Gas Generation Test Support for Transportation and Storage of Plutonium Residue Materials - Part 1: Rocky Flats Sand, Slag, and Crucible Residues

by

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Revision 0

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August 1999

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Strategic Materials Technology Department
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Section I – Introduction to Gas Generation Testing

Executive Summary

The purpose of this report is to present experimental results that can be used to establish one segment of the safety basis for transportation and storage of plutonium residue materials. Gas generation testing of actual Sand, Slag and Crucible (SS&C) residues from the Rocky Flats Environmental Technology Site (RFETS) and surrogate compositions representing SS&C contents demonstrates that hydrogen gas (H_2) is generated from both chemical and radiation induced reactions. The chemical reaction of adsorbed moisture with calcium metal is very rapid at elevated temperature and produces H_2 much faster than expected from radiolysis of adsorbed moisture. The rate of H_2 production from radiolysis of adsorbed moisture varies based upon matrix composition. In tests of surrogate materials and actual SS&C samples, the current analytical radiolysis model was found inadequate when weight loss at 210°C was used to estimate moisture content. In addition, test results show that partial oxygen gas (O_2) depletion occurs for many of the SS&C residue materials, and no net increase in O_2 is observed for all the SS&C residue materials when weight loss at 210°C is maintained below 2.3 percent. The observed depletion of O_2 in sealed containers of SS&C residue is supported by external studies of moist air radiolysis and gas sample data from plutonium oxide (PuO_2) containers after many years of storage.

Description of Document Content

This report was written to summarize what has been learned about gas generation for SS&C residues. The presentation is divided into several sections to impose a level of organization to an otherwise sprawling topic. The Table of Contents provides a detail listing of the document sections and should be referenced to help the reader understand the flow of information provided in this report.

Section I includes the executive summary and background on the need for gas generation tests to support transportation and storage of plutonium (Pu) residues. Section II provides an overview of gas generation test methods and a description of test data collected at the Savannah River Technology Center (SRTC). Section II also provides a platform for interpreting the results of this study and supports the ideas presented in the remaining sections.

One of the early priorities for gas generation testing was to validate the capability of an analytical radiolysis model. This effort is described in Section III, which includes a description of the model developed at SRTC and a comparison with actual test results for SS&C surrogates.

A key parameter influencing gas generation rates and gas composition is moisture content of the residue. Section IV discusses the current means for measuring H_2O in SS&C, and presents data from the tests used to measure H_2O adsorbed by residue matrix components.

Radiation is one of the two principal driving forces behind gas generation and the resulting gas composition in sealed containers. A brief literature review of radiolysis effects that are anticipated to impact residue storage are covered in Section V.

The next section of this report is dedicated to a discussion of the observed O_2 content in the gas generation testing for SS&C residues. Section VI includes the basis for "no net increase in O_2 " for sealed containers of SS&C.

The final section of this report attempts to summarize what has been learned in the initial stages of the SRTC Gas Generation Test Program (GGTP) and draw conclusions based on the observed behavior of SS&C residue and surrogate materials. Our current understanding of gas generation in Pu residue from radiolysis of adsorbed moisture is presented as a conceptual model.

Background on Gas Generation Testing

The transportation of Pu bearing residue materials requires a well-designed shipping package that has been rigorously tested to withstand normal and accident conditions. Pu-bearing contents can contribute to shipping package internal pressure by producing heat and gases from chemical and radiochemical reactions.^{1,2,41} Of particular concern is the production of H_2 , which could result in flammable gas mixtures within the shipping package. The Safety Analysis Report for the 9975 Package³ (9975 SARP) uses an analytical model⁴ to predict the radiolysis of moisture in residue materials. The model estimates gas production as a linear function of the energy released by radioactive decay, the relative stopping power of matrix components including water, and the fraction of energy absorbed by water. The model assumes that water adsorbed by residue materials is decomposed by radiolysis to form stoichiometric proportions of H_2 and O_2 at a rate similar to what is reported for aqueous solutions. The contents and shipping time are then constrained to prevent the formation of gas mixtures and pressures that would exceed limits for the 9975 package.

The 9975 SARP currently provides content descriptions for two categories of Pu residues. These descriptions are based on process knowledge of RFETS SS&C and fluoride residues. In February 1999, SRTC initiated the GGTP for Pu residues. The purpose of this test program is to support safe packaging, transportation and storage of Pu residues. The first tests conducted under this program were designed to show that the gas generation model used in the 9975 SARP provides conservative H_2 generation rates when applied to RFETS SS&C and fluoride residues. Many of the initial tests were conducted using surrogates composed of PuO_2 and a single non-radioactive component from the SS&C list of contents. Additional gas generation measurements were made using samples of actual RFETS SS&C. Efforts to study fluoride residues have been delayed pending definition of the treatment steps to be used prior to packaging.

A mid-study review of the test results indicated that the analytical radiolysis model is not adequate for all materials allowed by the SS&C content description. Comparison of measured versus calculated H_2 generation rates showed the model under-predicts for some materials by nearly a factor of ten for the seven-day test period. A rapid reaction of calcium metal with moisture in the surrogate materials also was observed. The same pressure rise associated with

rapid gas production was observed for the actual SS&C samples at elevated temperatures. Chemical reactions, which contribute to the H_2 concentration, are not considered in the analytical radiolysis model. The strong tendency toward O_2 depletion for the SS&C samples and the expected increase in H_2 generation rate with elevated moisture on PuO_2 also were noted during the mid-study review of the test results. Based on these observations, the GGTP changed the focus of the tests to determine a moisture limit (based on weight loss) that would provide no net increase of O_2 for the SS&C residues. The terminology "no net increase" has been selected since there are several reaction mechanisms that contribute to the observed O_2 concentration.

The purpose of this report is to summarize what has been learned about gas generation for SS&C residues during the initial months of the GGTP for Pu residues. This report will primarily evaluate the gas generation experimental results that can be used to establish one segment of the safety basis required for packaging and transportation of RFETS SS&C residues. Many of the test results may also be applied to storage of the SS&C residue.

Section II – Gas Generation Testing

Experimental Apparatus

The first task associated with measuring the gases generated by Pu residues during transportation and storage was to assemble an apparatus for experimental measurements. The apparatus was designed to allow monitoring gas generation rates and determining final gas compositions. The general approach used in the gas generation testing at SRTC was to seal test materials in sample vessels that were connected to pressure transducers and a gas manifold that was equipped for gas sampling. The details of the experimental set-up and test protocol are provided in the Task Technical and Quality Assurance (QA) Plan⁵ written at the initiation of the GGTP in SRTC. Figure 1 is a diagram of the laboratory set-up.

Figure 1 – The GGTP Diagram of Laboratory Apparatus

The sample vessels used in the SRTC testing were designed to be heated and have redundant temperature controls. The actual system used had six test positions that could be operated simultaneously. The sample vessels were maintained at ambient temperature or 90°C to assess the impact of thermal conditions. The 90°C temperature was selected because this was the highest sustained temperature expected for transportation of SS&C residue. Thermocouples mounted in the side-wall of each sample vessel provided the temperature measurements. The heated zone of the apparatus included only the primary container, so that the valve and pressure transducer was not heated. The pressure measurements were made using high accuracy Baratron™ pressure transducers.

Sample vessel sizes varied depending on the quantity of actual residue or surrogate material to be tested. Each of the test vessels is constructed of stainless steel with nominal container volumes ranging from 5 cubic centimeters (cc) up to about 100cc. The volume of each container with residue was determined using Pressure-Volume-Temperature (PVT) data collected after each test run by expansion from a known volume. The vessels were attached to the larger apparatus using a Cajon® VCR® fitting with stainless-steel gasket. Frequently the gaskets used in these tests contained sintered metal frits to minimize the spread of sample powders into the test apparatus. The face seals used by Cajon® are considered very reliable and are advertised to consistently provide helium leak rates less than 4×10^{-9} cc per second (cc/sec).

Each sample vessel was connected to a test stand, which was designed to retain the gases generated during testing and allowed continuous pressure measurements. The Baratron™ pressure transducers provided all stainless-steel parts in contact with the sample gas, which is ideal for H₂ applications. The valves used to isolate each test stand from the gas manifold were NUPRO® stainless steel bellows valves with Kel-F valve seats. These valves were selected for their demonstrated ability to retain H₂ and are frequently used in H₂ applications at the Savannah River Site. The gas manifold was constructed from 1/8th inch stainless tubing to minimize total volume.

The sample container, Baratron™, and valve portion of the test stand were assembled and leak tested prior to installation in the glovebox and connection to the manifold. Three of the six test assemblies used for gas generation testing were shown to have helium leak rates less than 8×10^{-10} cc/sec at 150 PSIG prior to installation. For the other three test assemblies, leak rates were shown to be less than 1×10^{-6} cc/sec by measuring pressure change with time for the evacuated apparatus.⁶ Additional leak tests of installed system components were conducted by evacuating the system and monitoring for pressure rise with time.

Gas Generation Test Protocol

Each sample vessel was filled with a designated sample or surrogate material in an air atmosphere. The vessels' bulk contents were measured by change in vessel mass before and after filling. All operations were carried out in a glovebox containment unit to prevent the spread of alpha contamination associated with handling Pu materials. After a sample vessel was filled and mounted on the test stand, thermocouples were installed. When test conditions required elevated temperatures, a band heater and insulation were added. The temperature controllers used were on-off devices and maintained the temperature in about a 10°C window above the 90°C set point. Pressure and temperature measurements were displayed and logged during the nominal seven-day test period using a LabVIEW™ based computer program. Figure 2 provides an example of the data logged for each test. Sampling the vessel gas mixture and measuring the test stand volume concluded each test.

Figure 2 – Sample Pressure and Temperature Profile for Gas Generation Testing

Gas samples were collected by first evacuating the common manifold using a vacuum pump, then opening the valve of a selected test position to expand the gas generated during testing into the evacuated manifold. A portion of the test gas was then removed from the manifold using gas-tight syringes. This sample gas was pulled through two 0.05 μ M filters that were located in the sample line to remove any potential radioactive particulate materials. Gas Chromatography (GC) was used to measure the H₂ and O₂ concentration in each sample⁷. Gas generation rates were subsequently calculated based on the measured gas concentrations, container volumes, temperatures, pressures, elapsed times.

Additional information on the sample and surrogate materials was required to support gas generation testing. This required measuring isotopic composition and moisture content of the test materials. Many of the samples were measured for moisture content using thermogravimetric analysis (TGA) following a protocol similar to the procedure used by RFETS. Isotopic composition was measured on a small subset of samples. Additional information on the analytical measurements used to characterize the test materials will be provided later in this report.

Samples and Surrogate Materials Used for GGTP

There were two challenges that had to be addressed when selecting representative materials for gas generation testing of RFETS SS&C. The first required selection of matrix components that would represent the content of SS&C during transportation and storage. The range of

SS&C compositions is fairly broad as a consequence of variation in the production process and selective sorting of SS&C components prior to storage at RFETS. To understand the potential impact of matrix content on the gas composition and gas generation rate from SS&C residue, surrogate materials were needed that would provide a cross section SS&C contents. The second challenge was to select a PuO_2 representative of the actual RFETS SS&C that could be used to generate surrogate compositions. Each of these issues will be addressed separately beginning with the selection of matrix materials need to develop SS&C surrogates.

Gas generation testing for RFETS SS&C was initially constrained to surrogate materials that were selected based on the SS&C content description provided in the 9975 SARP. Additional data on the variability and composition of RFETS SS&C was also available from flow sheet development efforts.^{8,9,10,11} The contents of RFETS SS&C, based on SRTC measurements as part of flow sheet development, are presented in Table 1.

Table 1 – Content of RFETS SS&C

SS&C Matrix Component	-----Weight Percent-----	
	Low Value	High Value
PuO_2	2	50
CaF_2	20	60
MgO	2	40
CaCO_3	1	7
Ca(OH)_2	1	10
CaO	5	40
Calcium Metal	0	11

The contents and variability of RFETS SS&C is similar to SS&C generated at other Department of Energy Pu processing facilities.¹²

The initial approach selected by the GGTP, described in the Technical Task and QA Plan, required a series of 19 tests to evaluate the accuracy of the analytical radiolysis model. This approach used PuO_2 and mixtures of PuO_2 and SS&C components listed above. This effort was expected to demonstrate that the analytical radiolysis model provided conservative H_2 generation results for a cross section of residue materials, not to bound SS&C contents by testing a large number of material mixtures. A nominal seven-day test period was selected to support rapid evaluation of model predictions and required an estimated minimum of 5 to 10g of PuO_2 . This quantity of PuO_2 was expected to produce sufficient H_2 for GC measurements. A standard ratio of 1:3 (Pu : Matrix) was selected for mixtures of PuO_2 with each SS&C component to prevent having to use container volumes greater than 100cc. Additional tests then were planned to follow-up on data points identified as inconsistent with anticipated material behavior.

