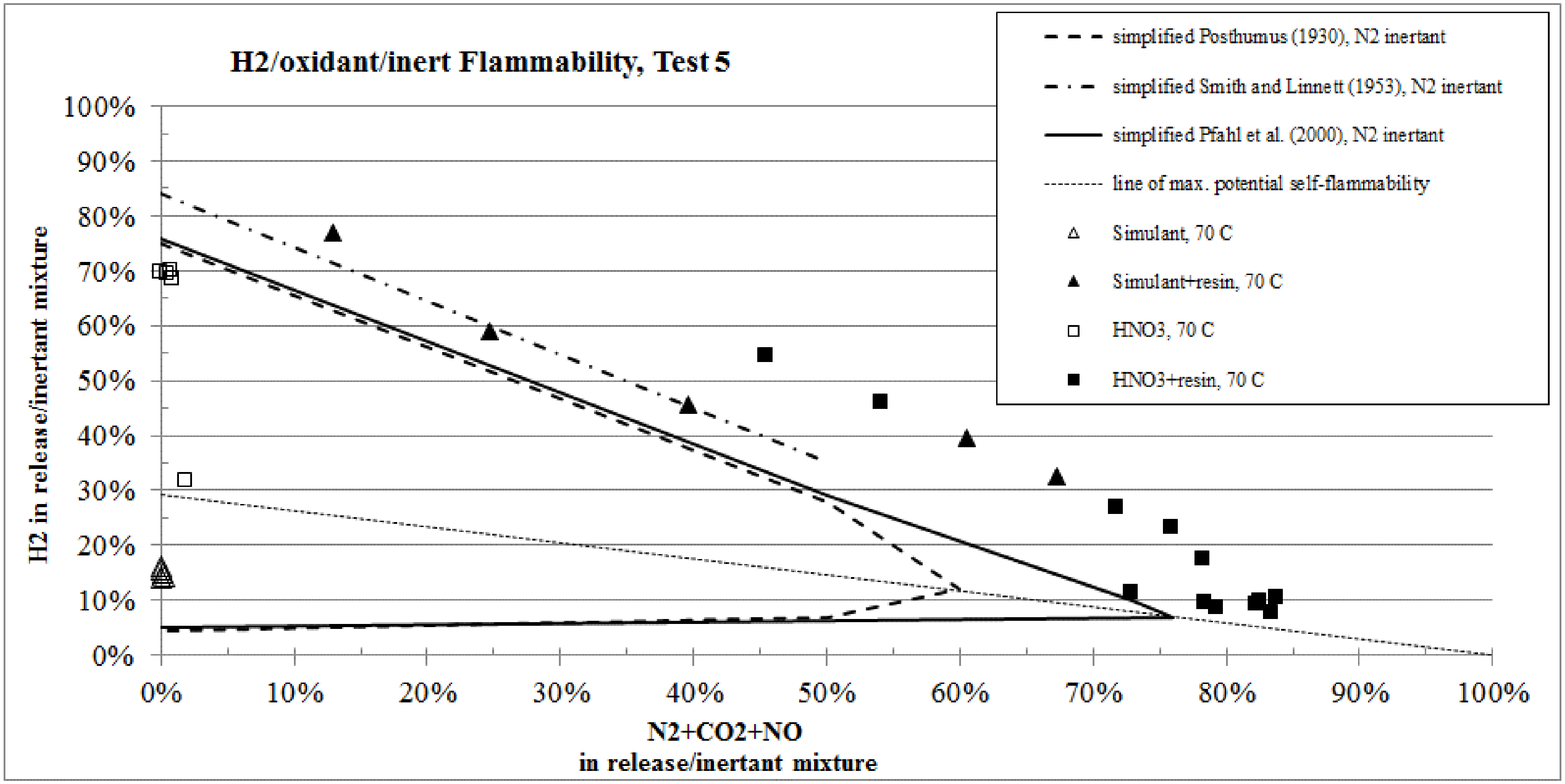

Figure 7.5. Flammability characteristics of gases from Test 5.

8.0 Summary

Prior to this project work, there was a limited number of well-controlled studies of the impact of sRF resin on hydrogen generation. The current safety basis for the LAWPS for hydrogen is 1.4 times the Hu model output for water as derived by WRPS based on previous studies of hydrogen generation of sRF resin. The testing conducted here is to support this safety basis with the addition of sRF resin to different liquids that will be used in the LAWPS. Test 1 was conducted using laboratory-grade DI water and demonstrated results well below the Hu model with water alone and results below the Hu model with the addition of resin. However, the use of less-pure grades of water will likely result in higher hydrogen generation rates as there may be species present to scavenge hydroxyl radicals and increase the hydrogen concentration in the headspace based on the experiments conducted and presented in the literature (Pastina et al. 1999). The prompt radiolytic hydrogen generation describes the initial production of molecular hydrogen in an open system under radiolytic conditions. Most experiments to determine the prompt hydrogen value of water or other aqueous species add a reductant such as bromide to preserve the molecular hydrogen from attack by hydroxyl radicals. The water-only values do not match the prompt hydrogen value of 0.45 likely because the experiment was performed in a closed system with laboratory grade deionized water in the absence of reductant species. The values obtained were found to reasonably match literature values for a pure water experiment in a closed system (Pastina and Laverne 2001) as well as the rate constant information in the literature (Buxton et al. 1988).

The remaining tests on other ion exchange process liquids and simulated feed demonstrated hydrogen generation rates less than the anticipated modeled generation rate for water using the Hu model, i.e., G-values less than 0.45, and in some cases less than the Hu model predicted values for those liquids. It should be noted that towards the end of the simulant tests, the G-values were higher than the Hu model prediction for the simulant, likely due to oxidative degradation of the resin and further scavenging of hydroxyl radicals by the resin. The thermal-only experiments yielded very little hydrogen (less than 1%) as compared to the radiolytic system experiments.

Visual examination of the resin and liquids after testing showed significant resin darkening in the irradiated resin cases, which is an indicator of oxidation. The exact impact on cesium loading capacity this damage would cause is not known. The liquids showed discoloration, likely from leaching and reaction of the liquid with the organic resin. In addition, self-heating behavior was observed in the nitric acid testing at elevated temperatures in the presence of resin.

9.0 References

Birdwell J, D Schuh, P Taylor, R Collins, and R Hunt. 2010. *An Engineering Evaluation of Spherical Resorcinol Formaldehyde Resin*. ORNL/RM-2010/200, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Bryan SA and LR Pederson. 1994. *Composition, Preparation, and Gas Generation Results from Simulated Wastes of Tank 241-SY-101*. PNL-10075, Pacific Northwest Laboratory, Richland, Washington.

Bryan SA and LR Pederson. 1995. *Thermal and Combined Thermal and Radiolytic Reactions Involving Nitrous Oxide, Hydrogen, and Nitrogen in the Gas Phase; Comparison of Gas Generation Rates in Supernate and Solid Fractions of Tank 241-SY-101 Simulated Waste*. PNL-10490, Pacific Northwest Laboratory, Richland, Washington.

Bryan SA, CM King, LR Pederson, SV Forbes, and RL Sell. 1996. *Gas Generation from Tank 241-SY-103 Waste*. PNNL-10978, Pacific Northwest National Laboratory, Richland, Washington.

Buxton GV, CL Greenstock, WP Helman, and AB Ross. 1988. “Critical Review of Rate Constants for Reactions of Hydrated Electrons, Hydrogen Atoms and Hydroxyl Radicals *(·OH/·O-)* in Aqueous Solution.” *Journal of Physical and Chemical Reference Data* 17, 513; doi: 10.1063/1.555805.

Duffey CE and DD Walker. 2006. *Radiolytic, Thermal, and Physical Degradation Testing of Spherical Resorcinol-Formaldehyde Resin*. WSRC-TR-2005-0075, Savannah River National Laboratory, Aiken, South Carolina.

Golcar GR, NG Colton, JG Darab and HD Smith. 2000. *Hanford Tank Waste Simulants Specification and Their Applicability for the Retrieval, Pretreatment, and Vitrification Processes*. PNWD-2455 (BNFL-RPT-012, Rev. 0), Battelle, Pacific Northwest Division, Richland, Washington.

Hu TA. 2004. *Empirical Rate Equation Model and Rate Calculations of Hydrogen Generation for Hanford Tank Waste*. HNF-3851, Rev. 1, CH2M Hill Hanford Group, Inc., Richland, Washington.

Hu TA. 2012. “Improved Model for Hydrogen Generation Rate of Radioactive Waste at the Hanford Site.” *Nuclear Technology* 178, 39-54, April, 2012.

King CM and SA Bryan. 1998. *Thermal and Radiolytic Gas Generation from Tank 241-A-101 Waste.* TWS98.78, Pacific Northwest National Laboratory, Richland, Washington.

King CM, LR Pederson, and SA Bryan. 1997. *Thermal and Radiolytic Gas Generation from Tank 241-S-102 Waste*. PNNL-11600, Pacific Northwest National Laboratory, Richland, Washington.

King CM and SA Bryan. 1999. *Thermal and Radiolytic Gas Generation Tests on Material from Tanks 241-U-103, 241-AW-101, 241-S-106, and 241-S-102: Status Report.* PNNL-12181, Pacific Northwest National Laboratory, Richland, Washington.

Mahlman HA. 1961. “The OH yield in the Co^{60} γ Radiolysis of HNO_3.” *J. Chem. Phys.*, **35**, (3) 936-939.

Mahoney LA. 2015. *Self-Flammability of Gases Generated by Hanford Tank Waste and the Potential of Nitrogen Inerting to Eliminate Flammability Safety Concerns*. PNNL-24194 Rev. 1 (WTP-RPT-237 Rev. 1), Pacific Northwest National Laboratory, Richland, Washington.

NQA-1-2000, *Quality Assurance Requirements for Nuclear Facility Applications*. The American Society of Mechanical Engineers, New York, New York.

NQA-1-2008, *Quality Assurance Requirements for Nuclear Facility Applications*. The American Society of Mechanical Engineers, New York, New York.

NQA-1a-2009, *Addenda to ASME NQA-1-2008*. The American Society of Mechanical Engineers, New York, New York.

Pastina B, JA LaVerne, and S Pimblott. 1999. “Dependence of Molecular Hydrogen Formation in Water on Scavengers of the Precursor to the Hydrated Electron.” *J. Phys. Chem. A*, 103 (29) 5841-5846.

Pastina B and JA LaVerne. 2001. “Effect of Hydrogen on Hydrogen Peroxide in Water Radiolysis.” *J. Phys. Chem. A*, 105, 9316-9322.

Pfahl UJ, MC Ross, JF Shepherd, KO Pasamehmetoglu, and C Unal. 2000. “Flammability limits, ignition energy, and flame speeds in H_2–CH_4–NH_3–$N2_O$–O_2–N_2 mixtures.” *Combustion and Flame* **123**(1–2):140-158.

Posthumus K. 1930. “On explosion regions of gas mixtures, in which one or two of the gases are endothermic.” *Rec. trav. chim.* **49**: 309-347.

Russell RL, DE Rinehart, and RA Peterson. 2014. *Ion Exchange Testing with SRF Resin FY 2012*. PNNL-21645, Rev. 1 (WTP-RPT-223, Rev. 1), Pacific Northwest National Laboratory, Richland, Washington.

Russell RL, PP Schonewill, and CA Burns. 2017. *Simulant Development for LAWPS Testing*. PNNL-26165 (RPT-LPIST-001, Rev. 0), Pacific Northwest National Laboratory, Richland, Washington.

Smith S and JW Linnett. 1953. “The upper limits of inflammability of hydrogen-air and hydrogen-nitrous oxide mixtures.” *J. Chem. Soc. (London) Part I*, 37-43.