Table 2 provides brief descriptions and set-up data for the tests conducted by the SRTC GGTP that are relevant to SS&C contents. Six of the tests were conducted on actual RFETS SS&C samples (test runs 13, 20, 30, 32, 34, and 36). Two of these tests (20 and 36) were done at elevated temperature. Four tests (test runs 17, 44, 50 and 52) were conducted using "Pu Cake," which is a mixture of about 30% PuO_2 and 70% plutonium tetrafluoride (PuF_4). The

Table 2 – SS&C Test Content and Set-up Data

**Run #	Description	Time (days)	Container Volume	*Grams PuO ₂	Bulk Weight(g)	Measured Volume	Temp (degC)
2/20/99 Start – Set 1							
1	PuO ₂ + RF MgO sand & crucible	8.83	25cc	9.59	37.83	34.11	ambient
2	PuO ₂ + calcined CaO + Ca(OH) ₂	8.92	50cc	8.85	35.80	63.86	ambient
3	PuO ₂ Stored over desiccant	9.65	5cc	7.65	7.65	30.50	ambient
4	PuO ₂ stored in 76%RH humidor	9.71	5cc	8.54	8.54	30.90	ambient
5	PuO ₂ ~ 10% H ₂ O added	6.66	5cc	7.57	7.57	29.81	ambient
6	Standard Gas	3.73	50cc	0.00	0.00	62.33	ambient
3/1/99 Start – Set 2							
7	Standard Gas + Heat	6.31	50cc	0.00	0.00	49.71	90
8	#2 stored at 100% RH	6.14	50cc	7.73	31.30	64.10	ambient
9	PuO ₂ + 30g CaF ₂	6.83	50cc	9.83	39.85	62.91	ambient
10	PuO ₂ +Ca(OH) ₂ & MgO Crucible	5.75	25cc	7.90	15.80	43.46	ambient
11	#1 stored at 100%RH	6.12	25cc	9.32	36.76	38.51	ambient
12	PuO ₂ stored at 100%RH	6.82	5cc	9.52	9.52	30.72	ambient
3/8/99 Start – Set 3							
13	44g of RF SS&C sample H6	7.88	50cc	15.50	43.84	51.66	ambient
14	#9 heated	7.88	50cc	9.83	39.85	64.37	90
15	#8 heated	8.16	50cc	7.73	31.30	65.63	90
16	PuO ₂ stored at 100%RH + Heat	7.77	5cc	7.26	7.26	30.78	90
17	Pu Cake	7.61	25cc	32.01	35.66	42.04	ambient
18	#5 mixed with 2g Ca metal	7.56	5cc	4.88	6.93	30.34	ambient
3/17/99 Start– Set 4							
19	CaF ₂ at RT repeat #14 and #9	6.8	50cc	9.83	39.85	52.40	ambient
20	#13 heated	6.8	50cc	15.50	43.84	53.82	90
21	#10 heated	6.81	10cc	7.50	15.00	25.98	90
22	PuO ₂ +MgO 1:1 ratio	6.81	25cc	9.73	19.45	43.03	ambient
23	#11 heated	6.78	10cc	4.66	20.00	31.95	90
24	PuO ₂ + Mg(OH) ₂	6.79	25cc	7.26	17.26	43.83	ambient
3/26/99 Start– Set 5							
25	PuO ₂ + MgO with lo water	10.11	10cc	6.60	25.00	14.43	90
26	PuO ₂ + MgO with med water	9.74	10cc	6.24	23.43	25.67	90
4/6/99 Start– Set 6							
30	RFETS H2	7.69	50cc	8.18	43.10	63.26	ambient
31	PuO ₂ +MgO w/ hi water+heat	8.83	10cc	6.15	23.09	26.22	90C
32	RFETS H7	7.71	100cc	6.77	14.60	91.65	ambient
33	#18 repeated	7.71	10cc	4.65	6.60	38.54	ambient
34	RFETS H8	7.69	10cc	8.49	10.80	38.98	ambient
4/16/99 Start – Set 7							
36	RFETS Sample H2	5.61	50cc	8.18	43.10	61.32	90
37	#31 repeated	5.66	10cc	6.15	23.09	26.49	90
38	PuO ₂ + 5% H ₂ O	5.69	25cc	9.66	10.29	44.90	ambient
4/23/99 Start – Set 8							
41	PuO ₂ +100%RH ~2weeks	5.6	10cc	10.08	10.08	19.25	ambient
44	PuCake - like #17	5.77	100cc	27.65	30.80	123.67	ambient
45	PuO ₂ + 2.5% water	5.77	10cc	12.17	12.50	37.51	ambient
46	PuO ₂ + 2.5% water	5.84	10cc	9.83	10.32	38.12	ambient
4/29/99 Start – Set 9							
47	PuO ₂ +2.5% H ₂ O+Heat	6.77	10cc	12.17	12.50	18.96	90
50	PuCake - replicate1	6.76	100cc	27.34	30.46	122.76	ambient
51	#41 repeated	6.76	10cc	10.08	10.08	18.70	ambient
52	PuCake - replicate #2	6.77	25cc	14.98	16.69	45.15	ambient
5/18/99 Start – Set 10							
53	#51 heated	7.95	10cc	10.08	10.08	18.74	90
54	Blank+Heat	7.95	10cc	0.00	0.00	31.56	90
55	PuO ₂ +130mg H ₂ O	7.95	50cc	12.57	12.70	71.49	ambient
56	PuO ₂ +150mg H ₂ O	7.95	10cc	10.42	10.57	37.50	ambient
5/26/99 Start – Set 11							
57	PuO ₂ +150mg H ₂ O	7.75	10cc	10.42	10.57	18.49	90
58	Blank	8	10cc	0.00	0.00	31.27	ambient
59	PuO ₂ +130mg H ₂ O	7.78	50cc	12.57	12.70	59.55	90

* Test runs 17, 44, 50 and 52 were conducted using "Pu Cake", a mixture of about 30% PuO₂ and 70% PuF₄. The data were adjusted to represent the Pu content in "Pu Cake" as PuO₂.

** Test runs 28, 29, 35, 40, 42, 43, 48, and 49 contained materials that do not conform to the content description of SS&C residue. These test runs were not included in this report.

PuO₂ mass data, presented in Table 2 for the Pu Cake samples, have been adjusted to correct for the change in Pu composition. The Pu Cake was used to investigate the impact of PuF₄ on gas generation rates. SRTC measurements have not found PuF₄ in RFETS SS&C residue samples¹³, but process history suggests PuF₄ could be present.

The second issue that had to be addressed in creating SS&C surrogates was selection of an appropriate source of PuO₂. There are two likely sources of PuO₂ in SS&C. In the first case, the PuO₂ is formed from air oxidization of small Pu metal fragments that did not coalesce during formation of the Pu metal button. The second case includes PuO₂ present in the PuF₄ as an impurity prior to production of Pu metal and PuO₂ created in the initial stages of Pu metal production from hydrolysis of PuF₄. The PuO₂ present in the process prior to metal production was heated to temperatures in excess of 1000°C as part of the production process. Evidence from attempts to dissolve RFETS SS&C suggests that greater than 90% of the PuO₂ present in this SS&C is "high fired."¹³ This is similar to what has been observed for processing SS&C at the Savannah River Site¹⁴.

The surface area of PuO₂ decreases linearly as the material is heated over the range of 50°C to 900°C, and this trend is anticipated to continue for higher processing temperatures. Since the amount of moisture adsorbed by PuO₂ is a function of surface area,^{15, 16} PuO₂ from low temperature corrosion of Pu metal will adsorb more moisture than "high fired" material. The larger surface area PuO₂ can adsorb more moisture and should provide the highest gas generation rates from radiolysis of H₂O. The PuO₂ from corrosion of Pu metal was selected for use in creating SS&C surrogates.

Isotopic Analysis of Test Materials

Isotopic analysis of selected samples was obtained following dissolution of the material in nitric acid. The solutions were analyzed using gamma spectroscopy and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS).¹⁷ These isotopic values were subsequently used as input for the analytical radiolysis model. No impurities were identified in the PuO₂ using x-ray diffraction, and ICP-MS identified only trace metals normally associated with Pu metal production. The isotopic data and associated decay energy are provided based on the gamma ray spectroscopy data in Table 3.

Table 3 – Isotopic Data and Decay Energy for RFETS SS&C and SRS PuO₂

Isotope	Specific Activity	MeV per decay	SRS PuO ₂		RFETS H6	
			mass fraction	eV/day/g Pu	mass fraction	eV/day/g Pu
Pu-238	1.99864E+19	5.49	0.00013	3.91E+19	0.00007	2.10E+19
Pu-239	7.24294E+16	5.1	0.9439	9.55E+20	0.9447	9.56E+20
Pu-240	2.64688E+17	5.16	0.0542	2.03E+20	0.0534	2.00E+20
Pu-241	1.20263E+20	0.0053	0.0016	2.79E+18	0.0016	2.79E+18
Pu-242	4.58677E+15	4.89	0.002	1.23E+17	0.0023	1.41E+17
Am-241	3.99949E+18	5.48	0.00106	6.37E+19	0.00239	1.44E+20
Totals =			1.002890	1.26E+21	1.00446	1.32E+21

Based on the samples analyzed, there is less than 5% difference in the energy output of a representative RFETS sample and the PuO_2 used in SS&C surrogates. This small difference in radiation dose is anticipated based on the isotopic tolerances for "weapons grade" Pu. The worst case isotopic data provided by RFETS suggests the decay energy could be as much as 25% higher than what was found in sample H6 or about 30 % higher than found in the SRS PuO_2 . The reason for this difference in measured and worst case decay energy is the inclusion of 0.5% Pu-238 and a large amount of Am-241 from Pu-241 decay.

Gas Generation Test Standards

Several tests were conducted to confirm the capability to sample and analyze the gas in test vessels accurately. Test runs 6, 7, 54 and 58 were conducted without PuO_2 present in the vessels. Tests 6 and 7 used a 4% H_2 standard in unheated and heated configurations, and tests 54 and 58 used air as an O_2 standard in heated and unheated configurations. The H_2 standard also contained 76% nitrogen and nominally 4% of each of the following gases O_2 , CO_2 , CO, methane and ethane. Tests 6 and 7 demonstrated the ability to analyze for H_2 and confirmed that rapid recombination of H_2 and O_2 was not catalyzed by the sample vessel surfaces. Tests 54 and 58 demonstrated the ability to analyze for O_2 and confirmed the vessel walls are not rapidly oxidized under the test conditions. Test results for these standards are presented in Table 4.