Appendix A –
Gas Composition Analysis Results

Table A.1. Percent Composition of Gas Sampled (including argon) – Water-Only Data, 25 °C

					Mole Percent Gas, 25 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 1, Vessel 1-1	1-1 Day 11	259.00	259.00	9.16E+07	97.9	0.581	1.2	0.21		0.178						
	G-1-23-1	191.42	450.42	6.77E+07	95.55	2.94	0.191	1.15		0.168						
	G-1-30-1	192.00	642.42	6.79E+07	88.5	4.52	3.67	3.15		0.131						A
	G-1-44-1	216.08	858.50	7.64E+07	29.8	1.62	53.5	15		0.063			0.002			A
Test 1, Vessel 1-5	1-5 Day 11	259.00	259.00	9.16E+07	98.5	0.723	0.547	0.036		0.177						
	G-1-23-5	191.42	450.42	6.77E+07	96.3	2.55	0.087	0.93		0.163						
	G-1-30-5	192.00	642.42	6.79E+07	93.8	4.16	0.131	1.83		0.118						
	G-1-44-5	216.08	858.50	7.64E+07	91.38	3.63	2.62	2.26		0.098						
Test 1, Vessel 2-1	2-1 Day 10	236.08	236.08	0	99.61		0.284	0.091		0.01						
	G-1-24-1	191.17	427.25	0	99.53	0.011	0.374	0.076		0.012						
	G-1-31-1	191.50	618.75	0	99.82		0.133	0.038		0.009						
	G-1-45-1	215.58	834.33	0	99.48	0.012	0.395	0.087		0.026						
Test 1, Vessel 2-5	2-5 Day 10	236.08	236.08	0	99.65		0.286	0.055		0.009						
	G-1-24-5	191.17	427.25	0	99.84	0.004	0.142	0.005		0.008						
	G-1-31-5	191.50	618.75	0	99.82		0.133	0.038		0.009						
	G-1-45-5	215.58	834.33	0	99.79		0.165	0.038		0.009						

A - Corrected for air in-leakage based on the nitrogen content
Blank values indicate < 0.001 mol % gas

Table A.2. Percent Composition of Gas Sampled (including argon) – Water-Only Data, 45 °C

					Mole Percent Gas, 45 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 1, Vessel 1-3	1-3 Day 11	259.00	259.00	9.16E+07	96.3	0.822	2.15	0.48		0.229						
	G-1-23-3	191.42	450.42	6.77E+07	99.01	0.401	0.332	0.081		0.175						
	G-1-30-3	192.00	642.42	6.79E+07	99.22	0.5	0.106	0.017		0.158						
	G-1-44-3	216.08	858.50	7.64E+07	99.4	0.388	0.075	0.016		0.123						
Test 1, Vessel 1-7	1-7 Day 11	259.00	259.00	9.16E+07	98.3	0.887	0.578	0.042		0.242						
	G-1-23-7	191.42	450.42	6.77E+07	99.29	0.432	0.073	0.021		0.188						
	G-1-30-7	192.00	642.42	6.79E+07	99.4	0.351	0.094	0.02		0.139						
	G-1-44-7	216.08	858.50	7.64E+07	99.49	0.315	0.061	0.024		0.109						
Test 1, Vessel 2-3	2-3 Day 10	236.08	236.08	0	99.58		0.363	0.051		0.008						
	G-1-24-3	191.17	427.25	0	96.49	0.01	2.94	0.55		0.011						
	G-1-31-3	191.50	618.75	0	99.89		0.09	0.009		0.007						
	G-1-45-3	215.58	834.33	0	99.81	0.011	0.131	0.032		0.015						
Test 1, Vessel 2-7	2-7 Day 10	236.08	236.08	0	99.62		0.308	0.066		0.008						
	G-1-24-7	191.17	427.25	0	97.94		1.63	0.423		0.006						
	G-1-31-7	191.50	618.75	0	99.86		0.113	0.023		0.004						
	G-1-45-7	215.58	834.33	0	98.91		0.916	0.166		0.013						

Blank values indicate < 0.001 mole % gas

Table A.3. Percent Composition of Gas Sampled (including argon) – Water-Only Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 4, Vessel 1-1	G-1-162-1	165.08	165.08	5.36E+07	96.7	0.928	1.73	0.384		0.251						
	G-2-8-1	168.17	333.25	5.46E+07	98.41	0.552	0.672	0.111		0.254						
	G-2-18-1	167.50	500.75	5.44E+07	92.9	4.83	0.08	2		0.249						
	G-2-28-1	168.08	668.83	5.46E+07	81.7	12.2	0.139	5.81		0.153						
	G-2-36-1	144.33	813.17	4.69E+07	73.6	13.3	5.33	7.77		0.088						A
	G-2-44-1	143.08	956.25	4.64E+07	78	14.8	0.105	7.06		0.072						
Test 4, Vessel 1-3	G-1-162-3	165.08	165.08	5.36E+07	96.5	1.14	1.66	0.493		0.226						A
	G-2-8-3	168.17	333.25	5.46E+07	81.3	12.5	0.095	5.82		0.2049	0.0051	0.0172				
	G-2-18-3	167.50	500.75	5.44E+07	74.8	16.8	0.06	8.255		0.1129						
	G-2-28-3	168.08	668.83	5.46E+07	73	18	0.05	8.85		0.0594						
	G-2-36-3	144.33	813.17	4.69E+07	74.8	16.93	0.048	8.21		0.0377						
	G-2-44-3	143.08	956.25	4.64E+07	75.7	16.3	0.056	7.89		0.0287						
Test 4, Vessel 2-1	G-1-163-1	166.25	166.25	0	99.35		0.54	0.096		0.012						
	G-2-9-1	168.17	334.42	0	99.787		0.188	0.006		0.019						
	G-2-19-1	167.58	502.00	0	2.28		79.6	18.1								C
	G-2-29-1	168.00	670.00	0	76.1		18.9	5		0.021						C
	G-2-37-1	144.08	814.08	0	99.8		0.153	0.026		0.013	0.009					
	G-2-45-1	143.08	957.17	0	99.868		0.104	0.017		0.01						
Test 4, Vessel 2-5	G-1-163-5	166.25	166.25	0	99.41		0.471	0.082		0.036						
	G-2-9-5	168.17	334.42	0	99.9	0.012	0.077	0.007		0.014						
	G-2-19-5	167.58	502.00	0	99.865	0.042	0.07	0.012		0.011						
	G-2-29-5	168.00	670.00	0	99.84	0.053	0.092	0.008		0.008						
	G-2-37-5	144.08	814.08	0	99.845	0.057	0.075	0.012		0.01						
	G-2-45-5	143.08	957.17	0	99.874	0.045	0.06	0.012		0.009						

A - Corrected for air in-leakage based on the nitrogen content

C - Significant air in-leakage, due to lack of H2, this was not corrected.

Blank values indicate < 0.001 mole percent gas

Table A.4. Percent Composition of Gas Sampled (including argon) - Water Plus Resin Data, 25 °C

					Mole Percent Gas, 25 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 1, Vessel 1-2	1-2 Day 11	259.00	259.00	9.16E+07	61.5	37.3	1.03	0.147		0.006			0.014		0.006	
	G-1-23-2	191.42	450.42	6.77E+07	66.2	33.1	0.104	0.57		0.005						
	G-1-30-2	192.00	642.42	6.79E+07	58.3	41.5	0.139	0.051		0.004			0.006			
	G-1-44-2	216.08	858.50	7.64E+07	38	61.9	0.059	0.04		0.008			0.006			D
Test 1, Vessel 1-6	1-6 Day 11	259.00	259.00	9.16E+07	75.2	24.2	0.55	0.022		0.006			0.011		0.008	
	G-1-23-6	191.42	450.42	6.77E+07	42.2	18.9	30.7	8.2		0.02			0.004			A
	G-1-30-6	192.00	642.42	6.79E+07	69.3	30.6	0.062	0.017		0.003						
	G-1-44-6	216.08	858.50	7.64E+07	54.9	45	0.052	0.018		0.005						
Test 1, Vessel 2-2	2-2 Day 10	236.08	236.08	0	99.3		0.61	0.088		0.005						
	G-1-24-2	191.17	427.25	0	94.71		4.31	0.97		0.014						
	G-1-31-2	191.50	618.75	0	99.77		0.188	0.036		0.005						
	G-1-45-2	215.58	834.33	0	99.8	0.013	0.149	0.024		0.012						
Test 1, Vessel 2-6	2-6 Day 10	236.08	236.08	0	96.5	0.009	2.91	0.58		0.009						
	G-1-24-6	191.17	427.25	0	99.81		0.16	0.028		0.005						
	G-1-31-6	191.50	618.75	0	99.85		0.129	0.021		0.004						
	G-1-45-6	215.58	834.33	0	82.9		13.6	3.5		0.013						C

A - Corrected for air in-leakage based on the nitrogen content

C - Significant air in-leakage, due to lack of H2, this was not corrected.

D - Sampling error that may have affected gas composition

Blank values indicate < 0.001 mole % gas

Table A.5. Percent Composition of Gas Sampled (including argon) - Water Plus Resin Data, 45 °C

					Mole Percent Gas, 45 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 1, Vessel 1-4	1-4 Day 11	259.00	259.00	9.16E+07	51.8	44	3.5	0.7		0.017			0.047	0.013	0.009	D
	G-1-23-4	191.42	450.42	6.77E+07	70.2	29.6	0.116	0.018		0.006			0.016			
	G-1-30-4	192.00	642.42	6.79E+07	68.8	30.8	0.316	0.062		0.005			0.013		0.011	
	G-1-44-4	216.08	858.50	7.64E+07	62.4	37.5	0.092	0.023		0.008			0.014			
Test 1, Vessel 1-8	1-8 Day 11	259.00	259.00	9.16E+07	64.8	34.5	0.64	0.023		0.006			0.039	0.011	0.011	
	G-1-23-8	191.42	450.42	6.77E+07	77.9	22	0.074	0.009		0.006			0.012			
	G-1-30-8	192.00	642.42	6.79E+07	61.4	38.5	0.102	0.013		0.004			0.017			
	G-1-44-8	216.08	858.50	7.64E+07	65.4	34.4	0.117	0.017		0.011			0.01			
Test 1, Vessel 2-4	2-4 Day 10	236.08	236.08	0	99.45		0.502	0.045		0.004						
	G-1-24-4	191.17	427.25	0	99.73	0.02	0.196	0.017		0.034						
	G-1-31-4	191.50	618.75	0	99.82		0.151	0.022		0.004						
	G-1-45-4	215.58	834.33	0	98.9		0.92	0.209		0.01						
Test 1, Vessel 2-8	2-8 Day 10	236.08	236.08	0	99.48	0.01	0.458	0.051		0.004						
	G-1-24-8	191.17	427.25	0	99.74	0.015	0.202	0.036		0.004						
	G-1-31-8	191.50	618.75	0	99.82	0.015	0.122	0.034		0.005						
	G-1-45-8	215.58	834.33	0	99.3	0.018	0.142	0.029		0.006						

D - Sampling error that may have affected gas composition
Blank values indicate < 0.001 mole % gas

Table A.6. Percent Composition of Gas Sampled (including argon) - Water Plus Resin Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 4, Vessel 1-2	G-1-162-2	165.08	165.08	5.36E+07	72.3	25.4	1.91	0.313		0.011	0.004		0.039	0.017	0.013	
	G-2-8-2	168.17	333.25	5.46E+07	67.4	32.3	0.175	0.0167					0.0311	0.0185	0.00126	
	G-2-18-2	167.50	500.75	5.44E+07	66.5	33.26	0.12	0.021		0.007			0.0266	0.0152	0.0115	
	G-2-28-2	168.08	668.83	5.46E+07	66.9	32.9	0.117	0.0145		0.004			0.0253	0.0135	0.0133	
	G-2-36-2	144.33	813.17	4.69E+07	68.2	30.9	0.7	0.1511		0.006	0.0059		0.0223	0.0132	0.009	
	G-2-44-2	143.08	956.25	4.64E+07	64.9	34.8	0.194	0.0224		0.008			0.0275	0.0137	0.0121	
Test 4, Vessel 1-4	G-1-162-4	165.08	165.08	5.36E+07	74.7	23.1	1.81	0.303		0.008	0.005		0.044	0.019	0.011	
	G-2-8-4	168.17	333.25	5.46E+07	67.3	32.4	0.133	0.0133			0.0055		0.0366	0.0206	0.0145	
	G-2-18-4	167.50	500.75	5.44E+07	69.3	30.5	0.125	0.0125		0.008			0.0293	0.0189		
	G-2-28-4	168.08	668.83	5.46E+07	72	27.8	0.097	0.013		0.007			0.0242	0.0152	0.0109	
	G-2-36-4	144.33	813.17	4.69E+07	62.1	29.9	6.29	1.64		0.01			0.0252	0.0112	0.0088	B
	G-2-44-4	143.08	956.25	4.64E+07	70.4	29.4	0.143	0.012		0.008			0.0282	0.0122		
Test 4, Vessel 2-2	G-1-163-2	166.25	166.25	0	99.5	0.022	0.418	0.0213		0.033						
	G-2-9-2	168.17	334.42	0	99.701	0.058	0.227	0.005		0.009						
	G-2-19-2	167.58	502.00	0	99.756	0.012	0.211	0.0128		0.008						
	G-2-29-2	168.00	670.00	0	86.6	0.014	10.7	2.7324		0.014						C
	G-2-37-2	144.08	814.08	0	99.757	0.035	0.181	0.0151		0.008	0.0039					
	G-2-45-2	143.08	957.17	0	99.841	0.027	0.115	0.0087		0.009						
Test 4, Vessel 2-6	G-1-163-6	166.25	166.25	0	99.21	0.12	0.6	0.0463		0.019						
	G-2-9-6	168.17	334.42	0	99.58	0.245	0.154	0.0031		0.017						
	G-2-19-6	167.58	502.00	0	99.671	0.193	0.111	0.0145		0.011						
	G-2-29-6	168.00	670.00	0	99.33	0.179	0.408	0.0706		0.008	0.0036					
	G-2-37-6	144.08	814.08	0	99.781	0.116	0.088	0.0069		0.008						
	G-2-45-6	143.08	957.17	0	99.824	0.07	0.082	0.0149		0.009						

B - Corrected for air in-leakage based on oxygen concentration
C - Significant air in-leakage, due to lack of H2, this was not corrected.
Blank values indicate < 0.001 mole % gas

Table A.7. Percent Composition of Gas Sampled (including argon) – Nitric Acid Only Data, 25 °C

Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Mole Percent Gas, 25 °C Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 3, Vessel 1-1	G-1-107-1	188.00	188.00	6.42E+07	85.4	10.3	0.133	4.23		0.2						
	G-1-118-1	195.58	383.58	6.68E+07	78.1	13.5	1.53	6.8		0.158						
	G-1-127-1	164.50	548.08	5.62E+07	81.9	12.1	0.198	5.85			0.017					
	G-1-135-1	170.83	718.92	5.84E+07	81.2	12.3	0.447	6.01		0.074						
	G-1-145-1	165.33	884.25	5.64E+07	82.2	11.9	0.099	5.738		0.059						
Test 3, Vessel 1-5	G-1-107-5	188.00	188.00	6.42E+07	85.7	9.4	0.76	4.13		0.018	0.022	0.004				
	G-1-118-5	195.58	383.58	6.68E+07	84.2	10.8	0.096	4.88		0.154						
	G-1-127-5	164.50	548.08	5.62E+07	74.2	7.77	11.3	6.62		0.126						A
	G-1-135-5	170.83	718.92	5.84E+07	86	9.38	0.056	4.4		0.112						
	G-1-145-5	165.33	884.25	5.64E+07	82.8	11.5	0.05	5.56		0.088						
Test 3, Vessel 2-1	G-1-108-1	185.67	185.67	0	99.16		0.598	0.22			0.022	0.011				
	G-1-119-1	196.17	381.83	0	4.36		75.5	20.1					0.002			C
	G-1-128-1	163.58	545.42	0	3.85		75.8	20.4								C
	G-1-136-1	171.17	716.58	0	3.45		76.1	20.4		0.056	0.008		0.002			C
	G-1-146-1	165.25	881.83	0	3.3		76.1	20.5		0.053			0.001			C
Test 3, Vessel 2-5	G-1-108-5	185.67	185.67	0	99.65		0.245	0.094			0.065	0.066				
	G-1-119-5	196.17	381.83	0	99.84		0.113	0.033		0.012						
	G-1-128-5	163.58	545.42	0	99.88		0.09	0.032								
	G-1-136-5	171.17	716.58	0	99.802		0.134	0.046		0.01	0.008					
	G-1-146-5	165.25	881.83	0	99.858		0.091	0.031		0.013	0.006					