Table 4 – Measurement of Gas Standards from Test Vessels

Run #	Vessel Temperature	H_2 Vol%		O_2 Vol%	
		Standard	Measured	Standard	Measured
6	ambient	4.0	4.2	4.0	3.9
7	90C	4.0	3.7	4.0	3.6
54	90C	0.0	0.0	20.9	20.0
58	ambient	0.0	0.0	20.9	20.5

The concentration of nitrogen gas (N_2) in ambient air is 78.08 vol%. The N_2 concentration results from measurement of these gas standards are found in Table 5, along with GC measurement data for all the SS&C tests. The N_2 values for tests 6 and 7 are larger than expected based on measurement statistics, but the measurements for H_2 and O_2 in the standard are accurate. The N_2 values for tests 54 and 58 are within the anticipated 2 sigma standard deviation of the known value. The error bars for GC concentration data, based on measurement of standards over a 30-day period, at the 95% confidence interval are $\pm 9.4\%$ for H_2 , $\pm 1.5\%$ for O_2 , and $\pm 7.1\%$ for N_2 .⁷

Some consideration has been given to scaling sample results using N_2 as an internal standard. However, the greater degree of statistical uncertainty in the N_2 value and evidence for N_2 being consumed in radiolysis of air has limited efforts to correct data based on N_2 recovery. Argon gas (Ar) is present in air at about 0.93 vol%. The inert nature of Ar suggests that it could be used as an internal standard to correct the GC results for sample recovery. However, the GC

Table 5 – Gas Measurement Data for SS&C Residue Testing

Run #	Sample #	H2 (vol%)	O2 (vol%)	N2 (vol%)	CO2 (vol%)	N2O (vol%)	CO (vol%)	sum (vol%)
2/20/99 Start – Set 1								
1	3-123637	0.55	18.8	84	0	0	0	103.35
2	3-123636	0.00	17.9	84.5	0	0	0	102.40
3	3-123635	0.00	21.1	82.3	0.05	0	0	103.45
4	3-123634	0.00	20.1	82.5	0.16	0	0	102.76
5	3-123633	10.80	22.8	61.7	0.1	0	0	95.40
6	3-123638	4.20	3.9	81.6	1.8	0.5	1.2	93.20
3/1/99 Start – Set 2								
7	3-123639	3.70	3.6	87	NR	NR	4.06	98.36
8	3-123640	0.05	19.6	86	0.1	0	0	105.75
9	3-123641	0.08	20.2	85.1	0.09	0.02	0	105.49
10	3-123642	0.62	20.2	83.8	0.06	0	0	104.68
11	3-123643	0.26	19.7	88.1	0.05	0.04	4.28	112.43
12	3-123644	0.54	20	84.8	0.12	0.12	0	105.58
3/8/99 Start – Set 3								
13	3-123645	6.19	3.1	90.8	0.03	1.6	0	101.72
14	3-123646	0.89	16.7	80	5.2	0.25	0	103.04
15	3-123647	0.00	11.7	82.6	0	0	0	94.30
16	3-123648	0.22	15.5	78.2	0.48	0.04	0	94.44
17	3-123649	1.64	20.6	79.6	0.06	0.05	0	101.95
18	3-123650	24.15	15.5	53.1	0.03	0	0	92.78
3/17/99 Start – Set 4								
19	3-123651	0.00	18.2	83.8	0.37	0.08	0	102.45
20	3-123652	80.00	0	23.6	0	0	0	103.60
21	3-123653	2.60	6	95.6	0.16	0.2	0	104.56
22	3-123654	0.13	15.4	86.3	0.09	0.11	0	102.03
23	3-123655	1.60	11.9	88.6	0.22	0.17	0	102.49
24	3-123656	5.00	19.7	76.6	0.03	0.09	0	101.42
3/26/99 Start – Set 5								
25	3-123658	2.17	12.6	82.7	<1	<1	<1	97.47
26	3-123659	1.19	16.2	79.4	<1	<1	<1	96.79
4/6/99 Start – Set 6								
30	3-125514	1.27	16.5	75.8	<1	<1	<1	93.57
31	3-125515	0.03	20.5	76	<1	<1	<1	96.53
32	3-125516	8.13	12.9	78.5	<1	<1	<1	99.53
33	3-125517	1.6	20.2	76.4	<1	<1	<1	98.20
34	3-125518	0.2	20.2	76.9	<1	<1	<1	97.30
4/16/99 Start – Set 7								
36	3-125520	74.70	1.3	17.9	0.02	<1	<1	93.92
37	3-125521	0.40	20	64.2	0.03	0.02	<1	84.65
38	3-125522	7.40	14.1	77.7	0.08	0.04	<1	99.32
4/23/99 Start – Set 8								
41	3-125525	0.7	19.9	81.2	NR	NR	<0.1	101.80
44	3-125528	0.2	18.6	82.4	0.32	<0.1	<0.1	101.52
45	3-125529	2.3	21	76.8	<0.1	<0.1	<0.1	100.10
46**	3-125530	1.2	21.1	62.1	<0.1	<0.1	<0.1	84.40
4/29/99 Start – Set 9								
47	3-125531	3.4	7.3	81.8	<0.1	<0.1	<0.1	92.50
50	3-125534	0.4	18.9	79.2	<0.1	<0.1	<0.1	98.50
51	3-125535	1.5	19.9	73.4	<0.1	<0.1	<0.1	94.80
52**	3-125536	0.55	20.14	78.36	<0.1	0.05	<0.1	99.10
5/18/99 Start – Set 10								
53	3-127169	1.32	13	85	<0.1	<0.1	<0.1	99.32
54	3-127170	0	20	74	<0.1	<0.1	<0.1	94.00
55	3-127171	0.36	19	84	<0.1	<0.1	<0.1	103.36
56	3-127172	0.25	20	84	<0.1	<0.1	<0.1	104.25
5/26/99 Start – Set 11								
57	3-127173	1.8	10.1	81.5	<0.1	<0.1	<0.1	93.40
58	3-127174	0	20.5	78.1	<0.1	<0.1	<0.1	98.60
59	3-127175	0.7	16.2	81.6	2.8	0.31	<0.1	101.61

**Measurement problems during GC analysis noted for test runs 46 and 52.

uses Ar as a carrier gas, which prevents it from being measured in the samples. Samples noted to have measurement recovery problems during GC analysis include test runs 46 and 52. The largest source of sample recovery problems stemmed from having insufficient sample volume for some of the tests.

Gas Generation Rate Calculations

The results from GC measurements are expressed as volume percent (vol%). Because the gas volume, pressure and temperature of each sample vessel were different, the vol% measurement was converted to micromoles (μmol) of gas to support comparison between tests. Using PVT measurements, the volume of each vessel and test stand volume was measured by expanding gas from a calibrated volume. For tests at elevated temperature, this measurement was made before and after the vessel had returned to ambient temperature. The PVT data from the end of each test run were used to calculate the total μmol s of gas in the system using the ideal gas law. Because the heated containers are not at uniform temperature, the average temperature for the gas is calculated based on the difference in system volume at ambient and elevated temperature.

The μmol s of H_2 in a selected test vessel were calculated as the product of measured vol% H_2 and the calculated total μmol s of gas in the vessel and associated test stand. These calculations have been completed using a spreadsheet format and were expanded to include changes in the μmol s of O_2 present in the system. For O_2 the only change from the above procedure required taking into account the initial μmol s of O_2 in the system. The above calculation was done twice using initial and final O_2 concentrations. The first time used the initial pressure, initial temperature, constant volume and the reference value of 20.946% vol% O_2 in air.¹⁸ The second calculation is for the end of test conditions and uses final pressure, final temperature, constant volume and the measured value for vol% O_2 . The final result is expressed as delta O_2 and is calculated as the difference between end and initial moles of O_2 . These calculations are presented in Table 6.

Chemical Reactions in SS&C Surrogate Materials and Residue Samples

The potential of chemical reactions in SS&C residues is important to transportation and storage safety because these reactions generate heat, pressure and potentially flammable mixtures of gases. The elevated temperatures possible during transportation of Pu residue materials could be a contributing factor to initiation of acceleration of potential chemical reactions. Calcium metal was used as a reductant in the production of Pu metal at RFETS, and a fraction of the unreacted calcium metal remains in the SS&C residue. The amount of calcium metal present in SS&C has been estimated by measuring the volume of gas produced when SS&C residue was allowed to react with water. These water reactivity tests to determine reactive metal content of RFETS SS&C have been done both at SRS and RFETS.^{19, 20} The amount of calcium remaining was estimated to be as high as 11% in some samples.

Table 6 – Spreadsheet Calculation of Initial and Final Gas Compositions

Run #	Volume (cc)	initial P (torr)	initial t (deg K)	start gas (umols)	start O2 (umols)	Final P (torr)	Final t (deg K)	end gas (umols)	H2 (vol%)	O2 (vol%)	end H2 (umols)	end O2 (umols)	delta O2 (umols)
2/20/99 Start – Set 1													
1	34.1	752.2	296.6	1388.0	290.7	743.2	295.7	1375.5	0.6	18.8	7.6	258.6	-32.1
2	63.9	741.9	294.7	2579.5	540.3	711.8	297.2	2454.0	0.0	17.9	0.0	439.3	-101.0
3	30.5	740.9	296.6	1222.4	256.1	741.3	295.9	1226.0	0.0	21.1	0.0	258.7	2.6
4	30.9	748.3	298.5	1242.9	260.3	751.5	295.4	1261.3	0.0	20.1	0.0	253.5	-6.8
5	29.8	755.5	297.3	1215.5	254.6	891.3	295.5	1442.7	10.8	22.8	155.8	328.9	74.3
6	62.3	775.7	295.5	2625.3	549.9	774.7	294.5	2630.8	4.2	3.9	110.5	102.6	N/A
3/1/99 Start – Set 2													
7	49.7	649.4	296.2	1748.7	366.3	808.1	331.0	1947.4	3.7	3.6	72.1	70.1	N/A
8	64.1	750.2	295.6	2610.2	546.7	735.1	295.7	2556.8	0.1	19.6	1.3	501.1	-45.6
9	62.9	734.5	299.1	2478.8	519.2	733.3	298.2	2482.2	0.1	20.2	2.0	501.4	-17.8
10	43.5	746.5	298.5	1743.9	365.3	746.5	295.8	1759.8	0.6	20.2	10.9	355.5	-9.8
11	38.5	755.7	296.4	1575.4	330.0	749.7	295.9	1565.5	0.3	19.7	4.1	308.4	-21.6
12	30.7	756.6	297.5	1253.5	262.6	753.7	296.1	1254.6	0.5	20.0	6.8	250.9	-11.6
3/8/99 Start – Set 3													
13	51.7	762.3	302.1	2091.6	438.1	655.9	295.9	1837.3	6.2	3.1	113.7	57.0	-381.1
14	64.4	765.1	296.3	2666.9	558.6	975.2	329.5	3057.0	0.9	16.7	27.2	510.5	-48.1
15	65.6	754.1	299.6	2650.5	555.2	806.3	327.6	2591.6	0.0	11.7	0.0	303.2	-252.0
16	30.8	760.2	296.1	1267.9	265.6	753.2	314.3	1183.7	0.2	15.5	2.6	183.5	-82.1
17	42.0	762.2	298.0	1725.3	361.4	779.1	297.2	1768.3	1.6	20.6	29.0	364.3	2.9
18	30.3	760.0	298.0	1241.5	260.0	1179.8	296.4	1937.7	24.2	15.5	468.0	300.3	40.3
3/17/99 Start – Set 4													
19	52.4	751.7	298.4	2118.0	443.6	744.5	297.4	2104.7	0.0	18.2	0.0	383.1	-60.6
20	53.8	753.4	297.6	2186.1	457.9	1178.3	321.3	3166.9	80.0	0.0	2533.5	0.0	-457.9
21	26.0	744.0	298.4	1039.3	217.7	803.2	323.0	1036.6	2.6	6.0	27.0	62.2	-155.5
22	43.0	749.4	298.3	1734.5	363.3	742.1	298.0	1719.3	0.1	15.4	2.2	264.8	-98.5
23	32.0	758.2	299.0	1299.9	272.3	806.3	307.8	1342.9	1.6	11.9	21.5	159.8	-112.5
24	43.8	764.4	298.1	1803.3	377.7	764.3	297.8	1804.9	5.0	19.7	90.2	355.6	-22.2
3/26/99 Start – Set 5													
25	14.4	749.5	295.9	586.5	122.8	800.2	324.7	570.5	2.2	12.6	12.4	71.9	-50.9
26	25.7	752.6	296.2	1046.5	219.2	789.2	317.1	1025.2	1.2	16.2	12.2	166.1	-53.1
4/6/99 Start – Set 6													
30	63.3	755.8	297.8	2576.0	539.6	724.6	297.6	2471.3	1.3	16.5	31.4	407.8	-131.8
31	26.2	733.8	369.5	835.5	175.0	738.8	367.5	845.7	0.0	20.5	0.3	173.4	-1.6
32	91.7	753.9	297.5	3726.5	780.5	772.2	296.9	3824.6	8.1	12.9	310.9	493.4	-287.2
33	38.5	760.0	298.8	1572.9	329.5	751.8	296.8	1566.4	1.6	20.2	25.1	316.4	-13.0
34	39.0	768.9	298.9	1608.9	337.0	760.5	296.9	1602.0	0.2	20.2	3.2	323.6	-13.4
4/16/99 Start – Set 7													
36	61.3	748.5	297.9	2472.1	517.8	3843.2	324.5	11652.5	74.7	1.3	8704.4	151.5	-366.3
37	26.5	741.6	297.4	1059.9	222.0	813.1	316.1	1093.3	0.4	20.0	4.4	218.7	-3.3
38	44.9	744.9	297.4	1804.4	378.0	802.2	297.9	1940.0	7.4	14.1	143.6	273.5	-104.4
4/23/99 Start – Set 8													
41	19.3	750.0	298.2	776.9	162.7	742.3	296.4	773.6	0.7	19.9	5.4	153.9	-8.8
44	123.7	750.5	300.6	4954.2	1037.7	722.7	297.4	4822.0	0.2	18.6	9.6	896.9	-140.8
45	37.5	756.9	298.5	1526.0	319.6	782.5	297.4	1583.5	2.3	21.0	36.4	332.5	12.9
46	38.1	763.9	298.9	1563.3	327.4	788.3	296.9	1624.1	1.2	21.1	19.5	342.7	15.2
4/29/99 Start – Set 9													
47	19.0	749.7	297.9	765.4	160.3	1197.3	370.0	984.2	3.4	7.3	33.5	71.8	-88.5
50	122.8	748.8	298.2	4945.9	1036.0	736.0	298.4	4858.1	0.4	18.9	19.4	918.2	-117.8
51	18.7	755.7	298.1	762.3	159.7	753.4	298.1	759.9	1.5	19.9	11.4	151.2	-8.4
52	45.1	762.5	298.8	1848.5	387.2	747.9	298.4	1815.5	0.6	20.1	10.0	365.6	-21.5
5/18/99 Start – Set 10													
53	18.7	754.9	297.6	762.7	159.8	872.6	338.2	775.8	1.3	13.0	10.2	100.9	-58.9
54	31.6	754.7	298.1	1282.2	268.6	775.2	315.6	1244.0	0.0	20.0	0.0	248.8	-19.8
55	71.5	743.3	298.4	2857.4	598.5	744.9	298.1	2866.5	0.4	19.0	10.3	544.6	-53.9
56	37.5	759.8	298.4	1532.1	320.9	774.6	297.5	1566.7	0.3	20.0	3.9	313.3	-7.6
5/26/99 Start – Set 11													
57	18.5	774.9	298.3	770.7	161.4	1048.9	300.6	1035.1	1.8	10.1	18.6	104.5	-56.9
58	31.3	750.4	298.5	1261.3	264.2	750.3	299.3	1257.8	0.0	20.5	0.0	257.8	-6.4
59	59.6	742.4	298.2	2378.8	498.3	1019.0	322.6	3018.4	0.7	16.2	21.1	489.0	-9.3

Test run number 18 contained a sample of SS&C surrogate created by mixing moist PuO_2 (from test #5 and #12) and small pieces of calcium metal. Test 18 showed a rapid pressure rise at ambient temperature immediately upon sealing the sample vessel. Results indicate that the pressure increase is primarily due to H_2 probably from the reaction of calcium metal with H_2O . It was recognized that this test with freshly cut calcium metal was not representative of RFETS SS&C conditions. The test sample was re-measured after several weeks and the gas generation rate was much smaller. However, these test results provided an indication of the pressure increase that should be anticipated with a reaction of calcium metal in SS&C residue.

Figures 3 and 4 show the pressure data for a RFETS sample with and without heating (Tests 30 and 36 respectively). When heated to 90°C this sample, which had demonstrated a pressure decrease at ambient temperature, rapidly increased in pressure. Analysis of the gas mixture at the end of test 36 showed an elevated H_2 concentration, similar to test run number 18. The initial pressure rise observed for test run 36 (Figure 4) is approximately 100 times greater than expected for radiolysis of water. During days 2 – 7 of test run 36, the pressure increase is still more than 10 times what is expected for radiolysis of water. The most probable cause for the observed H_2 production in test 36 is the reaction of calcium metal with water vapor.

Even though the calcium metal content of SS&C was expected to have a heavily oxidized surface and react slowly at ambient temperature in room air, the transport conditions for SS&C residues may cause the calcium to react with adsorbed moisture in the sealed container. The subsequent pressure rise and H_2 generation rate is far greater than what is predicted for radiolysis of adsorbed moisture. Furthermore, chemical reactions that produce H_2 are not considered as part of the analytical radiolysis model.

Figure 3 – RFETS Sample Test Run 30 at Ambient Temperature

Figure 4 – RFETS Sample Test Run 36 at Elevated Temperature

Section III – Gas Generation Modeling

Description of the Analytical Radiolysis Model

The analytical radiolysis model developed by N.M. Askew,⁴ as an adaptation of earlier work by M.L. Hyder,²⁰ uses a spreadsheet format to calculate the rates of H₂ and O₂ formation from the radiolysis of water. The key assumptions documented by Askew in describing this model are given below:

- All materials are finely divided and homogeneously mixed so the effects of self-shielding are neglected
- Gas phase recombination was neglected
- The effect of the substrate on radiolysis was neglected
- A G-value of 1.6 molecules per 100eV was used for H₂ formation
- Oxygen is generated at half of the H₂ molar generation rate

The model calculates gas production rates by first estimating the amount of energy deposited into the water, assuming that radiation absorbed by other materials, such as the matrix components, does not lead to gas production. The estimated amount of energy absorbed by the residue is based upon the energy released by decay of radioactive materials present. The relative stopping power (SP) of each matrix component determines the energy absorbed by that component. The range of stopping powers for non-radioactive components in SS&C residue is very small, so the stopping power of MgO was used to represent the bulk matrix. The ratio of water stopping power to matrix stopping power is then used to determine the effective dose absorbed by water. The G-value, or molecules per 100 electron volts (eV), is then applied to compute the H₂ generation rate. The equation for H₂ generation rate could be represented:

$$\text{H}_2 \text{ Generation Rate} = F * E * G * C$$

Where:

$$F = \text{SP}_{\text{H}_2\text{O}} * \text{mass}_{\text{H}_2\text{O}} / \Sigma (\text{SP}_{\text{matrix}} * \text{mass}_{\text{matrix}})$$

E = total decay energy rate in eV/day

G = G-value for H₂ production or G(H₂)

C = Constant used for unit conversions

The analytical radiolysis model includes a term to correct for decreasing water content as a result of radiolysis.

Predictions of H₂ Generation Rate using the Analytical Radiolysis Model

To compare observed H₂ generation rates with output from the analytical radiolysis model, the data are expressed as $\mu\text{mol/g PuO}_2/\text{day}$. This comparison is provided in Table 7 for several samples that cover a range of matrix contents, and moisture and temperature conditions. The weight loss of the sample at 210° C is used as the moisture input to the model. The model does not accurately predict the gas generation rate observed experimentally when using this weight loss value as an estimate of moisture content. Run number 10 shows that weight gains

can occur for materials that adsorb gas or react with air at elevated temperature. This is a problem associated with using this technique to estimate moisture content.

Table 7 – Comparison of Model Predictions with Measured H₂ Generation Rates

Run #	Model Prediction ($\mu\text{mol H}_2/\text{g Pu/day}$)	Measured Rate ($\mu\text{mol H}_2/\text{g Pu/day}$)	Surrogate Content PuO ₂ plus matrix:	%Wt Loss @ 210 deg C
10	0.00	0.27	CaO + MgO	-0.33
11	0.06	0.08	MgO	0.11
14	0.07	0.40	CaF ₂ @ 90 deg C	0.30
21	0.39	0.70	Ca(OH) ₂ + MgO	0.33
22	0.25	0.04	MgO	0.29
23	0.06	0.78	MgO @ 90 deg C	0.11
24	0.31	2.09	Mg(OH) ₂	0.65

Limitations of Modeling H₂ Generation

Two principal limitations have been identified for the analytical radiolysis model when used for SS&C residue materials. The first is the inaccuracy associated with using a G-value for bulk liquid water for moisture adsorbed on a matrix. The model assumes that the radiation dose absorbed by the SS&C matrix does not result in H₂ production and there is no energy transfer. But some materials like SiO₂ and MgO are observed to promote energy transfer to adsorbed species on the material surface.^{21,22} For these materials that support energy transfer, the G-value can be 10 to 100 times the G-value associated with radiolysis of homogeneous materials like an aqueous solution. G-values that reflect H₂ generation rates in the presence of matrix materials are necessary to fully correct for the energy transfer phenomena. These G-values could be used, based on bounding estimates of residue content, to more accurately predict H₂ generation rate.

Samples 22 and 23 contain MgO at ambient temperature and 90°C respectively. For the sample at ambient temperature, the measured H₂ generation rate is less than predicted by the analytical radiolysis model. In test run 23 the sample has a lower weight moisture content than sample 22, but the measured H₂ generation rate is a factor of 13 greater than the model result. The variation in H₂ generation rate that may result from the temperature difference between these samples is not understood. One possibility is the formation of Mg(OH)₂ at elevated temperature. Test run 24 showed a H₂ generation rate about 7 times larger than predicted by the analytical radiolysis model.

The second limitation identified for the analytical radiolysis model is the inaccuracy associated with estimating moisture based on weight loss measurements at 210°C. An extreme example of this problem is found in Table 7. Run number 10 generated H₂ although the weight loss measurement at 210°C shows a weight gain. This type of weight gain was observed with numerous samples known to contain CaO or Ca(OH)₂. The weight gain was attributed to the reactions of calcium metal with air or water and the reactions of CaO with H₂O to form Ca(OH)₂ or Ca(OH)₂ with CO₂ to form CaCO₃.²⁷ A more detailed evaluation of moisture adsorption and weight loss measurements is provided in the following sections.

Section IV – SS&C Moisture Content

RFETS has characterized much of the SS&C residues for moisture content using the 210°C weight loss measurement. A similar analysis was setup at SRTC to determine the utility of the analytical radiolysis model using weight loss measurements at 210°C as the moisture input.²³ The use of a 210°C weight loss method has been continued in an attempt to achieve maximum benefit from the existing RFETS data. This section discusses the factors that influence moisture adsorption in SS&C residues and shows the effect of moisture content on the H₂ generation rate. Use of the 210°C weight loss method is sufficient to determine physically adsorbed moisture and can be used as an indicator of the gas composition for SS&C residues.

Moisture Measurements based on Weight Loss

One of the most frequently used laboratory techniques for measuring the moisture content of a solid is based on weight loss after drying. Weight loss measurements are made frequently by weighing a sample, heating the sample to remove adsorbed moisture, and then weighing the dried sample. The moisture content is calculated as the difference between initial and final weights and reported as a percentage of sample mass. Selection of the proper drying temperature, to determine moisture content of a material by the weight loss method, requires specific understanding of the materials' weight loss properties. The weight loss properties of a material are determined using Thermogravimetric Analysis (TGA) to measure weight loss as a function of time and temperature. The TGA data are used to select the proper drying temperature for a simple weight loss determination of moisture. Weight loss measurements are not specific for H₂O and subsequently report any volatile compound as moisture content.

Based on TGA data for SS&C residues over a temperature range of 30 to 900°C, it is evident that the SS&C components continue to lose weight above 210°C. The primary components of SS&C are MgO, Ca metal, CaF₂, CaO, Ca(OH)₂, CaCO₃, Pu metal, PuO₂, and a possible trace of Mg(OH)₂. In the case of Ca(OH)₂ and Mg(OH)₂, these compounds begin to decompose and lose H₂O around 400°C. For PuO₂ the weight loss appears to be nearly continuous as temperature increases. For samples of PuO₂ containing less than 2% H₂O, about half of the adsorbed water is removed at 210°C.²⁴ Figures 5 through 7 show the TGA plots for some materials found in SS&C residue. Figure 8 is the TGA data for an actual SS&C sample.

Weight loss measurements at 210°C estimate moisture content based on the assumption that weight loss is caused by desorption of H₂O. The weight loss measurement at RFETS used an automated weight loss balance with a sample size of about 5 grams (g). The TGA analysis uses about 0.020g of sample. Both systems were set-up to heat the sample at 210°C until the sample weight was constant. The TGA accomplished this by holding the sample at 210°C for 30 minutes. The weight loss balance at RFETS was set to stop heating once the weight loss achieved a slope of less than 0.05%. In cases where the sample contains calcium or plutonium metals that react with air to form the heavier oxides, the weight loss measurement is offset by potential weight gains. Other sources of error in this type measurement include chemical reactions that increase the sample weight, such as conversion of Ca(OH)₂ to CaCO₃, and problems caused by sample handling. When samples have equilibrated to adsorb moisture in a

Figure 5 – TGA Plot of PuO_2 Figure 6 – TGA Plot of Ca(OH)_2

Figure 7 – TGA Plot of $\text{Mg}(\text{OH})_2$

Figure 8 – TGA Plot of RFETS Sample H2

high humidity environment, storing the samples in a dry environment prior to the weight loss measurements may cause the samples to lose a fraction of the adsorbed moisture. Thus the actual moisture content would be underestimated. The opposite is possible if "dry" samples are stored in a humid environment prior to analysis. Adsorbed moisture is defined as the quantity of H_2O that has condensed on a solid surface and has not penetrated within the solid.