A - Corrected for air in-leakage based on the nitrogen content
C - Significant air in-leakage, due to lack of H2, this was not corrected.
Blank values indicate < 0.001 mole % gas

Table A.8. Percent Composition of Gas Sampled (including argon) – Nitric Acid Only Data, 45 °C

					Mole Percent Gas, 45 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 3, Vessel 1-3	G-1-107-3	188.00	188.00	6.42E+07	87	9.11	0.1382	3.71		0.1984						
	G-1-118-3	195.58	383.58	6.68E+07	82.5	11.9	0.194	5.53								
	G-1-127-3	164.50	548.08	5.62E+07	83.9	10.7	0.096	5.22								
	G-1-135-3	170.83	718.92	5.84E+07	82.4	11.9	0.074	5.6		0.07	0.005					
	G-1-145-3	165.33	884.25	5.64E+07	82.1	12	0.039	5.86		0.053	0.003					
Test 3, Vessel 1-7	G-1-107-7	188.00	188.00	6.42E+07	86.3	9.63	0.112	3.89		0.023	0.026					
	G-1-118-7	195.58	383.58	6.68E+07	82.7	11.8	0.077	5.46		0.153						
	G-1-127-7	164.50	548.08	5.62E+07	84.6	10.3	0.067	4.95		0.116						
	G-1-135-7	170.83	718.92	5.84E+07	84.4	10.6	0.041	4.81		0.097	0.005					
	G-1-145-7	165.33	884.25	5.64E+07	84	10.6	0.042	5.19		0.078	0.007					
Test 3, Vessel 2-3	G-1-108-3	185.67	185.67	0	99.6		0.315	0.033				0.012				
	G-1-119-3	196.17	381.83	0	99.838		0.08	0.019		0.032	0.031					
	G-1-128-3	163.58	545.42	0	99.85		0.091	0.021			0.043					
	G-1-136-3	171.17	716.58	0	98.67		1.03	0.205		0.046	0.045					
	G-1-146-3	165.25	881.83	0	99.661		0.16	0.012		0.131	0.035					
Test 3, Vessel 2-7	G-1-108-7	185.67	185.67	0	99.7		0.253	0.047				0.023	0.0018			
	G-1-119-7	196.17	381.83	0	99.89		0.056	0.013		0.03	0.014					
	G-1-128-7	163.58	545.42	0	99.913		0.045	0.015			0.028					
	G-1-136-7	171.17	716.58	0	99.852		0.052	0.009			0.087					
	G-1-146-7	165.25	881.83	0	99.8		0.054	0.009		0.029	0.06	0.029				

Blank values indicate < 0.001 mole % gas

Table A.9. Percent Composition of Gas Sampled (including argon) – Nitric Acid Only Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 5, Vessel 1-1	G-2-63-1	193.33	193.33	6.16E+07	74.3	15.6	2.18	6.86		0.956	0.052	0.042				A
	G-2-76-1	192.33	385.67	6.13E+07	79	14.3	0.096	6.59			0.048					A
	G-2-89-1	193.67	579.33	6.17E+07	79	14.2	0.057	6.58		0.158	0.018					A
	G-2-102-1	189.17	768.50	6.03E+07	80	13.7	0.073	6.1			0.017					A
	G-2-116-1	190.92	959.42	6.08E+07	80.2	13.6	0.131	5.9		0.117	0.036					A
Test 5, Vessel 1-5	G-2-63-5	193.33	193.33	6.16E+07	17.2		60.4	22.4								A
	G-2-76-5	192.33	385.67	6.13E+07	82.6	12.1	0.215	5.02			0.038					A
	G-2-89-5	193.67	579.33	6.17E+07	74.7	11.3	7.01	6.78		0.199	0.017					A
	G-2-102-5	189.17	768.50	6.03E+07	82.2	12.1	0.228	5.23		0.2	0.022					A
	G-2-116-5	190.92	959.42	6.08E+07	82.5	12.1	0.268	4.92		0.17	0.024					A
Test 5, Vessel 2-1	G-2-64-1	194.08	194.08	0	99.129		0.126	0.012			0.704		0.03			
	G-2-77-1	192.50	386.58	0	14.8		67.2	18			0.017		0.002			C
	G-2-90-1	193.67	580.25	0	96.7		0.587	0.012		0.124	2.49		0.103			
	G-2-103-1	189.08	769.33	0	93.7			0.018		0.063	6		0.249			
	G-2-117-1	190.92	960.25	0	86.3		2.62	0.03			10.58		0.439			
Test 5, Vessel 2-5	G-2-64-5	194.08	194.08	0	99.36		0.155	0.01			0.454		0.018			
	G-2-77-5	192.50	386.58	0	98.11		0.078	0.012			1.73		0.072			
	G-2-90-5	193.67	580.25	0	95			0.016			4.81		0.198			
	G-2-103-5	189.08	769.33	0	90.6			0.018			8.99		0.372			
	G-2-117-5	190.92	960.25	0	85.1			0.029			14.264		0.591			

A - Corrected for air in-leakage based on the nitrogen content
C - Significant air in-leakage, due to lack of H_2, this was not corrected.
Blank values indicate < 0.001 mole % gas

Table A.10. Percent Composition of Gas Sampled (including argon) – Nitric Acid plus Resin Data, 25 °C

					Mole Percent Gas, 25 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 3, Vessel 1-2	G-1-107-2	188.00	188.00	6.42E+07	70.3	9.07	4.42			6.83		9.35	0.0116			
	G-1-118-2	195.58	383.58	6.68E+07	62	4.27	11.9			14.4		7.33	0.005			
	G-1-127-2	164.50	548.08	5.62E+07	71.8	6.26	2.88			17.7		1.31				
	G-1-135-2	170.83	718.92	5.84E+07	81.5	11.3	0.806	0.056		6.32	0.017					
	G-1-145-2	165.33	884.25	5.65E+07	71.3	18.8	0.41	0.075		9.34						
Test 3, Vessel 1-6	G-1-107-6	188.00	188.00	6.42E+07	71.5	8.1	2.85			8.4		9.09	0.0071			
	G-1-118-6	195.58	383.58	6.68E+07	59.9	4.88	13.6			15.4		6.17	0.003			
	G-1-127-6	164.50	548.08	5.62E+07	68.5	12.5	2.28			16.2		0.5				
	G-1-135-6	170.83	718.92	5.84E+07	73.6	17.5	0.566	0.07		8.23						
	G-1-145-6	165.33	884.25	5.65E+07	75.4	17.1	0.233	0.061		7.25						
Test 3, Vessel 2-2	G-1-108-2	185.67	185.67	0	99.1		0.618	0.016			0.047	0.198				
	G-1-119-2	196.17	381.83	0	99.623		0.287	0.015			0.04	0.036				
	G-1-128-2	163.58	545.42	0	99.61		0.276	0.02			0.095					
	G-1-136-2	171.17	716.58	0	99.635		0.158	0.018		0.077	0.112					
	G-1-146-2	165.25	881.83	0	3.3		76.11	20.5		0.053	0.008		0.001			C
Test 3, Vessel 2-6	G-1-108-6	185.67	185.67	0	26.4		58	15.5			0.005	0.006	0.0021			C
	G-1-119-6	196.17	381.83	0	99.8		0.125	0.013		0.059						
	G-1-128-6	163.58	545.42	0	99.89		0.091	0.017								
	G-1-136-6	171.17	716.58	0	99.85		0.116	0.029								
	G-1-146-6	165.25	881.83	0	99.853		0.085	0.02		0.042						

C - Significant air in-leakage, due to lack of H_2, this was not corrected.
Blank values indicate < 0.001 mole % gas

Table A.11. Percent Composition of Gas Sampled (including argon) – Nitric Acid plus Resin Data, 45 °C

					Mole Percent Gas, 45 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 3, Vessel 1-4	G-1-107-4	188.00	188.00	6.42E+07	62.5	8.08	1.96			15.3		12.2	0.0124			
	G-1-118-4	195.58	383.58	6.68E+07	50.8	9.7	8.8			26.4		4.32	0.003			
	G-1-127-4	164.50	548.08	5.62E+07	66.9	14	3.46	0.119		15.4	0.093	0.278				
	G-1-135-4	170.83	718.92	5.84E+07	59	26.5	1.21	0.108		13.1	0.021					
	G-1-145-4	165.33	884.25	5.65E+07	66.3	23.5	0.37	0.082		9.74						
Test 3, Vessel 1-8	G-1-107-8	188.00	188.00	6.42E+07	73.6	5.7	1.28			10.2		9.12	0.0152			
	G-1-118-8	195.58	383.58	6.68E+07	48	8.63	9.07			28.3		5.98	0.003			
	G-1-127-8	164.50	548.08	5.62E+07	64.5	14.2	0.228			16.2		0.542				
	G-1-135-8	170.83	718.92	5.84E+07	67	19.6	1.25	0.098		12	0.082					
	G-1-145-8	165.33	884.25	5.65E+07	64.9	23.3	0.714	0.081		10.9	0.056		0.005			
Test 3, Vessel 2-4	G-1-108-4	185.67	185.67	0	97.2		0.117			0.87	1.07	0.733	0.0554			
	G-1-119-4	196.17	381.83	0	96.33		0.702	0.022		1.94	0.419	0.57	0.011			
	G-1-128-4	163.58	545.42	0	95.57		0.017			2.51		1.89	0.007			
	G-1-136-4	171.17	716.58	0	96.26		0.759	0.032		2.74	0.207					
	G-1-146-4	165.25	881.83	0	47.3		40.7	10.7		1.03	0.082	0.22				C
Test 3, Vessel 2-8	G-1-108-8	185.67	185.67	0	98.1		0.115			0.584	1.07	0.103	0.05			
	G-1-119-8	196.17	381.83	0	98.07		0.18	0.012		0.476	1.05	0.17	0.043			
	G-1-128-8	163.58	545.42	0	98.15					0.93	0.88		0.042			
	G-1-136-8	171.17	716.58	0	98.27		0.024			1.05	0.627		0.031			
	G-1-146-8	165.25	881.83	0	98.371		0.141	0.01		0.513	0.825	0.105	0.036			

C - Significant air in-leakage, due to lack of H_2, this was not corrected.
Blank values indicate < 0.001 mole % gas

Table A.12. Percent Composition of Gas Sampled (including argon) – Nitric Acid plus Resin Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 5, Vessel 1-2	G-2-52-2	50.83	50.83	1.62E+07	60.9	3.18	0.684			26	6.49	2.58	0.159			
	G-2-55-2	46.42	97.25	1.48E+07	58.2	3.46				28.76	6.03	3.44	0.116			
	G-2-59-2	46.75	144.00	1.49E+07	61.2	3.6				27.4	4.52	3.12	0.077			
	G-2-63-2	49.33	193.33	1.57E+07	67.4	3.37				23.4	3.84	1.9	0.08			
	G-2-66-2	48.58	241.92	1.55E+07	67.4	3.59				23.6	2.9	2.48	0.044			
	G-2-70-2	46.25	288.17	1.47E+07	60.6	3.48				29.9	1.62	4.44	0.014			
	G-2-73-2	48.83	337.00	1.56E+07	59.9	4.64				30.6		5.7				
	G-2-76-2	48.67	385.67	1.55E+07	70.7	4.93				22.4		1.48				
	G-2-82-2	94.92	480.58	3.02E+07	62.9	8.82				28	0.203	0.11				
	G-2-89-2	98.75	579.33	3.15E+07	69.2	9.69				21.5						
	G-2-102-2	189.17	768.50	6.03E+07	68.1	17.7	0.671	0.105		13.5	0.018		0.007			B
	G-2-116-2	190.92	959.42	6.08E+07	69.2	18.3	0.412	0.094		12	0.018		0.008			B
Test 5, Vessel 1-6	G-2-52-6	50.83	50.83	1.62E+07	65.8	3.87	0.404			21.8	4.89	3.08	0.1	0.053		
	G-2-55-6	46.42	97.25	1.48E+07	8.14	0.15	71.1	18.8		1.45	0.15	0.243	0.002			A
	G-2-59-6	46.75	144.00	1.49E+07	63.3	3.36				24.23	5.71	3.27	0.111			
	G-2-63-6	49.33	193.33	1.57E+07												E
	G-2-66-6	48.58	241.92	1.55E+07	62	3.14				26.8	2.13	6	0.02			
	G-2-70-6	46.25	288.17	1.47E+07	64.5	2.93				26.2	1.71	4.63	0.015			
	G-2-73-6	48.83	337.00	1.56E+07	62	4.31				27.9		7.04	0.008			
	G-2-76-6	48.67	385.67	1.55E+07	71.2	5				22.3		1.01				
	G-2-82-6	94.92	480.58	3.02E+07	63.8	8.25				27	0.5	0.456				
	G-2-89-6	98.75	579.33	3.15E+07	64.6	8.2				25.9	0.321	0.895				
	G-2-102-6	189.17	768.50	6.03E+07	61.4	14	4.13	0.215		20.1	0.156					B
	G-2-116-6	190.92	959.42	6.08E+07	69.5	14.9	0.982			14.5	0.23					
Test 5, Vessel 2-2	G-2-53-2	51.67	51.67	0	51.3					40.8	5.18	2.59	0.107			
	G-2-56-2	46.58	98.25	0	56.8					37.6	3.68	1.82	0.075			

	G-2-64-2	95.83	194.08	0								F
	G-2-77-2	192.50	386.58	0	55	0.71				44.3	0.03	
	G-2-90-2	193.67	580.25	0	61.4	1.78		31.5	2.09	3.21	0.025	
	G-2-103-2	189.08	769.33	0	84.2	1.46	0.094	13.1	1.05		0.03	
	G-2-117-2	190.92	960.25	0	86.2	0.829	0.093	12.5	0.39			
Test 5, Vessel 2-6	G-2-53-6	51.67	51.67	0	64.6			29.3	3.96	2.1	0.079	
	G-2-56-6	46.58	98.25	0	74.7			21.5	2.45	1.3	0.048	
	G-2-64-6	95.83	194.08	0	63.563	0.304		36.086			0.046	
	G-2-77-6	192.50	386.58	0	52.5	0.692		40.4		2.64	0.06	
	G-2-90-6	193.67	580.25	0	58.6	0.867		35.1	3.78	1.58	0.09	
	G-2-103-6	189.08	769.33	0	82.9	1.58	0.099	14.9	0.492		0.007	
	G-2-117-6	190.92	960.25	0	88.2	0.544	0.077	10.9	0.334			

A - Corrected for air in-leakage based on the nitrogen content
B - Corrected for air in-leakage based on oxygen concentration
E - Sample missing. Values estimated for calculations.
F - Sample was lost in the mass spec laboratory.
Blank values indicate < 0.001 mole % gas

Table A.13. Percent Composition of Gas Sampled (including argon) – Simulant Only Data, 25 °C

					Mole Percent Gas, 25 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 2, Vessel 1-1	G-1-55-1	161.50	161.50	5.63E+07	90.6	5.5	2.16	1.62		0.005		0.08				
	G-1-65-1	168.92	330.42	5.88E+07	74.8	5.8	13.6	5.68		0.007		0.111				A
	G-1-81-1	287.42	617.83	1.00E+08	77.6	10.8	6.8	4.8		0.083	0.022					A
	G-1-97-1	241.92	859.75	8.43E+07	88.6	8.9	0.379	2			0.002	0.085				
Test 2, Vessel 1-5	G-1-55-5	161.50	161.50	5.63E+07	93.4	5.2	0.149	1.16		0.006		0.067				
	G-1-65-5	168.92	330.42	5.88E+07	91.9	6.4	0.065	1.43		0.006		0.114				
	G-1-81-5	287.42	617.83	1.00E+08	87.3	10.3	0.078	2.21				0.076				
	G-1-97-5	241.92	859.75	8.43E+07	89.4	8.6	0.051	1.88				0.082				
Test 2, Vessel 2-1	G-1-56-1	164.83	164.83	0	99.31		0.472	0.198		0.0161						
	G-1-66-1	168.67	333.50	0	93.3		5.3	1.35		0.017						C
	G-1-82-1	287.42	620.92	0	98.9		0.832	0.276		0.021						
	G-1-98-1	241.67	862.58	0	97.2	0.013	2.21	0.55		0.016						
Test 2, Vessel 2-5	G-1-56-5	164.83	164.83	0	99.84		0.117	0.034		0.007						
	G-1-66-5	168.67	333.50	0	99.78		0.174	0.043								
	G-1-82-5	287.42	620.92	0	99.8		0.185	0.04		0.005						
	G-1-98-5	241.67	862.58	0	99.8		0.195	0.032								

A - Corrected for air in-leakage based on the nitrogen content
C - Significant air in-leakage, due to lack of H_2, this was not corrected.
Blank values indicate < 0.001 mole % gas

Table A.14. Percent Composition of Gas Sampled (including argon) – Simulant Only Data, 45 °C

					Mole Percent Gas, 45 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 2, Vessel 1-3	G-1-55-3	161.50	161.50	5.63E+07	85.3	5.6	0.128	8.8		0.007		0.082				
	G-1-65-3	168.92	330.42	5.88E+07	81.4	6.8	0.049	11.6		0.005		0.115				
	G-1-81-3	287.42	617.83	1.00E+08	72.4	10.6	0.08	16.8		0.009		0.074				
	G-1-97-3	241.92	859.75	8.43E+07	5.6	0.4	75.1	20.3		0.036		0.007	0.001			A
Test 2, Vessel 1-7	G-1-55-7	161.50	161.50	5.63E+07	87	5.4	0.132	7.4		0.006		0.074				
	G-1-65-7	168.92	330.42	5.88E+07	82.4	7.2	0.029	10.2		0.002		0.118				
	G-1-81-7	287.42	617.83	1.00E+08	17.6	2.01	61.3	19		0.039	0.039	0.007				A
	G-1-97-7	241.92	859.75	8.43E+07	77.9	9.16	0.049	12.9		0.019		0.055				
Test 2, Vessel 2-3	G-1-56-3	164.83	164.83	0	1.73		77.5	20.8		0.047	0.002		0.002			C
	G-1-66-3	168.67	333.50	0	99.83		0.149	0.013		0.009						
	G-1-82-3	287.42	620.92	0	99.91		0.06	0.007		0.018		0.003				
	G-1-98-3	241.67	862.58	0	99.84		0.128	0.013		0.015						
Test 2, Vessel 2-7	G-1-56-7	164.83	164.83	0	99.8		0.189	0.005		0.007						
	G-1-66-7	168.67	333.50	0	99.92		0.066	0.008		0.009						
	G-1-82-7	287.42	620.92	0	99.92		0.052	0.012		0.016						
	G-1-98-7	241.67	862.58	0	99.9		0.081	0.006				0.016				

A - Corrected for air in-leakage based on the nitrogen content

C - Significant air in-leakage, due to lack of H_2, this was not corrected.

Blank values indicate < 0.001 mole % gas

Table A.15. Percent Composition of Gas Sampled (including argon) – Simulant Only Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 5, Vessel 1-3	G-2-63-3	193.33	193.33	6.16E+07	50.1	7.13	0.134	42.6			0.036					A
	G-2-76-3	192.33	385.67	6.13E+07	60.9	6.25	0.035	32.8			0.015					A
	G-2-89-3	193.67	579.33	6.17E+07	54.4	6.65		33.9			0.019					
	G-2-102-3	189.17	768.50	6.03E+07	60.5	6.29		33.2		0.035	0.009					
	G-2-116-3	190.92	959.42	6.08E+07	59.7	6.18		34.1		0.025	0.01					
Test 5, Vessel 1-7	G-2-63-7B	193.33	193.33	6.16E+07	50.6	6.71	0.531	42			0.066					G
	G-2-76-7	192.33	385.67	6.13E+07	62.5	6.15	0.015	31.2			0.07					A
	G-2-89-7	193.67	579.33	6.17E+07	58	6.28	0.002	35.64			0.067					A
	G-2-102-7	189.17	768.50	6.03E+07	58.6	5.32		35.8		0.186	0.045					
	G-2-116-7	190.92	959.42	6.08E+07	61.5	5.66	0.01	32.76		0.076	0.025					A
Test 5, Vessel 2-3	G-2-64-3	194.08	194.08	0	95.5		3.607	0.91			0.032					
	G-2-77-3	192.50	386.58	0	99.779		0.144	0.021			0.056					
	G-2-90-3	193.67	580.25	0	99.842		0.102	0.008			0.048					
	G-2-103-3	189.08	769.33	0	99.763		0.117	0.006		0.081	0.033					
	G-2-117-3	190.92	960.25	0	99.545		0.079	0.006			0.356		0.014			
Test 5, Vessel 2-7	G-2-64-7	194.08	194.08	0	99.34	0.01	0.58	0.03			0.05					B
	G-2-77-7	192.50	386.58	0	99.3		0.539	0.115			0.068					
	G-2-90-7	193.67	580.25	0	99.742		0.149	0.028			0.082					
	G-2-103-7	189.08	769.33	0	99.76		0.084	0.017		0.084	0.055					
	G-2-117-7	190.92	960.25	0	99.838		0.071	0.016			0.075					

A - Corrected for air in-leakage based on the nitrogen content
B - Corrected for air in-leakage based on oxygen concentration
G - Sampling error, makeup sample shown here.
Blank values indicate < 0.001 mole % gas

Table A.16. Percent Composition of Gas Sampled (including argon) – Simulant Plus Resin Data, 25 °C

					Mole Percent Gas, 25 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 2, Vessel 1-2	G-1-55-2	161.50	161.50	5.63E+07	98.6	1.26	0.065	0.014				0.021				
	G-1-65-2	168.92	330.42	5.88E+07	86.2	11.9	0.97	0.024				0.236				
	G-1-81-2	287.42	617.83	1.00E+08	74.4	22.8	1.79			0.16	0.044	0.81				
	G-1-97-2	241.92	859.75	8.43E+07	78.8	17.1	2.53	0.016			0.347	1.24				
Test 2, Vessel 1-6	G-1-55-6	161.50	161.50	5.63E+07	96.2	3.58	0.141	0.059				0.032				
	G-1-65-6	168.92	330.42	5.88E+07	93.5	6.1	0.24	0.003				0.121				
	G-1-81-6	287.42	617.83	1.00E+08	79.5	18.5	1.15			0.178		0.6				
	G-1-97-6	241.92	859.75	8.43E+07	80.7	16.1	1.7				0.002	1.47				
Test 2, Vessel 2-2	G-1-56-2	164.83	164.83	0	99.88		0.092	0.012		0.011						
	G-1-66-2	168.67	333.50	0	99.8		0.181	0.007		0.012						
	G-1-82-2	287.42	620.92	0	99.8		0.145	0.009		0.01						
	G-1-98-2	241.66	862.58	0	99.2		0.66	0.121		0.01						
Test 2, Vessel 2-6	G-1-56-6	164.83	164.83	0	99.9		0.078	0.0148		0.005						
	G-1-66-6	168.67	333.50	0	99.9		0.085	0.006		0.005						
	G-1-82-6	287.42	620.92	0	99.91		0.064	0.016		0.006						
	G-1-98-6	241.66	862.58	0	99.88		0.097	0.012		0.008						

Blank values indicate < 0.001 mole % gas

Table A.17. Percent Composition of Gas Sampled (including argon) – Simulant Plus Resin Data, 45 °C

					Mole Percent Gas, 45 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 2, Vessel 1-4	G-1-55-4	161.50	161.50	5.63E+07	45.2	3.35	40.4	11		0.018		0.027				A
	G-1-65-4	168.92	330.42	5.88E+07	85.4	13.2	1.02	0.155		0.003		0.117				
	G-1-81-4	287.42	617.83	1.00E+08	83.3	14.1	1.47					1.16				
	G-1-97-4	241.92	859.75	8.43E+07	81.6	13	3.22				0.014	2.1	0.009			
Test 2, Vessel 1-8	G-1-55-8	161.50	161.50	5.63E+07	97.8	2.09	0.113	0.012		0.016						
	G-1-65-8	168.92	330.42	5.88E+07	80.2	17	2	0.28		0.007		0.49				
	G-1-81-8	287.42	617.83	1.00E+08	74.5	21.5	2.5					1.49	0.009			
	G-1-97-8	241.92	859.75	8.43E+07	72.6	19.1	5.2				0.009	3.09	0.012			
Test 2, Vessel 2-4	G-1-56-4	164.83	164.83	0	99.84		0.121	0.017			0.006	0.02				
	G-1-66-4	168.67	333.50	0	99.83		0.128	0.012				0.022				
	G-1-82-4	287.42	620.92	0	99.81		0.123	0.022		0.034		0.011				
	G-1-98-4	241.67	862.58	0	99.8		0.189	0.015				0.027				
Test 2, Vessel 2-8	G-1-56-8	164.83	164.83	0	99.75		0.219	0.018		0.017						
	G-1-66-8	168.67	333.50	0	99.88		0.085	0.014		0.004		0.118				
	G-1-82-8	287.42	620.92	0	99.84		0.113	0.014				0.027				
	G-1-98-8	241.67	862.58	0	99.8		0.129	0.013				0.02				