It is evident that additional information about the chemical composition of SS&C can be obtained from Figures 5-8. The RFETS sample shown in Figure 8, for example, contains $\text{Ca}(\text{OH})_2$ and CaCO_3 based on the TGA curve and the transition temperatures for decomposition of these species. The presence of CaCO_3 and $\text{Ca}(\text{OH})_2$ have been confirmed using x-ray diffraction measurements. Based on measurement of the weight change at each transition, a quantitative analysis of the species could be accomplished. The error associated with the SRTC TGA weight loss measurements has been estimated by looking at the reproducibility of measurements on a reagent grade surrogate. The relative standard deviation of this measurement is $\pm 3.2\%$ at the 95% confidence interval. For actual SS&C and surrogate materials, the difficulty associated with obtaining a representative sample would add to the measurement uncertainty. Obtaining representative samples can be difficult because the dense PuO_2 tends to settle to the bottom of a container. Accurate sampling is also hindered by materials at the surface of a filled storage container adsorbing moisture more rapidly than materials at the center of the container. The impact of these effects on moisture analysis methods for SS&C residues has not been evaluated.

Adsorption of Moisture on PuO_2

As part of the efforts associated with testing the analytical radiolysis model, various components of the SS&C residue were exposed to high humidity environments to monitor the adsorption of moisture. PuO_2 was found to adsorb a significant quantity of H_2O . The PuO_2 used for these tests was obtained from the air oxidation of Pu metal buttons and has never been intentionally heated above approximately 110°C . Thermal calculations on storage conditions of the Pu metal suggest the PuO_2 may have been heated to about 170°F ($\sim 77^\circ\text{C}$) during storage.²⁵ Based on literature reports, this oxide should have a surface area of about $7 \text{ m}^2/\text{g}$, which would decrease in nearly a straight line fashion to about $2 \text{ m}^2/\text{g}$ on heating to 900°C .¹² Because the PuO_2 used in these tests has a higher surface area than PuO_2 anticipated to be in SS&C, the moisture content of this material will be higher and provide conservative estimates of moisture adsorption. Increasing moisture content is expected to provide a conservative estimate of gas generated from radiolysis.

Figure 9 shows the weight gained by PuO_2 from adsorption of moisture in humid atmospheres over an extended period of time. This PuO_2 was originally generated by air oxidation of plutonium metal. The 100% humidity environment was produced by filling the bottom of a standard glass desiccator with water, and samples containing about 10g of PuO_2 were stored in a beaker in the upper section of the desiccator. The 76% constant humidity was created by keeping an excess of sodium acetate in contact with a saturated solution of sodium acetate.²⁶ The initial weight loss at 210°C for the samples of PuO_2 , before exposure to elevated humidity, was about 0.6%, and the total weight loss by this sample at 900°C was about 1.6%.

Figure 9 – Weight Gain of PuO_2 in Humid Environments

Figure 9 plots the percent weight gained for the samples stored in 76% and 100% humidity environments. A similar sample of PuO_2 (not shown in Figure 9) was maintained in the 100% humidity environment for about two weeks and showed an average weight loss at 210°C of approximately 2.3%. The difference between these results suggests the estimate of starting moisture content for Figure 9 may be low.

Adsorption of Moisture on SS&C Residue Components

Moisture adsorption tests were also conducted on SS&C residue components including MgO (both sand and crucible), CaF_2 , and CaO . The CaO and CaF_2 are reagent grade laboratory chemicals and the MgO components were obtained from RFETS. The test was conducted by first drying the materials to constant weight using a muffle furnace at 800°C . No appreciable weight loss was observed during the drying step except for the CaO sample. The samples were placed in constant humidity storage as described above for about 100 hours. Humidity levels of 100%, 76%, and 52% were used along with a desiccator containing CaSO_4 desiccant. The 52% humidity level was achieved using magnesium nitrate as described above for the 76% humidity environment.

These tests showed that CaF_2 and MgO adsorb less than 0.1% moisture over the course of 100 hours even at 100% relative humidity. Although MgO with a very low density can adsorb H_2O and CO_2 , the sand and crucible in this application are refractory materials with a high density that do not readily adsorb significant quantities of H_2O or CO_2 .²⁷ The CaO sample demonstrated that it is a far better desiccant than even CaSO_4 and was able to readily adsorb moisture under "dry" conditions. The moisture adsorbed by CaO is chemically reacted to form

Ca(OH)_2 . Calcium metal was not tested under these conditions but is known to form a protective layer of calcium oxide which breaks down in the presence of humid air to allow additional formation of CaO and Ca(OH)_2 .²⁸

Each of the primary non-radioactive components of SS&C has been shown either not to adsorb appreciable amounts of moisture or to adsorb moisture that can not be recovered at 210°C . One exception to this statement is Ca(OH)_2 formed from oxidation of calcium metal. The adsorption of moisture on Ca(OH)_2 was evaluated and shown to be on the order of 2% from air at uncontrolled humidity levels.²⁹ The moisture content of reagent grade Ca(OH)_2 , from this same set of tests, was limited to about 1% under similar conditions. Based on these observations, the weight loss at 210°C for SS&C residue is expected to provide primarily information on the moisture adsorbed by PuO_2 and Ca(OH)_2 . Heating Ca(OH)_2 to 210°C does not remove H_2O to form CaO , but simply removes the adsorbed moisture.

Moisture Measurement Data for Actual Samples of SS&C

For actual SS&C samples, some of the PuO_2 is expected to have been heated above 1000°C and will have a smaller surface area than the PuO_2 used for these tests. So, the PuO_2 in actual SS&C should adsorb less moisture from the storage environment than described by the SRTC studies. Calcium hydroxide is not initially present in SS&C residues, but is formed as excess calcium metal is oxidized to CaO , which then reacts with water to form Ca(OH)_2 . Calcium hydroxide can also be formed directly from the reaction of calcium metal with water vapor.²⁸ The other components of SS&C have been shown to physically adsorb only small amounts of moisture. With the foregoing background information on the compounds present in RFETS-SS&C, the limit for moisture adsorption in SS&C should be about 2%, since this is the approximate moisture limit for both PuO_2 and Ca(OH)_2 .

The statistical analysis of moisture determinations, made by RFETS for about 700 cans of SS&C residue, shows a mean weight loss at 210°C of 1.3% ³⁰. The upper bound, at the 95% confidence interval for the moisture content on all SS&C samples in this statistical study, was about 1.9%. This observed upper limit for the actual moisture measurements matches the 2% estimate determined by evaluating weight gain of individual SS&C components. A comparison of TGA data from SRS, with data on the same samples analyzed at RFETS is presented in Table 8. The RFETS measurements used an automated moisture balance to determine moisture content.

Table 8 – Comparison of SRS TGA and RFETS Weight Loss Data

Sample ID	RFETS initial Value	Sister Can Value	TGA Value @ 210°C
H2	0.16	0.29	0.5
H6	1.08	0.44	0.5
H7	0.86	0.3	0.3
H8	1.87	---	0.7

The SS&C materials identified in Table 8 were crushed then sieved through a ¼ inch screen at RFETS prior to packaging in produce cans. The volume of SS&C in the original storage container may require packaging in multiple produce cans after processing. Each of the cans packaged from the original container are called "sister cans." The samples for moisture measurement were originally pulled from only one of the sister cans. As part of the effort to understand the difference between SRS TGA values and RFETS weight loss at 210°C the sister cans from each of the Table 8 samples were analyzed by RFETS where possible.³¹

Samples from the sister cans were only exposed to the ambient air for about one day. Handling of the initial samples at RFETS is uncertain, but may have included storage in the lab for up to 30 days. Exposure of the samples to humid air could explain the observed difference in weight loss values presented in Table 8. The sister can values are much closer to the SRS data than the initial data points. The SRS weight loss values appear conservative with respect to the RFETS measurements with the exception of sample H2. The statistical analysis of the RFETS weight loss measurement may help interpret these results.

Based on statistical analysis of 178 sister cans, the two sigma standard deviation of the RFETS weight loss method is about 0.6%³². The statistical analysis further demonstrated that the SS&C moisture results are normally distributed with an average moisture content of 1.3%. With all SS&C considered to represent a single population, 95% of the RFETS results are within a range of $1.3 \pm 0.6\%$ based on analysis at 210°C.

The RFETS replicate weight loss values for sample H2, from Table 8, are outside the normal statistical distribution for SS&C residues. Based on the composition of sample H2, there is no evident reason for this difference in results. The average difference between RFETS replicate measurements presented in Table 8 is 0.44% moisture, which is consistent with the $\pm 0.6\%$ standard deviation associated with replicate measurements. The SRS TGA values are within the $\pm 0.6\%$ window attributed to normal variation for the RFETS analysis.

Addition of Liquid Water to PuO₂

Several of the gas generation test runs with PuO₂ were designed to help evaluate the effect of elevated moisture content on H₂ generation rate. Weight loss measurements at 210°C measured typically only a fraction of the anticipated moisture content when H₂O was added directly to the test vessel. Table 9 shows the variation between added water and measured values at 210°C.

Table 9 – Comparison of TGA Data with Known Water Addition to PuO₂

Run #	Added H ₂ O Content	Total H ₂ O Content	Wt Loss @ 210°C	Fraction Recovered
5	10%	10.6%	4.5%	42%
38	5%	5.6%	3.3%	59%
47	2.5%	3.1%	1.8%	58%

Water in these instances was added directly to the PuO_2 using a pipette to obtain elevated levels of moisture. The weight of the test vessels was measured before and after H_2O addition to confirm H_2O content of the sample. Plotting the TGA curves for PuO_2 samples, measured as part of the GGTP, shows that any moisture content greater than approximately 1.5% was lost by heating to approximately 60°C and only about 1% moisture remains after heating to 210°C . Several TGA plots for these PuO_2 samples, normalized to the dry PuO_2 mass at 500°C , are shown in Figure 10.

Figure 10 – TGA Plots of Normalized Moisture Content on PuO_2

The fraction of water that is easily removed from PuO_2 could desorb in dry air. An example of how easily excess water can be removed from PuO_2 was observed when storing the PuO_2 for test run 3 in a desiccator containing a CaSO_4 desiccant. The moisture content of this PuO_2 dropped from 0.56% to 0.14% based on weight loss at 210°C . This behavior explains why samples loaded with high percentages of water for test runs like numbers 5, 38 and 45 could have lost water to the environment prior to measurement by TGA.

Published Data for Adsorption of H_2O on PuO_2

Published data^{16, 33} on the adsorption of water vapor show similar results to those obtained by the SRTC efforts. These two publications demonstrate that much of the adsorbed moisture above about 1% is physically adsorbed and can be removed under vacuum without heating. The remaining water is removed in a stepwise fashion that requires heating to remove water that is contained in chemically adsorbed layers. The first chemically adsorbed layer forms by dissociation of the water molecules to form hydroxyl groups on the PuO_2 surface, and the second layer of water molecules is hydrogen bonded to these surface hydroxyls.

These publications show that at 95% humidity, the equilibrium moisture content of low fired PuO_2 was about 3.2%. At 75% humidity, the equilibrium moisture content was about 1.7%. Achieving the equilibrium moisture content required up to eight repeated adsorption and desorption cycles with the moisture content of the PuO_2 increasing after each cycle. These publications also reported that about 0.7% of the adsorbed H_2O will remain on the PuO_2 at 200°C. This is comparable to the 1% found in the SRTC measurements shown in Figure 10. From the literature reports, we can calculate the expected weight loss at 200°C, for a sample of PuO_2 repeatedly exposed to 95% humidity, to be 2.5%. The SRTC sample of PuO_2 stored at 100% humidity for two weeks showed a 2.3% weight loss at 210°C. This sample was not cycled to remove and re-adsorb moisture, which possibly accounts for the 0.2% difference between the SRTC data and the literature reports.