A - Corrected for air in-leakage based on the nitrogen content

Blank values indicate < 0.001 mole % gas

Table A.18. Percent Composition of Gas Sampled (including argon) – Simulant Plus Resin Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 5, Vessel 1-4	G-2-63-4	193.33	193.33	6.16E+07	76.9	17.8	3.01	0.008			0.012	2.26	0.009			
	G-2-76-4	192.33	385.67	6.13E+07	77	13.3	5.83				0.011	3.85	0.017			
	G-2-89-4	193.67	579.33	6.17E+07	70.9	13.1	11.6				0.079	4.22	0.032			
	G-2-102-4	189.17	768.50	6.03E+07	69.1	12.1	15.4	0.02		2.5	0.738		0.039			B
	G-2-116-4	190.92	959.42	6.08E+07	64.8	11.7	19.9	0.019		2.71			0.049			B
Test 5, Vessel 1-8	G-2-63-8	193.33	193.33	6.16E+07	74.5	19.5	3.28				0.009	2.68	0.01			
	G-2-76-8	192.33	385.67	6.13E+07	73.7	15.7	6.34				0.015	4.2	0.02			
	G-2-89-8	193.67	579.33	6.17E+07	66.5	15.2	13				0.176	5.07	0.032			
	G-2-102-8	189.17	768.50	6.03E+07	63.4	13.9	19.5	0.008		2.46	0.7		0.04			B
	G-2-116-8	190.92	959.42	6.08E+07	57.6	13.2	27.2	0.01		1.54	0.455		0.47			B
Test 5, Vessel 2-4	G-2-64-4	194.08	194.08	0	99.3	0.01	0.562	0.035			0.109					B
	G-2-77-4	192.50	386.58	0	99	0.011	0.86	0.033			0.097					
	G-2-90-4	193.67	580.25	0	98.33		1.58	0.013			0.078					
	G-2-103-4	189.08	769.33	0	30.1		55	14.8		0.071	0.014		0.002			
	G-2-117-4	190.92	960.25	0	98.67		1.27	0.008			0.047					
Test 5, Vessel 2-8	G-2-64-8	194.08	194.08	0	99.3	0.012	0.57	0.021			0.094					B
	G-2-77-8	192.50	386.58	0	98.92		1	0.012			0.068					
	G-2-90-8	193.67	580.25	0	98.64		1.29	0.009			0.059					
	G-2-103-8	189.08	769.33	0	96.88	0.011	2.77	0.012		0.253	0.071					
	G-2-117-8	190.92	960.25	0	97		2.94	0.019			0.046					

B - Corrected for air in-leakage based on oxygen concentration
Blank values indicate < 0.001 mole % gas

Table A.19. Percent Composition of Gas Sampled (including argon) – Simulant w/ TOC Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 4, Vessel 1-5	G-1-162-5	165.08	165.08	5.36E+07	42.8	4.88	7.49	1.08			0.09	43.6	0.038	0.013		B
	G-2-8-5	168.17	333.25	5.46E+07	41.9	6.28	3.01				0.056	48.7	0.063	0.027		
	G-2-18-5	167.50	500.75	5.44E+07	50	7.76	12.5				0.043	29.4	0.051	0.272	0.02	
	G-2-28-5	168.08	668.83	5.46E+07	65.2	9.56	10.9				0.037	14.1	0.037	0.121	0.018	
	G-2-36-5	144.33	813.17	4.68E+07	81.2	9.87	4.7	0.06			0.041	4	0.037			B
	G-2-44-5	143.08	956.25	4.64E+07	75.3	9.06	3.64	10			0.041	2.1	0.034	0.014		
Test 4, Vessel 1-7	G-1-162-7	165.08	165.08	5.36E+07	48.9	5.08					0.099	45.9	0.0412	0.01		
	G-2-8-7	168.17	333.25	5.46E+07	44.1	5.85	2.06				0.0472	47.9	0.0626	0.013		
	G-2-18-7	167.50	500.75	5.44E+07	52.3	7.04	10.2				0.0425	30.3	0.0481	0.043	0.0154	
	G-2-28-7	168.08	668.83	5.46E+07	62.6	7.91	12.4				0.0266	16.9	0.0389	0.167	0.0232	
	G-2-36-7	144.33	813.17	4.68E+07	81.6	8.35	4.9				0.0299	5.2	0.0537			
	G-2-44-7	143.08	956.25	4.64E+07	84.7	8.36	3.2	1.28			0.047	2.62	0.0754			A
Test 4, Vessel 2-3	G-1-163-3	166.25	166.25	0	99.5		0.363	0.0458		0.047	0.014					
	G-2-9-3	168.17	334.42	0	99.796		0.158	0.0075			0.0391					
	G-2-19-3	167.58	502.00	0	99.1		0.657	0.139		0.093	0.0381					
	G-2-29-3	168.00	670.00	0	99.7		0.157	0.0064		0.091	0.0253					
	G-2-37-3	144.08	814.08	0	99.8	0.006	0.128	0.0113		0.073	0.0309					
	G-2-45-3	143.08	957.17	0	99.75	0.007	0.125	0.0144		0.072	0.0319					
Test 4, Vessel 2-7	G-1-163-7	166.25	166.25	0	99.4		0.455	0.052		0.076	0.031					
	G-2-9-7	168.17	334.42	0	98.81		0.981	0.1687			0.0369					
	G-2-19-7	167.58	502.00	0	99.36		0.492	0.0456		0.077	0.0243					
	G-2-29-7	168.00	670.00	0	99.41		0.431	0.0528		0.074	0.0296					
	G-2-37-7	144.08	814.08	0	99.48		0.393	0.0438		0.063	0.0234					
	G-2-45-7	143.08	957.17	0	99.442	0.006	0.408	0.0594		0.061	0.0243					

A - Corrected for air in-leakage based on the nitrogen content
B - Corrected for air in-leakage based on oxygen concentration
Blank values indicate < 0.001 mole % gas

Table A.20. Percent Composition of Gas Sampled (including argon) – Simulant w/ TOC plus Resin Data, 70 °C

					Mole Percent Gas, 70 °C											
Sample	Laboratory ID	Δ T (hrs)	Cumulative Run Time (hrs)	Δ Dose (Rad)	Ar	H_2	N_2	O_2	CO	CO_2	NO	N_2O	CH_4	C_2H_6	Other hydrocarbons	Notes
Test 4, Vessel 1-6	G-1-162-6	165.08	165.08	5.36E+07	81.5	8.57	2.45	0.015			0.017	7.46	0.014			
	G-2-8-6	168.17	333.25	5.46E+07	73.7	11.12	8.33				0.0095	6.86	0.0179			
	G-2-18-6	167.50	500.75	5.44E+07	62.9	14.6	16.6				0.0075	5.81	0.0346			
	G-2-28-6	168.08	668.83	5.46E+07	63.8	12.4	18.3				0.0113	5.46	0.0372			
	G-2-36-6	144.33	813.17	4.68E+07	65.7	10.5	18.9				0.0201	4.95	0.0405			
	G-2-44-6	143.08	956.25	4.64E+07	59.5	11.4	23.9				0.0161	5.14	0.0474			
Test 4, Vessel 1-8	G-1-162-8	165.08	165.08	5.36E+07	77.4	12.4	3.14	0.182			0.014	6.86	0.02			
	G-2-8-8	168.17	333.25	5.46E+07	69.4	16.8	9.07				0.0049	4.63	0.022			
	G-2-18-8	167.50	500.75	5.44E+07	64	17.1	14.4				0.0059	4.42	0.029			
	G-2-28-8	168.08	668.83	5.46E+07	62.1	16.6	16.9				0.0135	4.34	0.037			
	G-2-36-8	144.33	813.17	4.68E+07	58.1	13.9	23.7				0.0169	4.38	0.04			
	G-2-44-8	143.08	956.25	4.64E+07	53.6	13	28.9				0.0134	4.35	0.042			
Test 4, Vessel 2-4	G-1-163-4	166.25	166.25	0	98.93		0.935	0.0553		0.055	0.0208					
	G-2-9-4	168.17	334.42	0	99.44		0.532	0.0053			0.0224					
	G-2-19-4	167.58	502.00	0	98.72		1.17	0.01		0.079	0.0219					
	G-2-29-4	168.00	670.00	0	98.7		1.27	0.015			0.0138	0.025				
	G-2-37-4	144.08	814.08	0	98.3		1.64	0.018		0.042	0.0165					
	G-2-45-4	143.08	957.17	0	98.3		1.65	0.014		0.038	0.0117					
Test 4, Vessel 2-8	G-1-163-8	166.25	166.25	0	99.38		0.511	0.055		0.039	0.0176					
	G-2-9-8	168.17	334.42	0												F
	G-2-19-8	167.58	502.00	0	98.94		0.922	0.0119			0.0288	0.1				
	G-2-29-8	168.00	670.00	0	98.64		1.28	0.0075			0.016	0.028				
	G-2-37-8	144.08	814.08	0	98.69		1.23	0.023		0.041	0.0125					
	G-2-45-8	143.08	957.17	0	98.84	0.013	1.09	0.0185		0.032	0.011					

F - Sample was lost in the mass spec laboratory
Blank values indicate < 0.001 mole % gas

Appendix B –
Total Carbon Analysis Results

Table B.1. Water Data

Sample	Test Temperature (°C)	Rad Exposure?	Resin Contact?	TIC (mg C/L)	TOC (mg C/L)
Test 1, Vessel 1-1	25	Y	--	7.2	52.2
Test 1, Vessel 1-2	25	Y	Y	296	67.5
Test 1, Vessel 1-4	45	Y	Y	684	105
Test 1, Vessel 1-6	25	Y	Y	408	91
Test 1, Vessel 1-8	45	Y	Y	391	81.5
Test 1, Vessel 2-1	25	--	--	9.7	47.2
Test 1, Vessel 2-2	25	--	Y	82.8	87.9
Test 1, Vessel 2-4	45	--	Y	47.0	104
Test 4, Vessel 1-1	70	Y	--	8.2	34.4
Test 4, Vessel 1-2	70	Y	Y	406	119.24
Test 4, Vessel 1-4	70	Y	Y	364	108
Test 4, Vessel 2-1	70	--	--	10.1	26.7
Test 4, Vessel 2-2	70	--	Y	45.2	104

Table B.2. 0.45M HNO_3 Data

Sample	Test Temperature (°C)	Rad Exposure?	Resin Contact?	TIC (mg C/L)	TOC (mg C/L)
Test 3, Vessel 1-1	25	Y	--	4.5	39
Test 3, Vessel 1-2	25	Y	Y	16	60
Test 3, Vessel 1-4	45	Y	Y	20	70
Test 3, Vessel 1-6	25	Y	Y	22	69
Test 3, Vessel 1-8	45	Y	Y	19	76
Test 3, Vessel 2-1	25	--	--	7.2	28
Test 3, Vessel 2-2	25	--	Y	13	44
Test 3, Vessel 2-4	45	--	Y	11	47
Test 5, Vessel 1-1	70	Y	--	3.5	28.00
Test 5, Vessel 1-2	70	Y	Y	31	79
Test 5, Vessel 1-6	70	Y	Y	29	48
Test 5, Vessel 2-1	70	--	--	8.3	32
Test 5, Vessel 2-2	70	--	Y	8.3	125

Table B.3. 5.6M Na Simulant Data

Sample	Test Temperature (°C)	Rad Exposure?	Resin Contact?	TIC (mg C/L)	TOC (mg C/L)
Test 2, Vessel 1-1	25	Y	--	6512	273
Test 2, Vessel 1-2	25	Y	Y	7630	1390
Test 2, Vessel 1-4	45	Y	Y	7400	1380
Test 2, Vessel 1-6	25	Y	Y	7370	1250
Test 2, Vessel 1-8	45	Y	Y	7560	1520
Test 2, Vessel 2-1	25	--	--	6350	330
Test 2, Vessel 2-2	25	--	Y	5270	354
Test 2, Vessel 2-4	45	--	Y	5490	522
Test 5, Vessel 1-3	70	Y	--	6720	333
Test 5, Vessel 1-4	70	Y	Y	5180	2500
Test 5, Vessel 1-8	70	Y	Y	5100	3010
Test 5, Vessel 2-3	70	--	--	6370	299
Test 5, Vessel 2-4	70	--	Y	2640	517

Table B.4. 5.6M Na Simulant with 1%(w/w) Total Organic Carbon Data

Sample	Test Temperature (°C)	Rad Exposure?	Resin Contact?	TIC (mg C/L)	TOC (mg C/L)
Test 4, Vessel 1-5	70	Y	--	14900	2220
Test 4, Vessel 1-6	70	Y	Y	3650	2150
Test 4, Vessel 1-8	70	Y	Y	3430	1690
Test 4, Vessel 2-3	70	--	--	5950	9800
Test 4, Vessel 2-4	70	--	Y	935	1220

Appendix C – Gamma Dose Calibration Report

Pacific Northwest
NATIONAL LABORATORY

CALIBRATION LABORATORY – IONIZING RADIATION
Radiation Measurements and Irradiations
P.O. Box 999 | Richland, WA 99352

REPORT of CALIBRATION

Page 1 of 18

Client: PNNL Heather Colburn, Sam Bryan LAWPS Integrated Testing Project: 203493 / 67535 PM: Phillip Schonewill	**Tracking No.:**	15349
	Task:	Calibration of Absorbed Dose Rate to Water within liquid-filled lower half of reaction vessels centered approximately 5.7 cm from Co-60 source.
	Measurement Dates:	January 6-13, 2016
	Final Report Date:	February 22, 2016

Measurements Performed and Reported by:

2/22/2016

Roman K. Piper — Date
Scientist
Phone: (509)375-7339; Email: kim.piper@pnnl.gov

Reviewed by:

Mark Murphy 2/22/2016

Mark K. Murphy — Date
Scientist
Phone: (509)375-7331; Email: mark.murphy@pnnl.gov

Overview:

This report provides a summary of the measurements and calculations conducted for the 318 Gamma Bunker using ^{60}Co source 318-420 to obtain preliminary estimates of the average absorbed dose rate to the liquid phase (e.g., water or water plus resin) within each of 8 reaction vessels placed radially around the source. This effort is in support of the initial phase Gas Reaction Vessel irradiations. These have concentrated on three evaluation methodologies: air-equivalent ionization chamber measurements, radiochromic film irradiations, and MCNP modeling. Eventually, results of this assessment are anticipated to be applied for the determination of absorbed dose to other waste simulant compounds and those compounds mixed with resin. Since the initial phase testing focuses only on water and water plus resin, only these aspects are discussed within this summary. Because the source and/or reaction vessels may vary in precise positioning within the carousel, measurements and modeling methods focused on determination of a nominal average dose rate to all eight vessels placed in the carousel during a single irradiation campaign.