Effect of Moisture and Matrix Content on H_2 Generation

Figure 11 is a plot of H_2 production rate as a function of moisture content on PuO_2 . The curve

Figure 11 – H_2 Generation Rate as a Function of Adsorbed H_2O on PuO_2

added to Figure 11 was done using Microsoft® Excel® and is intended only to help guide the eye, not provide an accurate fit to support data interpolation. The moisture value is from TGA data providing weight loss at 210°C. Similar increases in H₂ generation rate as a function of moisture content have been reported for irradiation of other systems such as zeolite and ion exchange resin.^{34,35,36}

The H₂ generation rate for SS&C surrogate materials as a function of moisture content are plotted in Figure 12. Samples containing calcium metal and PuO₂ with greater than 0.7% weight loss at 210°C are not included. The calcium metal samples are excluded to emphasize the effects of radiolysis. The data for PuO₂ at greater than 0.7% weight loss at 210°C were presented in Figure 11. Figure 12 shows a marked increase with elevated temperature for three of the surrogate materials. The mechanism leading to the increased H₂ production rate is uncertain, but the results indicate that a thermally sensitive reaction to produce H₂ is possible.

Figure 12 – Hydrogen Gas Generation Rate for SS&C Surrogate Materials

Additional Observations on H₂ generation

Several additional interesting observations can be made in review of the H₂ generation data for SS&C residues. Perhaps most relevant to packaging of Pu bearing residue materials is the fact that flammable mixtures of H₂ and O₂ can be present in sealed containers. Such mixtures were observed in test runs 5, 18, 24 and 32. Tests 5, 18 and 24 are surrogate materials while test run 32 was an actual SS&C sample. Because 5% oxygen is considered sufficient to support

combustion³⁷ there is anticipated to be a transition period in many sealed systems where potentially flammable mixtures of H_2 and O_2 are formed.

In many of the tests, O_2 was slowly depleted from the gas phase of these sealed systems by some mechanism (see further discussion in Section VI). Because H_2 generation rate is a function of moisture content and radiation dose, the H_2 concentrations increased fastest with a high moisture content. The potentially flammable mixture of H_2 and O_2 would be present once the H_2 concentration exceeded 4% and remain until the O_2 content is depleted to less than 5%. Because the rate of O_2 depletion in these systems is uncertain, the best way to minimize the time frame, where a flammable mixture of gases may coexist, is to reduce the moisture content of the Pu residue. With the use of produce cans to store Pu residue, this problem is compounded by potential leaks that allow air to enter the container and replenish depleted O_2 or allow H_2 to leak into a secondary container filled with air.

Significant H_2 concentrations have been found both in test vessels that pressurize and those which remain at ambient pressure. So, it is clear from this data set that pressure is not a good indicator of gas composition and facilities should not rely on observation of container pressurization to detect flammable mixtures.

One interesting observation from the GGTP was that mixtures of $Ca(OH)_2$ and PuO_2 had much slower H_2 generation rates than anticipated. Three tests were run with mixtures of PuO_2 and CaO plus $Ca(OH)_2$ and the observed H_2 generation rate was very small when compared with a similar mixture of PuO_2 and $Mg(OH)_2$. This suggests that CaO could be added as a desiccant to Pu residue with elevated moisture content to reduce the H_2 generation rate.

These test results showing formation of flammable H_2 mixtures are substantially different from data in recent reports published by Los Alamos National Laboratory (LANL).^{38,39,40} The LANL reports postulate that H_2 is produced primarily by chemical reaction of adsorbed H_2O on PuO_2 to produce H_2 and the super-stoichiometric oxide, PuO_{2+x} . The recombination of H_2 and O_2 by radiolytic and chemical catalytic mechanisms is reported to be faster than the H_2 production. Based on LANL's observations, less than 2% H_2 would be anticipated to build up in the storage container until all the O_2 is consumed. There are substantial differences in the amount of H_2O and the quality of PuO_2 used by LANL and what is found in SS&C residue materials.

The LANL work was done using PuO_2 processed to meet the 3013 standard.⁴¹ This standard requires heating the PuO_2 at $950^\circ C$ for 2 hours in an oxidizing atmosphere and maintaining the total moisture content at less than 0.5%. The moisture content for many of the 3013 quality PuO_2 materials is less than 0.1%. This suggests that there may be a competing mechanism that changes as a function of moisture content. At low moisture content, surface chemistry is the dominant component of H_2 generation. As moisture content increases, radiolytic gas generation becomes a larger component of the observed gas production.

Section V – Radiolysis Effects In Residue Materials

Brief Presentation of Radiolysis Theory

There are a substantial number of published reports that suggest radiolysis of adsorbed H₂O will not necessarily generate O₂. The primary reason for this is found in reviewing the primary reaction pathways associated with radiolysis of H₂O. The following explanation for the lack of O₂ observed during radiolysis of water in a heterogeneous environment is an excerpt from A.S. Wagh et.al.⁴²

For water, the primary reaction pathways for H₂ generation in the radiolytic decomposition of water are shown below.

O₂ is not a primary radiolytic product, but is generated by secondary reactions of oxygen-containing intermediates and products such as the reaction of perhydroxyl radicals. Significantly less O₂ should be generated relative to H₂ because oxygen-containing transients will react with other ... constituents before they can build high-enough concentrations in solution to form O₂.

In this study, Wagh et al were evaluating the radiation effects on chemically bonded phosphate ceramics. Their work showed that no O₂ was produced in samples containing 5% Pu and H₂O concentrations that ranged from about 1% to 19%. The lack of O₂ production suggests that matrix materials are scavenging the O₂ precursors. Under conditions that allow OH radicals to be produced faster than the matrix scavenges them, intermediates like H₂O₂ and HO₂ are formed that may subsequently react to form O₂.

Other reports have also identified the lack of O₂ production associated with radiolysis of moisture on adsorbed species. These include the work of Nakashima and Aratono³⁶, who studied the gamma radiolysis of water adsorbed on zeolites. They observed that O₂ was produced only at sufficiently high rates of absorbed energy. Bibler, Wallace and Ebra demonstrated O₂ depletion during gamma radiolysis of zeolite with 5% and 16% adsorbed water³⁵. The radiolysis of water on silica gel was studied in the early 1960s at Oak Ridge National Lab. They report no O₂ detected for adsorbed water up to about 16% during gamma radiolysis.⁴³ In studying the alpha radiolysis of moisture in concrete waste forms, Bibler identified that at 7.4% H₂O in cement radiolysis yielded no O₂ and pressure of the storage containers dropped.⁴⁴ He notes that the water used as part of the cement structure is evidently more stable than water driven off by heating at 200°C

Radiolysis of Moist Air

The radiolysis of moist air has been demonstrated in numerous instances to result in the production of N_2O and NO_3^- . The NO_3^- is readily adsorbed on metal oxide surfaces to form up to 10 monolayers²¹. N_2O is present as a non-condensable gas and is readily measured in air systems. Argonne National Laboratory has studied both alpha and gamma radiolysis of moist and dry air systems to support storage of High Level Waste in an underground repository.^{45,46} Reed and Konynenburg provide a review of several reports on radiolysis in moist air systems.^{47,48} Included in this review are data from the following authors. Primak and Fuchs demonstrate the formation of HNO_3 in a moist air system and the subsequent corrosion of nickel wire. Corrosion of the wire continued until water was depleted from the air. Jones used spectroscopic techniques (infrared absorption) to monitor the gas composition of an irradiated gas cell. This effort demonstrated that HNO_3 and O_3 are the major products formed until all the water was consumed. A final study, Tokunaga and Suzuki, suggested that HNO_3 is formed by reaction of OH. This mechanism is proposed to explain the observation in each instance that HNO_3 formation is dependent on the presence of water.

The following excerpt from Reed and Konynenburg provides a good summary of anticipated products from the radiolysis of moist and dry air:

In dry air systems, the primary radiolytic products formed upon irradiation are nitrogen dioxide and nitrous oxide (minor amounts of ozone, nitric oxide and nitrogen pentoxide are also formed). Irradiation in a closed system resulted in the formation of a steady-state concentration of the nitrogen oxides that depended on the dose rate, temperature, total pressure, and initial nitrogen/oxygen ratio....

The addition of water to the dry air system resulted in the formation of nitric acid in place of nitrogen dioxide with nitrous oxide being generated to a lesser extent. Initial rate data indicated that nitrogen dioxide was formed first and subsequently oxidized to nitric acid by reaction with the OH free radical. In high dose experiments, nitric acid was preferentially formed until the water in the gas phase was depleted...

Since O_2 is not produced by radiolysis of water except via very reactive intermediates like OH radicals, the production of oxygen in Pu bearing residue materials should only be anticipated at very high moisture levels and dose rates. Additionally, the radiolysis of air in a residue storage container is expected to result in production of NO_3^- , which is readily absorbed by many metal oxides. Without O_2 being produced from the radiolysis of H_2O , the radiolysis of air should subsequently deplete the O_2 content of a residue storage container.

Los Alamos National Laboratory has recently performed headspace gas analysis on multiple cans of PuO_2 that have been in storage for as long as 18 years³⁸. Each of these cans which had been packaged in air showed extensive oxygen depletion when the can did not leak. Four of the cans were at least 13 years old and had 0.1% O_2 or less. One can was 1 year old and contained 4.9% O_2 . Each of the materials had a moisture content of less than 1.3% moisture

based on interstitial gas analysis. These materials ranged in composition from a mixed uranium-plutonium oxide to reactor grade PuO_2 and included "weapons grade" PuO_2 from RFETS. The loss of O_2 in the headspace of these containers offers external support for the observation that O_2 content is depleted in sealed containers of Pu residue that have sufficiently low moisture content.

Recent efforts to "understand fundamentally the radiolytic processes occurring on metal oxide surfaces," have led the authors of a recent publication⁴⁹ to conclude that, "...one cannot make reliable predictions of the course of radiolytic reactions under nonhomogeneous conditions using yields and rate data acquired in homogeneous systems." Similarly, radiolysis of moisture adsorbed on residue surfaces is a nonhomogeneous condition and should be anticipated to produce quite different results from radiolysis of aqueous solutions.

Other mechanisms for the depletion of O_2 in the sealed system have been proposed. These include oxidation of metal storage container surfaces and adsorption of O_2 on the active sites created by radiation damage to matrix materials. However, the fate of O_2 removed from the air of these sealed systems remains uncertain. Some of the mechanisms anticipated to remove O_2 from the air can be reversed at sufficiently high temperature or produce other gases, such as N_2O , that support combustion of H_2 . Evaluating the entire range of mechanisms for O_2 depletion is beyond the scope of this report, but has been recently addressed by Graham et al.⁵⁰

Section VI – Oxygen Content in SS&C Gas Generation Tests

The O_2 content of residue containers has a big impact on determining the gas pressure for shipping and storage packages. The assumption of simple stoichiometric production of H_2 and O_2 from radiolysis of H_2O would yield only a 33% increase in gas pressure. However, combustion of stoichiometric H_2 and O_2 mixtures at elevated pressures is considered far more dangerous than an equivalent amount of H_2 mixed with air. Oxygen generation is not expected from radiolysis of adsorbed moisture and potential mechanisms for O_2 depletion have been identified. By demonstrating “no net increase” of O_2 for SS&C residues with sufficiently low moisture content, the possibility of stoichiometric H_2 and O_2 mixtures at H_2 concentrations greater than about 30% is eliminated.

Contributors to O_2 Depletion

Several investigators have measured the O_2 content of the headspace gas in sealed containers of PuO_2 and identified reduced O_2 concentrations.^{51,38} SS&C residues show O_2 depletion similar to what has been identified for storage of pure PuO_2 . The mechanism associated with H_2 generation and O_2 consumption may change as a result of increased H_2O content in the containers. The net change in O_2 content of the headspace gas is the sum of reactions that produce and consume O_2 . The design of the current tests does not allow us to determine the relative contribution from forward and reverse reactions. As described earlier, O_2 is not produced directly from radiolysis of H_2O , but results from additional reactions involving OH and OH_2 radicals. If O_2 is not generated by radiolysis of adsorbed H_2O (because the PuO_2 or other materials present in the residue matrix rapidly scavenge OH and OH_2 radicals) any radiation induced or chemical reaction that consumes O_2 will result in O_2 depletion.