Measurements were conducted in four vessels at 90° relative positions. For the purpose of these measurements, they were labeled 1, 3, 5 and 7, with Position 1 corresponding to the vessel just clockwise of the vent tube near the edge of the carousel and the subsequent numbers following a clockwise sequence (see Figure 1). All eight carousel positions were occupied with reaction vessels during the ionization chamber and film measurements in order to provide the likely scattering conditions during irradiations. Only the measurement vessels and an additional vessel used for temperature monitoring were water-filled.

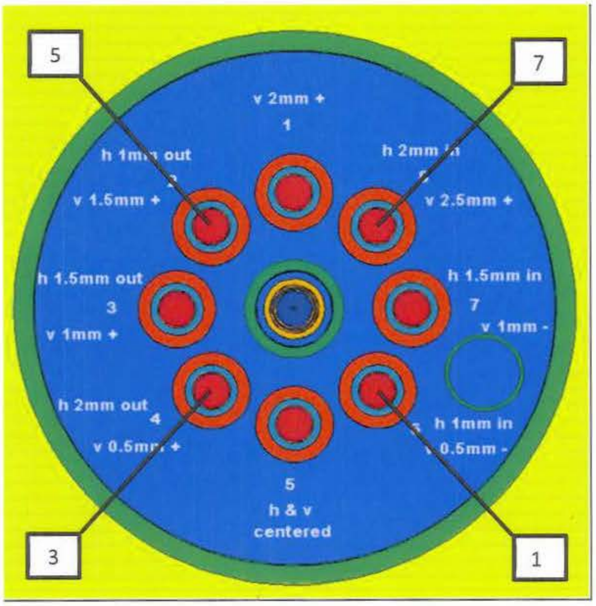

Figure 1: Top view of reaction vessels arrangement within Co-60 Bunker ("h" and "v" indications represent vessel offsets applied within MCNP simulations, discussed later in this report).

Air-Equivalent Ionization Chamber Measurement:

Radiation detectors used to evaluate the exposure rate within the reaction vessels included four Exradin air-equivalent ionization chambers (AEIC); two Model A12 and two Model A12S with approximate sensitive volumes of 0.64 and 0.24 cm^3, respectively. These detectors were placed in various combinations of height within the vessels, including centered at 1.5 cm, 6.75 cm and 12.0 cm above the inside base of the vessels. Each AEIC sensitive volume was retained coincident with the cylindrical axis of the vessel volume via the use of custom constructed, low mass plastic spacers. Initial measurements (June 6-7) focused on evaluating the exposure rate at the central height of the fluid-filled portion of the vessels (nominally set at 6.75 above the inside base). As the two detector models have different regions of the sensitive volume, it was necessary to locate the respective chambers at slightly different locations. Measurements were conducted with the AEICs placed directly within the water and/or water plus resin materials, without the use of their respective build-up caps, anticipating that the surrounding medium would provide sufficient charged particle equilibrium (CPE). Calibration of each chamber, with build-up cap applied, was performed prior to these measurements using the 318 Building High Exposure Facility (HEF) ^{60}Co source 318-464 at a distance of 150 cm in air. The transfer standard used for these direct replacement measurements was a Capintec Model PM-30, with build-up cap. The equipment listed in Table 1 was used to support these measurements. All listed equipment, with the exception of the thermocouple and associated Omega readout listed in the table, were calibrated in a method traceable to the National Institute of Standards and Technology.

Table 1: Measuring and Test Equipment

Device	S/N	Calibration Exp. Date	Application/Notes
AEIC Exradin A12 AIC	XA102351	12/2016	Bunker Vessel Position 1
AEIC Exradin A12 AIC	XA151686	12/2016	Bunker Vessel Position5
AEIC Exradin A12S AIC	XZ151955	12/2016	Bunker Vessel Position 3
AEIC Exradin A12S AIC	XZ151956	12/2016	Bunker Vessel Position 7
AEIC Capintec PM-30	CII30.7502	8/2016	^{60}Co Transfer Standard used to calibrate Exradin A12 and A12S AEICs
Keithley 617 Electrometer	383823	1/2017	Calibration and Bunker measurements (Positions 5 and 7)
PTW Unidos E Electrometer	002096	1/2017	Bunker AIC current readout Positions 1 and 3
Timer	SWFI3-0002	2/2016	Calibration of Exradin AIC charge integration time and for Film irradiation duration.
Thermometer	PTVA1-0001	6/2016	
DigiSense Readout Omega Thermocouple	577785 3197	1/2017	Reaction Vessel in water (Top) – Calibrated against working standard (PTVA1-0001)
Omega Readout Omega Thermocouple	876237 3196	Ind. Only	Reaction Vessel in water (Bottom) (Used only for relative readings)
Barometer	PTVA1-0001	6/2016	
Distance	DRLS1-0003	4/2020	Measuring vessel dimensions and AEIC placement

AEICs were placed within the vessels filled (roughly half-full) with 31 mL of deionized water. This was intended to provide a 13.5 cm depth (not including chamber displacement). The air-vent and signal cable protection tube for each chamber was marked at three positions to indicate the intended depths. When aligned with the top of the open flange, this placed the centroid of each AEIC volume at the respective intended position (e.g., 1.5, 6.75 and 12.0 cm relative to the inside base of the vessel).

Temperature monitoring was accomplished using Type K thermocouples (TC) placed within a surrogate reaction vessel half filled with deionized water. One TC was placed near the bottom of the vessel, while the second was placed higher in the vessel. Both were located within the water-filled region. To correct AEIC measurements, the TC placed near the top of the water-filled region was used.

Dose rate to water was determined using the following equation:

$$\dot{D}_w = I_{ioniz} \cdot k_{TP} \cdot k_e \cdot N \cdot k_{D/X} \cdot 3600$$

Where: $\dot{D}_w$ is the average absorbed dose rate to water over the sensitive volume of the AEIC (commonly attributed to the position of the centroid of the chamber), in rad/h,

I_{ioniz} is the measured ionization current, in A (C/s),

k_{TP} is the unitless correction for density of air within the AEIC volume,

k_e is the unitless correction for the readout of the electrometer,

N is the efficiency of each respective AEIC determined through comparison with the secondary transfer standard using the same photon energy, in R/C,

$k_{D/X}$ is the conversion coefficient from exposure (Roentgen) to absorbed dose to water (rad). A value of 0.966 was used, as referenced from ICRU 30 (1979), *Quantitative Concepts and Dosimetry in Radiobiology*,

3600 converts the time interval from seconds to hours.

Initial measurements conducted on January 6-7 included a six-replicate source transition assessment with the AEICs at the 6.75 cm position, as well as one measurement each with the chambers placed at the 1.5 cm and 12.0 cm positions. The replicate assessment provided data regarding potential source placement variation within the carousel due to inherent source anisotropy, as well as potential side to side position variations due to the diameter tolerance needed for source travel.

During the preparation for these measurements, it was noted that some of the vessels appeared to be slightly angled within the carousel. It was then alleged that the upper vessel alignment/retaining disk appeared to be inverted, thus slightly misaligning the flange cutouts with the lower plate troughs.

Follow-up measurements on January 13 were focused first on assessing the dose rate within resin-filled vessels. Additional measurements were conducted in deionized water to repeat the assessment of January 6-7 (repeating the replicate source alignment study was deemed unnecessary). Prior to commencing measurements on January 13, the upper alignment plate was inverted to enable better alignment of the reaction vessels.

The results of measurements near the ends of the liquid region of the vessels indicated approximately 50% of the dose rate observed at 6.75 cm above the inner chamber base (i.e., source mid-point). The replicate source positioning evaluation indicated that dose rate within individual vessels could be expected to vary up to about 1.8%. Furthermore, there is evidence that dose within the vessels placed radially around the source varied (i.e., within single irradiations). This is most likely to be associated with reaction vessel positioning. This distribution ranges approximately ±4% of the average measured dose rate.

AEIC measurements on January 13 provided the basis for the quoted absorbed dose rate to water at the three heights within the vessels. The central height (6.75 cm) measurement is considered to be the estimate of the traceable absorbed dose rate to water within the volume least affected by geometric conditions (e.g., scatter, stem effects, water/gas interface, etc.) within the volume. **The average dose rate to water indicated at 6.75 cm height within the vessels (aligned with the source center) was approximately 488 krad/h, and the near end points (1.5 and 12.0 cm above the inner base of the vessel) indicate 245 krad/h.** Measurements conducted within the resin medium appeared to be very similar to measurements within the water, without indication of unidirectional bias among the three measurement points. Data is provided in Table 2.

Table 2: AEIC Measurement Summary

Liquid Level in Vessel[1] (cm)	Measured Dose Rate to Water (krad/h)		
	January 13, 2016 (In Water)	January 13, 2016 (in Resin + Water)	January 6-7, 2016 (in Water)[3]
13.5			
12.5	245.2 ± 25.8	215.3 ± *5.1*[2]	250.5 ± 16.2
11.5			
10.5			
9.5			
8.5			
7.5	487.5 ± 22.9	493.2 ± 8.0	470.8 ± 12.4
6.5			
5.5			
4.5			
3.5			
2.5	244.6 ± 15.0	263.1 ± *6.2*[2]	238.5 ± 20.6
1.5			
0.5			

1. Value corresponds to top of labeled row.
2. One AEIC measurement only. AEIC is the smaller volume A12S, which only covers about 8 mm of length. Represents estimated standard deviation based on other related measurements.
3. Initial measurements consisted of four 90° relative positions around source at all heights and six replicate measurements at the 6.75 cm level for reproducibility studies. However, all data (except data regarding reproducibility) is suspect due to later-revealed issue with alignment due to inverted Upper Plate on the Carousel.

Radiochromic Film

Radiochromic film has a leuco dye layer within a polymeric matrix that darkens with increasing dose. Film used for these evaluations is the Ashland Model HD-V2, which has a stated range of 10 to 1000 Gy (1 to 100 krad). A film set was calibrated specifically for this effort, using ^{60}Co irradiations – with film placed within suitable build-up materials – ranging from 50 to 260 Gy (5 to 26 krad). Initial calibration and readout of the film (absorbance vs. dose) was performed using a HP Model Digital Sender 9250C scanner and a 24 hour post-exposure growth interval; however, the resolution of this scanner beyond about 24 krad was lacking. Fortunately, an Epson 10000XL flatbed scanner with 48-bit RGB format - more suitable to radiochromic film analysis - had recently become available. This scanner was calibrated (see Figure 2) using the same films used for the HP 9250C previous scanner, but with a post-exposure growth interval of about 17 days. In order to have data available in time for the initial gas generation irradiation phase, dosimetry films needed to be read with about 12 to 13 days post-exposure growth interval. It was anticipated this would provide a slight deficit in the dose estimate.

Film measurements were configured within the same reaction vessels as the AEIC measurements, albeit with the water removed. In place of the water, special film phantoms (see Figure 3) were constructed using polylactic acid (polyester) to hold 5 film strips, each within a nominal material density near 1.25 g/cm^3. Due to micro-air voids inherent with 3-D printing, and air voids between assembled components, the average density of these phantoms was measured to be ~0.86 g/cm^3. The film phantoms each were made up of a cylindrical holder, of diameter just less than the inner diameter of the reaction vessels, containing six layers of the material, five of which were crafted with insets just large enough to retain the precut film strips. When assembled, these layers formed a solid cylinder that fit into the cylindrical holder. These phantoms enabled film strips of about 11.2 cm in length to be centered – with the aid of shims – within the central irradiation region, although they unfortunately did not replicate the entire depth normally filled with liquid within the vessels. The region covered by the film extended from about 1.15 cm above the inner base of the vessels to 12.35 cm above the inner base of the vessels.

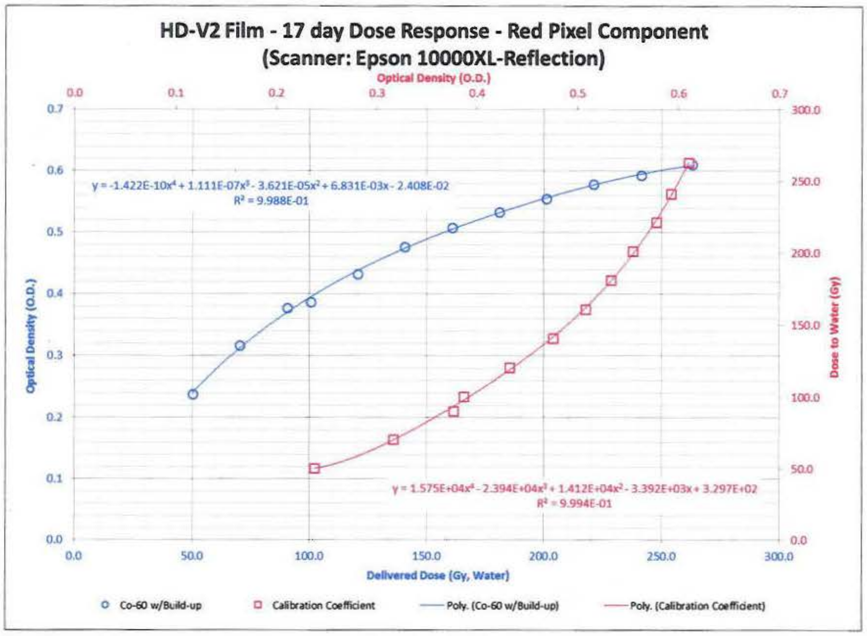

Figure 2: Calibration data for HD-V2 radiochromic film over the range of 50 to 260 Gy (5 to 26 krad) to water

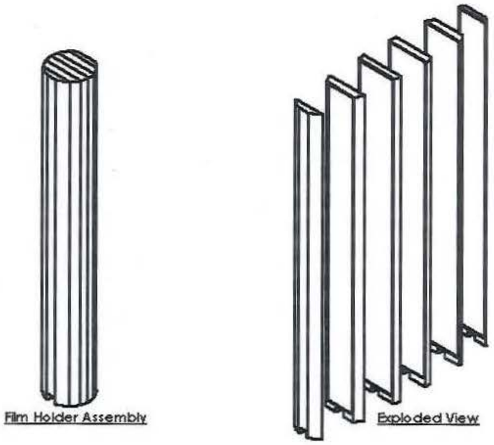

Figure 3: Radiochromic film holder (phantom) for placement of films within reaction vessels.