To help identify the factors that influence net changes in O_2 content, the available data for O_2 content of the sealed containers in the GGTP are examined and presented in graphical form. These observations include the relationships between O_2 content and H_2 production rate, H_2 concentration, moisture content, dose rate, sample temperature, and matrix content. Each of these relationships or factors seems to have some influence on O_2 content of the vessel. The most evident controlling factor on sample net O_2 content is moisture. If the moisture is limited to about 2.3%, based on weight loss at 210°C, no net increase of O_2 was observed in the vessel headspace. A statistical evaluation of the change in O_2 data was completed and supports the conclusion that no net O_2 is produced when weight loss at 210°C is limited to 2.3%.⁵²

Observations on O_2 Content of SS&C Residues

The change in O_2 content for each sample in the GGTP is presented in Table 6 under the heading of “delta O_2 .” Delta O_2 is calculated as the final minus the initial moles of O_2 . The “Change in O_2 (%)” was calculated as delta O_2 divided by the initial moles of O_2 , then multiplied by 100 to represent the value as percent change. “Change in O_2 (%)” is used in Figures 13 – 17 to show the impact of other measured or calculated parameters on O_2 content from gas generation testing of SS&C residue. In many of the figures, test number is used to identify some of the data points. Based on run number, the reader can find additional information on selected samples using Tables 2, 5, and 6.

Figure 13 shows the change in moles of O_2 for a given test versus the H_2 concentration in the same test. Hydrogen concentrations are plotted on a log scale to allow observation of the full range of concentration values. The GC results for H_2 have been used without any correction for vessel volume. Since the containers have measured gas volumes that range from about 14cc to 124cc, the concentration data does not provide a good indication of how much H_2 has been generated. Note however that O_2 content is not increasing along with H_2 concentrations as would be anticipated for stoichiometric production of O_2 from radiolysis of aqueous solutions. Figure 13 includes all samples in this data set that do not contain calcium metal.

Figure 13 – Change in Oxygen v. Hydrogen Concentration

Also of interest in discussion of flammability issues is the observation that O_2 in these tests was diminished as H_2 concentration approached the lower flammable limit (LFL) of 4% H_2 in air. One clear exception to this observation is test run 5, which generated about 10% H_2 and initially contained about 10% H_2O on PuO_2 . The other tests which have a positive change in O_2 are experiments with PuO_2 containing elevated moisture from the addition of liquid H_2O . No evidence was found for O_2 increasing when samples were simply allowed to adsorb moisture from humidified air. In general, it was noted that samples with matrix content in addition to PuO_2 had a more evident decrease in O_2 content.

Figure 14 demonstrates little correlation between increasing H_2 generation rates and the observed change in O_2 . Hydrogen gas generation rates should be a function of moisture content and dose rate for a particular material type. If the mechanism for O_2 depletion was dependent on the same factors as H_2 generation rate, good correlation between change in O_2 content and H_2 generation rate should be observed. If O_2 is removed from the gas phase by

radiolysis of air, the change in O_2 content should correlate with radiation dose to the air and increase with higher dose rates. However, the actual effect of radiation dose on O_2 depletion mechanism for SS&C residues remains uncertain. Other factors expected to impact the rate of O_2 depletion would include the volume of air irradiated and factors that control rates of NO_3^- being deposited in the matrix. The dose rates to air in these vessels were expected to be nearly constant for the PuO_2 samples because a single source of PuO_2 was used and the material mass in each vessel covered a narrow range. Little change in O_2 content for PuO_2 samples, that were not heated, was seen in Figures 14 and 15. This slow rate for O_2 depletion is consistent with the O_2 depletion observed in long term storage of PuO_2 .

Figure 14 – Change in Oxygen v. Hydrogen Generation Rate

When the PuO_2 was mixed with matrix materials to form the SS&C surrogates, there was a significant impact on the sample bulk density. PuO_2 has the highest bulk density of materials used in these tests. The calcium salts in SS&C have bulk densities on the order of 0.3 to 0.6g/cc. Plutonium dioxide and MgO used in these tests have bulk densities of 1.9 and 1.8 respectively. The PuO_2 that is not mixed with matrix components will irradiate an enclosed volume of air substantially smaller than PuO_2 in SS&C surrogates. On the other hand, adding matrix components will adsorb some portion of the radiation and reduce the exposure to air. These are competing factors that make it difficult to estimate that actual radiation dose absorbed by air.

Based on literature review, the factors identified for O_2 production in the non-homogeneous system are high dose rate and high moisture (physically adsorbed). The radiation dose to adsorbed water would be highest for PuO_2 that is not mixed with additional matrix materials. When matrix materials are present, these absorb part of the radiation dose. PuO_2 has been shown to have more physically adsorbed water than other SS&C components. The water adsorbed by CaO is chemically reacted to form $Ca(OH)_2$, which appears resistant to radiolytic decomposition in the SS&C surrogates. So, the greatest dose to water will occur when PuO_2 is the only matrix component in a sample. The application of literature reports, combined with observations for SS&C residues, suggest that PuO_2 is the matrix most likely to produce O_2 . Evaluating the change in O_2 content as a function of moisture on PuO_2 is expected to provide the most conservative moisture limit for establishing "no net increase" of O_2 from radiolysis of adsorbed moisture.

Selection of a Moisture Limit for "No Net Increase" in O_2

Figure 15 shows the change in O_2 content for the SS&C materials as a function of weight loss at $210^\circ C$. The values that have high weight loss are PuO_2 (# 5 and #38) and one sample (#17) of "Pu Cake". Test 5 is the only sample with 10% moisture, and the only sample that shows a statistically significant increase in O_2 in this data set. Test 45 has a slight increase in O_2 but is within the statistical confidence interval established for air⁵². It should be noted that the sample

Figure 15 – Change in Oxygen v. Moisture Content for SS&C Surrogates

for test 45 was known to have started with greater than 3% moisture (as discussed in Section IV). The weight loss measurement for this sample was made after the sample was used for test 47. Realistic placement of this data point, and others with direct addition of liquid H_2O , would be at a higher moisture content.

Increasing the moisture content of the PuO_2 , represented by weight loss at $210^\circ C$ above 2.3% suggests a change in the gas generation mechanism and the potential for a net increase of O_2 . This transition may have a curve shaped similar to what was presented for H_2 generation rate as a function of moisture content (see Figure 11).

Sample 38 does not fit the general trends observed for O_2 content in Figure 15. For this reason, the result for sample 38 has been discounted in selecting the moisture limit that is acceptable without a net increase in O_2 content. Having additional data to define the shape of this curve for O_2 generation would be helpful. However, after eliminating the data point for test 38, there are duplicate gas generation tests for a sample that has 2.3% moisture. By establishing the moisture limit at 2.3% for "no net increase" in O_2 , SS&C residues with a measured weight loss of less than 2.3% will have a headspace O_2 concentration less than or equal to air.

Statistical analysis of the SS&C surrogate data supports the assertion that "no net oxygen" is produced at less than 2.3% weight loss at $210^\circ C$.⁵¹ The 2.3% value was the highest moisture content achieved for PuO_2 without addition of liquid H_2O to the test vessel. A weight loss of 2.3% is also near the 2.5% upper limit anticipated for water adsorption from 95% humidity in air at ambient temperatures reported in literature. There would seem to be little chance that SS&C residue could exceed this moisture content based on weight loss at $210^\circ C$. The surface area of the PuO_2 is important to drawing this conclusion and should be limited to PuO_2 generated from oxidation of metal or other PuO_2 sources which have a similar low surface area around $7\text{ m}^2/\text{g}$ or less.

Effects of Radiation Exposure, Matrix Content and Temperature on O_2 Content

Figures 16 and 17 are added to support the conclusion that net oxygen content of residue containers will decrease with storage time provided the moisture content is sufficiently low. Figure 16 demonstrates a possible decrease in O_2 content as a function of exposure rate for each of the matrix materials present in SS&C.

The decrease in O_2 is a trend that can be observed in Figure 16 for each matrix component as exposure rate increases. Exposure values are computed as electron volts (eV) per hour, based on the PuO_2 mass and isotopic distribution for each sample. This rate is then divided by the total gas volume of a sealed system to correct for the variations in gas volume and thus the O_2 content of each test stand. The observed decrease in O_2 content as a function of dose rate is consistent with radiation induced mechanisms for O_2 depletion, such as radiolysis of moist air.

Figure 17 shows the impact of various SS&C matrix components on the O_2 content. In addition, the actual SS&C samples measured as part of the GGTP are included in this graph.

Figure 16 – Change in Oxygen v. Dose Rate

Figure 17 – Change in Oxygen v. SS&C Matrix Contents

Other test runs that contain calcium metal (runs 18 and 33) have been excluded from Figure 17. None of the samples that include matrix components had a positive value for change in O₂ content and many had statistically significant decreases in O₂. However there are no evident trends for O₂ content as a function of matrix content or percentage of gross weight.

Table 10 shows the change in O₂ content of eight containers of surrogate SS&C before and after heating. There were no changes in container, sample volume, moisture content, etc., between the heated and unheated tests. Each of the test vessels was removed from the apparatus prior to heating to ensure the sample vessel was re-equilibrated with air. The results shown in Table 10 for heating SS&C residues demonstrate a dramatic change in the O₂ content of the test vessels. Based on these observations, there is apparently a thermal reaction that depletes O₂. The results for test runs 55 and 59 do not show the large decrease in O₂ content found in the other samples. The reason for this difference is not known. On average (including runs 55 and 59), there was 549% or about 5.5 times more O₂ removed from heated vessels than from vessels maintained at ambient temperature.

Table 10 – Effect of Elevated Temperature on O₂ content of SS&C Residue

Sample Description	Run Numbers		O ₂ Content		% Change when heated
	Ambient	Heated(90C)	Ambient	Heated(90C)	
PuO ₂ + CaF ₂	9	14	-18	-48	267%
PuO ₂ + 100% RH	8	15	-45	-252	560%
RFETS H6	13	20	-381	-457	120%
PuO ₂ + Ca(OH) ₂ + MgO	10	21	-10	-155	1550%
PuO ₂ + 100% RH	11	23	-22	-112	509%
PuO ₂ + 100% RH 2 weeks	41/51	53	-9/-8	-59	694%
PuO ₂ + 130mg H ₂ O	55	59	-54	-9	-17%
PuO ₂ + 150mg H ₂ O	56	57	-8	-57	713%
Average					549%

To summarize these observations for change in O₂ content, there have been no factors identified in the gas generation test data, other than moisture content, that cause significant O₂ production. Many of the tests show that species are present that cause O₂ depletion in SS&C residues.

Statistical Evaluation of Oxygen in Gas Generation Tests

A statistical evaluation of the O₂ data⁵² reported in this study has been completed and is provided as Attachment 1. The statistics associated with O₂ data support the assertion that "no net O₂ increase" is produced in test cases if moisture values were maintained below the established 2.3% weight loss limit recommended for SS&C residues.

There are four important parts in the statistical review of O₂ data from the GGTP needed to support transportation and storage of SS&C residues. The first is a propagation of error to determine the normal variation expected from sampling and measuring errors. The second is application of the propagated errors. The propagated errors were used to determine if the change in O₂ content for each sample is statistically different from values determined for measurement of room air. This allowed the tests to be categorized as "O₂ Depleted," "No Difference," or "O₂ Generated." The third aspect of the statistical evaluation was to determine how decreasing the measurement uncertainty impacted the initial categorization of tests. The final aspect of the statistical review was to select samples with 2.3% or less moisture and calculate the level of confidence for "no net increase" in O₂ content.

The propagation of error provides an average uncertainty of 55 μmol in the delta O₂ measurement. This value can be as low as 8.3 μmol after decreasing the estimated uncertainty for each input measurement (volume, temperature, vol% O₂ and pressure) by a factor of 5. The reduced uncertainty increases the number of samples that fell into the category of "increased O₂" from 4 to 7. The initial 4 samples that are suspected of producing O₂ were from test runs 5, 28, 48, and 49. Test 5 was spiked at about 10% moisture and had a weight loss at 210°C of about 4.5%. The Tests 28, 48 and 49 were representative of the fluoride residue and not SS&C. When the input measurement uncertainty used to propagate error was reduced by a factor of two, test run 18 was added to the group of samples which showed "increased O₂." This test had a high moisture level, similar to Test 5, but was not analyzed for weight loss. When the input measurement uncertainty was decreased by a factor of 5, samples 45 and 46 were added to the group of samples that showed "increased O₂." The PuO₂ samples, used for runs 45 and 46, were spiked with 2.5% water by adding an aliquot of water to each test vessel.