Films were irradiated during the January 13 measurement campaign. The irradiation consisted of a single trial with all four film phantoms loaded in vessels at positions 1, 3, 5 and 7 (see Figure 1). To restrain the dose to within the calibration region of the film, the target dose was about 14 krad to water (center film layer), which limited the irradiation to about 105 seconds. The short irradiation time was anticipated to be significantly influenced by the transit of the source in and out of the carousel. During the June 6-7 irradiation campaign, a source transit evaluation was conducted and yielded an estimate of -1.8 seconds of transit influence (i.e., a 105 second irradiation would actually be 103.2 seconds). This offset was applied to the irradiation time. Due to some difficulties with the vacuum/control system used for the source transit, it was observed that the time for the source to arrive on-station was somewhat slower than the time for the source to depart (and slower than observed during the transit study). As such, this remains a significant uncertainty in the absolute dose delivered to the film. Despite this uncertainty upon the estimate of the true dose level within the volume of the vessels, the influence of this source transit time on the average distributed dose delivered within vessel volumes (i.e., the volume dose profile) was expected to be relatively small.

Film readout was conducted on January 25-26 with scan resolution set to 300 dpi, yielding a pixel dimension of about 85 µm. All scanner post processing enhancements were deactivated. The scanned images were analyzed within the red pixel region using ImageJ software, focusing primarily on a region of interest along a central 1 to 3 mm strip extending from the top to the bottom of the ~11.2 cm filmstrip (see images in Figure 4). Lateral profiles of the dose were not evaluated for this initial assessment.

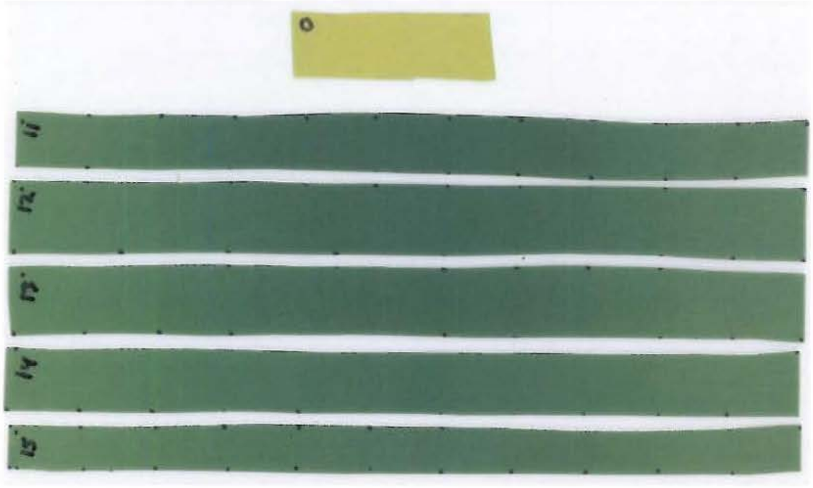

Figure 4: Radiochromic films exposed within reaction vessel placed at Bunker position 7. Film 11 placed nearest to source. Film 15 placed furthest from source. Uncorrected exposure time is 105 seconds delivering nominal dose to center of vessel of 140 Gy (14 krad).

Data from initial film analysis formed five response profiles (each >1300 pixels in length) representing dose at increasing depth within the cylindrical volume of each phantom (or water). From these five profiles, a single profile was derived simply by calculating the average pixel level of the five layers. Then, the average reading from each of the four vessels were combined to attain an overall profile. The average dose to the volume may be approximated by the mean of the >1300 pixels, converted to absorbed dose to water using the calibration function (polynomial in Figure 2). The average dose profile for each of the four reaction vessels, and the mean of those four profiles, is provided in Figure 5. From this figure, data variability is evident. **The initial dose estimate at the central AEIC region for positions 1, 3, 5, and 7 range from 421 to 469 krad/h, while the volume average dose for these vessel positions ranges from 325 to 357 krad/h and a combined average absorbed dose rate to water of 336 krad/h.**

MCNP Simulation:

The reaction vessel irradiation profile within the bunker was simulated through the use of MCNP5. Within this simulation, radiation energy deposited within the water content of the reaction vessels was separated into multiple cells. The distribution enabled the comparison of relative dose intensities for the various film and AEIC measurements facilitating a means to calibrate the average distributed dose within the volume. It also provided a means to combine the deposited energy proportionally such that the calculated average is weighted appropriately. Also included within the simulations were slight variations in the lateral and height distribution of the reaction vessels within the carousel that will aid in the final estimation of uncertainties associated with the determined mean absorbed dose to water.

Simulation data output via the F6 tally provided the total energy deposited (MeV/total mass) within the water content of each vessel cell per ^{60}Co disintegration. Post processing of this data translated the deposited energy to absorbed dose to water. The calculated dose to water (per disintegration) was then translated to total dose rate assuming the manufacturer's estimate of activity (with estimated accuracy of ±10%), decayed to the January 13, 2016. The resulting mean simulated dose rate at the center position of each cell (i.e., aligned with 6.75 cm above the inside base of the vessel) was approximately 2% less than the dose rate at the same position measured via AEIC. The dose rate to each vessel was calculated as the mean dose rate of all cells within the water-filled region of the vessel. This mean dose rate assessment was incremented by 2% to match overall intensity assessed via the NIST-traceable AEIC outcome.

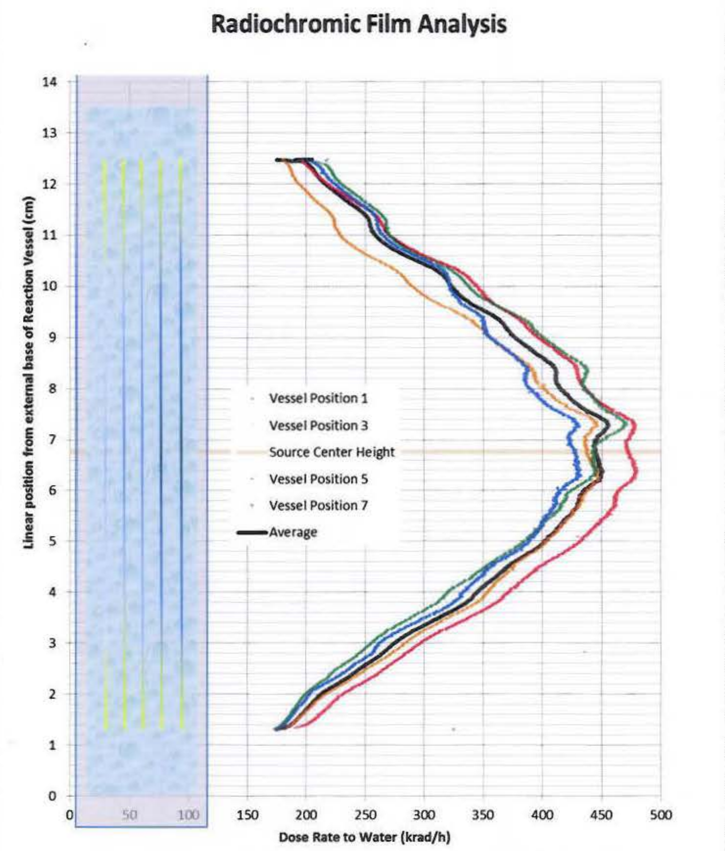

Figure 5 - Radiochromic Film measurement results showing dose rate calculated at increments of about 33 µm from about 1.3 cm to 12 5 cm above the inside base of each reaction vessel. For each vessel data shown, data is the average of 5 films placed as shown (as viewed edge on) within each reaction vessel. Radiation is incident from the right of the vessel shown.

Two simulations were performed. One simulation was conducted with reaction vessels intentionally misaligned in elevation (extending from −1 mm to +2.5 mm), while the second simulation was conducted with reaction vessels intentionally misaligned in lateral vessel position (extending from −2 mm to +2 mm). The vessel at position 2 in both simulations was aligned at the intended reference position and the dose tallied at 30 individual regions within the liquid-filled region of the vessel. The volume average dose rates from these two vessels differed by only 1.4 krad/h (about 0.3%). **The mean of the two rates, 346.8 krad/h, represents the MCNP determined value.**

All other vessels liquid volumes were split into 15 separate regions. Calculating the mean of the volume average dose rate for each set of simulation results provides a basis for uncertainty for possible variations in placement within the simulated offsets. **For elevation variations, the half-range of variation is about 0.7 krad/h; while for lateral variations, the half-range of variation is about 17.6 krad/h.** Data from these elevation and lateral variation simulations is provided in Tables 3 and 4.

Simulated relative distributed dose within the reaction vessels are provided within Figure 6.

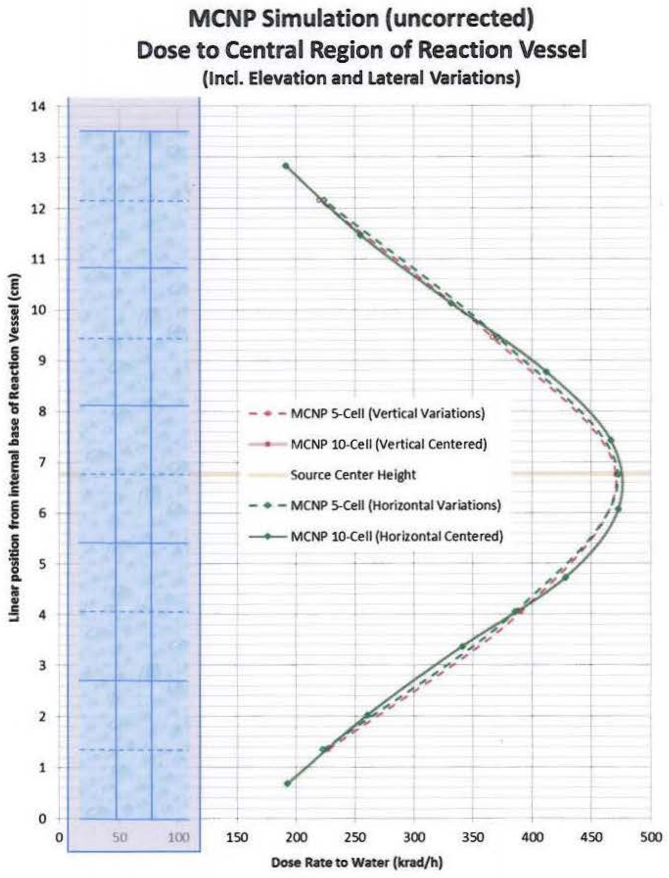

Figure 6 - MCNP simulation results showing total dose rate calculated to central region. 5-Cell results show dose rate to regions bounded by horizontal solid lines in diagram at left. 10-Cell results show dose rate to regions bounded by respective horizontal solid and dashed lines.

Table 3: Summary of MCNP calculated dose rates (corrected to AEIC) to individual reaction vessels with slight vertical (elevation) variations.

Bunker Position (Variation)	**Elevation (cm):**	**0.675**	**2.025**	**3.375**	**4.725**	**6.075**	**7.425**	**8.775**	**10.125**	**11.475**	**12.825**
	Lateral Vessel Region	**Dose to Water within Region (krad/h)**									
2 **(Reference)**	Near Source	215.7	300.2	410.3	528.0	598.8	584.6	506.8	394.2	296.8	213.0
	Central	199.7	269.9	353.4	443.5	490.0	483.4	426.9	343.8	264.1	198.6
	Away from Source	186.2	243.4	312.1	380.3	413.9	406.0	366.7	303.9	237.6	184.6
	Elevation (cm):	**1.35**	**4.05**	**6.75**	**9.45**	**12.15**					
1 (-0.5 mm)	Near Source	249.3	465.7	592.2	454.7	258.8					
	Central	226.3	395.8	488.3	388.0	234.1					
	Away from Source	207.6	342.8	412.3	336.4	214.6					
3 (+0.5 mm)	Near Source	258.6	474.6	593.5	447.2	250.5					
	Central	233.0	402.3	488.2	382.8	227.5					
	Away from Source	212.4	348.1	411.6	333.3	208.3					
4 (+1.0 mm)	Near Source	261.6	477.7	591.2	444.2	251.9					
	Central	236.2	405.1	486.5	379.6	228.1					
	Away from Source	214.0	350.5	410.5	330.4	208.0					
5 (+1.5 mm)	Near Source	264.6	483.8	591.7	438.0	245.3					
	Central	238.5	408.9	487.9	373.9	225.1					
	Away from Source	217.8	355.6	412.3	326.3	206.3					
6 (+2.0 mm)	Near Source	269.3	484.1	592.8	436.7	243.2					
	Central	241.8	411.6	488.0	371.7	221.9					
	Away from Source	219.9	356.2	413.6	323.9	205.6					
7 (+2.5 mm)	Near Source	270.2	490.7	585.0	432.3	241.8					
	Central	245.7	413.6	482.3	370.1	220.9					
	Away from Source	223.4	358.3	406.9	322.3	203.0					
8 (-1.0 mm)	Near Source	248.9	461.4	596.4	458.9	262.9					
	Central	226.3	392.9	491.5	390.8	237.7					
	Away from Source	206.1	341.4	414.9	339.5	217.4					

Average Response of Combined Cells

Position	krad/h (water)
1	3.511E+02
2	**3.519E+02**
3	3.515E+02
4	3.517E+02
5	3.517E+02
6	3.520E+02
7	3.511E+02
8	3.525E+02
Mean:	3.517E+02
Std. Dev.:	4.600E-01
CoV:	0.1%

Table 4: Summary of MCNP calculated dose rates (corrected to AEIC) to individual reaction vessels with slight horizontal (lateral) variations

Bunker Position (Variation)	**Elevation (cm):**	**0.675**	**2.025**	**3.375**	**4.725**	**6.075**	**7.425**	**8.775**	**10.125**	**11.475**	**12.825**
	Lateral Vessel Region	**Dose to Water within Region (krad/h)**									
2 **(Reference)**	Near Source	215.1	299.0	408.7	525.7	596.4	582.4	504.6	392.5	295.4	212.1
	Central	198.9	268.7	352.0	441.7	487.9	481.3	425.1	342.3	262.9	197.8
	Away from Source	185.5	242.4	310.9	378.8	412.2	404.2	365.2	302.8	236.5	183.8
	Elevation (cm):	**1.35**	**4.05**	**6.75**	**9.45**	**12.15**					
1 (-1.0 mm)	Near Source	254.8	482.0	611.7	462.1	257.7					
	Central	231.4	408.4	503.0	393.7	234.2					
	Away from Source	212.1	353.1	423.8	341.7	214.5					
3 (+2.0 mm)	Near Source	247.6	442.4	550.4	426.0	245.9					
	Central	223.0	376.8	455.7	365.1	223.2					
	Away from Source	203.4	327.1	385.7	318.3	203.2					
4 (+1.5 mm)	Near Source	248.7	447.8	558.4	431.7	251.7					
	Central	224.9	381.2	461.9	369.2	226.8					
	Away from Source	204.5	331.3	391.4	321.0	206.4					
5 (+1.0 mm)	Near Source	250.8	454.9	572.0	434.3	250.6					
	Central	227.0	387.0	472.1	371.3	228.3					
	Away from Source	207.4	338.1	399.8	324.1	208.6					
6 (Reference)	Near Source	255.5	465.8	593.8	449.5	254.9					
	Central	231.5	396.5	488.6	381.8	231.0					
	Away from Source	210.6	345.3	413.7	331.8	212.9					
7 (-2.0 mm)	Near Source	259.9	496.6	631.0	476.0	262.5					
	Central	236.6	420.0	516.8	403.1	239.2					
	Away from Source	217.2	362.9	434.0	349.5	218.4					
8 (-1.5 mm)	Near Source	259.5	489.3	627.1	468.0	261.1					
	Central	235.7	414.5	514.4	398.3	236.9					
	Away from Source	214.6	358.3	432.6	347.0	216.2					

<u>Average Response of Combined Regions</u>

Position	krad/h (water)
1	3.589E+02
2	**3.504E+02**
3	3.329E+02
4	3.371E+02
5	3.417E+02
6	3.509E+02
7	3.682E+02
8	3.649E+02
Mean:	3.506E+02
Std. Dev.:	1.287E+01
CoV:	3.7%

Discussion and Results:

Combining the data from the above measurements and simulations for the initial estimate of average dose to the liquid- or resin-filled volumes of the eight test vessels was initially challenging, due in part to some disparity between the film and AEIC data (see Figure 7). While, in theory, both measurement methods should provide equally valid results due to their respective calibrations and irradiation configurations, the uncertainty is much higher for the film than for the AEIC data. Certain unknown irradiation influences (e.g. source transit) and analysis uncertainties (e.g., film uniformity, calibration function parameters, etc.) contribute to the higher uncertainty of the film methodology.

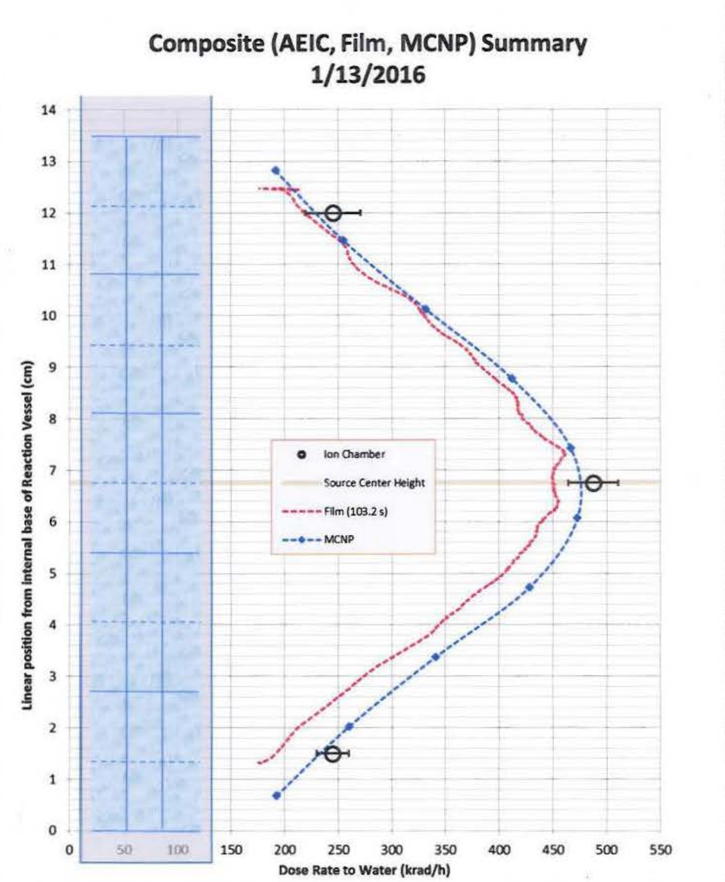

Figure 7 - Initial (uncorrected) radiochromic film and MCNP data compared to AEIC absorbed dose rates to water. Film data represents average of three innermost films from each of four measurement positions. MCNP data represents estimated dose to central region of vessel. Both data sets are intended to coincide with AEIC position along central axis of vessels.

Such differences could be the result of contributors from both the film and AEIC measurements. With respect to the film *measurements*, the source transit effect may significantly influence both the total dose as well as the dose profile depicted by the film – especially in the upper region of liquid. There are also several sources of uncertainty in the film *analysis*, not the least of which includes the previously mentioned 4 to 5-day latency differential between the calibration film analysis and the irradiated film analysis. Other influences on uncertainty are the uniformity of the film itself as well as scanner bed uniformity.

From the AEIC perspective, it is possible that the measurements may be influenced by the amount of liquid displacement as the chamber penetrates to increasing depth. This reaches maximum potential with the chamber near the bottom of the vessel, as the radiation interacts more directly with the air-filled cavity and stem of the AEIC, which offsets the attenuating property of the water that has been displaced by the chamber. At the mid-level (6.75 cm position), the chamber stem is also fully within the water, but less direct radiation from the source must transit that volume prior to interaction in the small volume of the sensitive chamber. Near the top of the vessel, most of the AEIC stem is outside of the water and very little deficit in water attenuation is anticipated.

The disparity of the film and AEIC data created greater impetus for consideration of the MCNP simulation data. Data from the "reference" reaction vessels, ideally aligned and segmented into 30 regions of dose tally within the liquid-filled region, provided much closer alignment with the AEIC data. Figure 7 represents MCNP data before normalization to the AEIC result. Although it is also noted to be slightly different than the AEIC measurements, it is more consistently different at all correlated positions. The simulation results are not affected by the transit of the source, but they are also incapable of realizing influences of anisotropy, largely thought to be due to non-uniform distribution of the activity within the source. At close proximity, such anisotropy may contribute significantly to the average dose throughout the liquid volume of the reaction vessels.

The results of the AEIC measurements are considered to provide the most traceable assessment of dose rate at the three discrete measurement points, with the central elevation having the least associated uncertainty of the three. Regardless, simply combining the three data points to attain an estimate of the average dose to liquid or resin in each vessel would not provide sufficient resolution of the volume. Both film and simulation analysis provide the dose distribution detail needed to calculate a well distributed average dose rate. Both also have other benefits, as well as some weaknesses. To attain the best assessment of average dose rate, the film and central region MCNP simulation analyses were adjusted (normalized) to the AEIC measurement at the central elevation (i.e., the measurement point thought to be the least uncertain due to geometry considerations. The position and volume averaged film data was elevated by 9.9% at all points. As noted above, the MCNP simulation data [shown in Tables 3 and 4, were adjusted by an average of 2.1% (2.3% for data in Table 3 and 1.9% for data in Table 4)]. The corrected film and simulation analysis is shown in Figure 8.

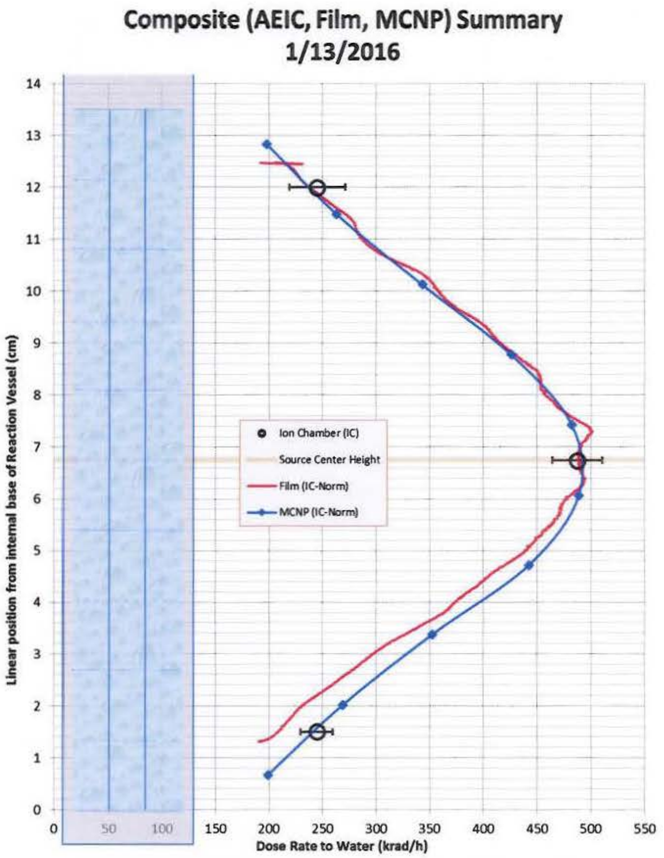

Figure 8 - Radiochromic film and MCNP data normalized to mid-level AEIC absorbed dose rate to water. Film data represents average of three innermost films from each of four measurement positions. MCNP data represents estimated dose to central region of vessel. Both data sets are intended to coincide with AEIC position along central axis of vessels.

With these corrections applied to all film and simulation data, the volume average dose rate was determined for each method. **Film data produced an estimated dose rate to water of 364.7 krad/h, while the MCNP simulation resulted in an estimate of 351.2 krad/h. These two results were combined to yield a mean dose rate estimate of 357.9 krad/h as of January 13, 2016.**

For the irradiation starting date of January 28, the absorbed dose rate to water is 356.0 krad/h, thus indicating an irradiation time of 842.7 h (35 days + 2.7 hours) to achieve 300 Mrad. Because the source output decays at about 0.036% per day, this will necessitate an increase in the total irradiation time. Based on a daily-compounded decay adjustment applied to the absorbed dose rate to water, the total time needed to attain an average dose rate of 300 Mrad will be just over 848.1 h (35 days + 8.1 hours).

Uncertainties:

A comprehensive evaluation of uncertainty has not been performed for this preliminary estimation of the dose rate. Instead, the major contributors of uncertainty for each measurement or simulation outcome are summarized in Table 5, below. Further analysis will be conducted for these contributors to uncertainty before a final estimate of the expanded combined absorbed dose rate uncertainty is stated.

Table 5: Identification of primary uncertainty constiuents

		Estimate (relative)	**Distribution**	**Std. Error**	**Std. Error^2**
Ionization chamber calibration	A	0.005	normal	0.005	0.000025
Ionization Chamber measurements					
statistical response	A	0.0004	normal	0.0004	0.0000002
electrometer (PTW)	B	0.006	rect.	0.003	0.000012
source anisotropy	A	0.018	rect.	0.010	0.000108
positioning of the vessels (from MCNP)	A	0.040	rect.	0.023	0.000533
				sum	0.000678
				sqrt (sum)	2.6%
Film irradiation (Negated via normalization to Ion Chamber)					
transit dose correction	A	0.001	normal	0.001	0.000001
error in timing/transit	B	0.039	normal	0.039	0.001521
				sum	0.001522
				sqrt (sum)	3.9%
Film Analysis					
film latency deficit	B	0.010	normal	0.010	0.000100
uniformity	B	0.030	rect.	0.017	0.000300
variation among vessels	A	0.068	rect.	0.039	0.001541
film calibration	B	0.030	normal	0.030	0.000900
film response	A	0.020	normal	0.020	0.000400
				sum	0.003241
				sqrt (sum)	5.7%

Distribution*

Washington River Protection Solutions
KE Ard
MR Landon
JG Reynolds
RM Russell
TE Sackett
WRPS Documents – TOCVND@rl.gov
LAWPS Documents – LAWPSVENDOR@rl.gov

Savanah River National Laboratory
DT Herman

DOE – Office of River Protection
SC Smith

Pacific Northwest National Laboratory
SR Adami
SA Bryan
DM Camaioni
HA Colburn
LA Mahoney
PP Schonewill
Project File
Information Release (pdf)

*All distribution will be made electronically.

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

Proudly Operated by **Battelle** *Since 1965*

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)

www.pnnl.gov