Based on our review of gas generation data for samples in the GGTP, an "operational window" was established for SS&C residue materials. This "operational window" is used to exclude tests on matrix components such as NaF that are not expected in RFETS SS&C residue and to limit moisture content to 2.3% based on weight loss at 210°C. After eliminating tests that were outside the "operational window," the statistical evaluation shows there is less than 1 chance in 100,000 that the remaining samples come from a population whose mean change in O₂ is zero or greater. This means that there is a very high probability that on average O₂ is depleted. When input measurement uncertainty is reduced by a factor of 5, as discussed above, about 80% of the test runs are categorized as "O₂ Depleted."

Measurement of Other Gases in the Test Apparatus

GC-MS measurements were made in parallel with the determinations of H_2 , O_2 , and N_2 in each sample. These measurements were performed to provide an indication of other gases that may be present. The typical gases detected included N_2O , CO_2 , and CO . Other gases were not observed in the headspace samples. The N_2O , CO_2 , and CO gases were generally a minor component of the overall gas content. The GC-MS gas measurement data is included in Table 6 along with GC results for H_2 , O_2 and N_2 . The detection limits reported for this measurement were estimated at 0.1 vol%.

There were two tests indicating that CO or CO_2 was generated in significant quantities during the test period. The source of carbon for creating CO or CO_2 is not known, but is assumed to be organic contamination from sample handling in the glovebox. Nitrous oxide (N_2O) is produced from the radiolysis of nitrogen in air. Nitric oxide (NO) and nitrogen dioxide (NO_2) were not detected in the headspace gases. No clear correlation between NO_x concentration and vessel contents was ever identified.

Section VII – Review of Gas Generation Test Program Findings

Conceptual Model for Gas Generation

Review of the technical literature on radiolysis of adsorbed species, gas generation related to PuO_2 storage, radiolysis of solutions, and the SRTC experience from gas generation testing has led to the conceptual model that is illustrated in Figure 18. This model suggests that as the water content of a heterogeneous Pu residue increases, the effects of bulk water and subsequent radiolysis increase while the surface effects decrease. Surface effects as previously noted would include adsorption of OH radicals, chemical decomposition of H_2O , and adsorption of O_2 . The bulk water effects include production of OH and OH_2 radicals in proportion to absorbed dose to yield a positive net O_2 production rate. As the bulk water in the system increases, a greater number of OH and OH_2 radicals produced can exceed the capacity of material surfaces to scavenge the radicals. The radicals can then recombine and lead to O_2 production. In concept, this explains the increased H_2 production rate observed as moisture content of a heterogeneous material increases and the observed threshold value for O_2 generation.

Figure 18 – Conceptual Model for Radiolysis of Adsorbed Species

Summary of GGTP Results for SS&C

Our current understanding of the transportation requirements for shipping Pu residue materials mandates that sufficient data is available for each material type to ensure that gas generation does not compromise package safety. The only means known, to provide the required level of information for gas generation of Pu residues, is laboratory testing to measure the gas generation from residue materials. SRTC established a GGTP to provide measurements for the RFETS SS&C and fluoride residues. The testing competed on SS&C residues used both actual samples and surrogate materials. The results of this test program have been presented in the foregoing sections along with a presentation of pertinent technical literature and potential reaction mechanisms. Several of the test program findings have significant impact on storage and transportation of Pu residue materials. These are enumerated below:

- 1) Hydrogen gas is generated from both chemical and radiation induced reactions in the SS&C residue. The reaction of calcium metal with moisture in SS&C residue produced H_2 much faster than anticipated for radiolysis of H_2O .
- 2) The rate of H_2 generation for adsorbed moisture on Pu residues varies based on the matrix composition. This change in H_2 generation rate may result from energy transfer mechanisms.
- 3) The observed hydrogen generation rate increased with increased moisture contents. This is consistent with observations for radiolysis of adsorbed water in other systems.
- 4) The gas generation analytical model tested was inadequate for predicting H_2 generation rates in SS&C surrogates when using moisture values estimated by weight loss at $210^\circ C$. Moisture analysis, based on weight loss at $210^\circ C$, underestimates the total adsorbed moisture of SS&C residues.
- 5) Oxygen depletion was observed in most of the SS&C surrogate gas generation tests. This observation is consistent with reports in the technical literature for irradiation of adsorbed moisture.
- 6) No net increase in oxygen is observed for SS&C residues when moisture is maintained below 2.3% as indicated by weight loss at $210^\circ C$. The decrease in O_2 content is consistent with headspace gas measurements for long term storage of PuO_2 .
- 7) RFETS SS&C residues exposed to 100% humidity at ambient temperature should not adsorb more than 2.3% moisture as measured by weight loss at $210^\circ C$. This H_2O would subsequently desorb when the SS&C residues are returned to a dry atmosphere.

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**Attachment 1 – A Statistical Review of the Oxygen Data from the Gas
Generation Tests Supporting the Revision of the 9975 SARP (U)**

A STATISTICAL REVIEW OF THE OXYGEN DATA FROM THE GAS GENERATION TESTS SUPPORTING THE REVISION OF THE 9975 SARP (U)

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A STATISTICAL REVIEW OF THE OXYGEN DATA FROM THE GAS GENERATION TESTS SUPPORTING THE REVISION OF THE 9975 SARP (U)

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July 15, 1999

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INTRODUCTION

The Chemical and Hydrogen Technology Section (CHT) of the Savannah River Technology Center (SRTC) has conducted a series of gas generation tests in support of the revision of the safety analysis report for packaging (SARP) for the 9975 container, developed at the Savannah River Site (SRS). The Packaging and Transportation Group of SRTC is coordinating the revision to this SARP. A Task Technical and Quality Assurance Plan directing this work was issued by CHT in February 1999 [1].

Initially, the primary interest in this testing was hydrogen generation. From [1], these gas "generation tests can be tracked in real-time by measuring the pressure of a sealed container of the materials being studied. Because multiple gas phase reactions are produced in the radiation field of the sample, material pressure measurements do not necessarily define the quantity of H_2 generated. However, the change in total molecules of gas can be calculated using the ideal gas law from the pressure measurement, known container volume and sample temperature. A measurement of the actual headspace gases must be completed to calculate the H_2 generation rate for a particular sample."

As the results from these tests were reviewed, however, questions arose regarding the oxygen in the headspace gases. Specifically, do the data from some tests indicate that oxygen was generated for those tests? And do the data for other tests indicate that the oxygen was depleted for them? A statistical analysis of the oxygen data derived from these tests is provided in this report to help answer these questions.

This analysis was conducted using JMP® Version 3.2.2, a commercial software package of the SAS Institute, Inc., in Cary, NC [2].

DISCUSSION

In this section various plots of the oxygen data are reviewed; the tests are grouped into similar types of experiments, which are then studied; measurement and analytical uncertainties are propagated through the equations used to determine the change in oxygen; and finally, the test results are judged for significant O_2 changes based upon their corresponding uncertainties. As part of this final assessment, the results from those tests that are thought to be most representative of the operational window for the 9975 package are summarized.

The data from these tests are provided in Table A1 of the Appendix. A test identifier is provided in the first column of this table. This identifier is used throughout this report to designate specific tests. Table A2 in the Appendix provides additional information for these tests designated using these same test identifying numbers.

As described above for H₂, the determination of interest for O₂ is the change in total O₂ molecules from the beginning to the end of each test in the sample vessel.

This determination is made using the following equation

$$r = n_2 - n_1 = \frac{mP_2V}{RT_2} - \frac{aP_1V}{RT_1} \quad (1)$$

where n_1 is an estimate of the initial moles of O₂ in the headspace gases of the container and n_2 is an estimate of the final moles of O₂ in the headspace gases. Equation (1) also shows how these estimates are determined using the ideal gas law. In equation (1), the term "a" represents the initial O₂ as a fraction of the headspace gas volume, V (in cubic centimeters, cc), at an initial pressure of P₁ (in torr) and temperature of T₁ (in degrees Kelvin, °K). R is the universal gas constant, $62324.73 \frac{\text{torr} \cdot \text{cc}}{\text{K} \cdot \text{mole}}$. The "m" term in equation (1) represents the final

O₂ concentration as a fraction of the headspace gases of volume V at a pressure of P₂ (in torr) and temperature T₂ (°K).

The value of "a" for each experiment is the fraction of O₂ in air, for which the reference value is 0.20946. The value for "m" was determined by gas chromatography utilizing a sample of the headspace gases taken by syringe at the end of the test. These values along with results from equation (1) are provided in Table A1.

INITIAL LOOK AT THE OXYGEN DATA

Exhibit A1 in the Appendix provides a plot of the initial O₂ molar value versus the corresponding final value by test. Some of those tests with final O₂ values larger than their initial values are labeled with their test number in this plot. Exhibit A2 in the Appendix provides a plot of the change in O₂ (final minus initial) by test number. A reference line at zero is also shown on this plot. Two questions of interest in this last plot are: "Which of these test results indicate a significant increase in O₂ (if any)?" and "Which of these tests indicate a significant decrease in O₂ (if any)?"

In order to answer these questions, an idea of the repeatability of the outcomes from similar tests must be determined. The test descriptions in Table A2 of the Appendix were used to group the tests into the categories indicated in Table 1.

Table 1: Types of Tests

Type	Tests
PuO ₂ + MgO	1, 11, 23H, 25, 26
PuO ₂ + CaF	9, 14, 19
Pu Cake	17, 44, 50, 52
PuO ₂	12, 16H, 41, 51
PuO ₂ + CaO	2, 8, 15H
Other	3, 4, 5, 6, 7, 10, 13, 18, 20, 21, 22, 24, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 45, 46, 47, 48, 49, 53, 54, 55, 56, 57, 58, 59

An "H" following a test number indicates that that particular test was heated, possibly differentiating it from the other tests in its group.

Exhibit A3 in the Appendix provides a look at the change in O_2 by group type. Descriptive statistics for each of these groups are also provided in this exhibit. Note that the heated tests (those with the "H" suffix in Table 1) are labeled (in addition to those that were labeled earlier) in this exhibit and that they result in a change in O_2 that appears to be different from their unheated counterparts. The average and standard deviation of each group containing a heated test are computed including and excluding this test.

The repeatability of a test of the 9975 package may be represented by the standard deviation in the measurements of set of identical experiments. Each of the first 5 groups from Table 1 (excluding the heated tests) is to be considered as a set of nearly identical experiments. Their standard deviations range from 0.000071 to 0.000002 moles of O_2 with a pooled estimate of the standard deviation across all five groups of 0.00004 moles. When considered on a percentage basis as a relative (to the mean O_2 change) standard deviation, they range from about 21% to about 101% of the average O_2 change for the group with a pooled relative standard deviation of about 88% (using a one-way analysis of variance approach). In summary, a 2-sigma uncertainty determined from these results would lead to a limit of ± 0.00008 moles and $\pm 176\%$ of reading for absolute and relative errors, respectively.¹ Obviously, assessing the O_2 changes using the relative errors leads to insignificant differences between the initial and final oxygen for all of the tests. For those tests showing a potential O_2 increase, the absolute error 2-sigma limit leads to only 28, 48, and 49 being significant at an approximate 95% confidence level.

Part of the variation seen among the results for each of these groups is from measurement and analytical uncertainty and part is from differences in the conditions among each set of repeated tests (i.e., the conditions of the tests in each group may not have been as "identical" as desired). The next section looks at the variation due to the first of these two categories via the approach of error propagation. Before moving on to that topic, consider two additional looks at these data.

The first is a plot of the O_2 change versus headspace volume (in cc) across all of the tests, which is provided in Exhibit A4 in the Appendix. The volume of headspace gases in the container of each test is plotted along the x-axis. Along the y-axis the initial moles of O_2 are plotted as a solid light-gray line. The final moles of O_2 are also plotted on the y-axis, and their values are indicated by the symbol "x". While several of the tests showing a potential increase in O_2 have a headspace gas volume in the interval from 65 to 75 cc, other tests with volumes of only 30 cc also show a potential increase in O_2 . Thus, there is no obvious

¹ Absolute and relative errors are discussed later in this section.

relationship between the initial headspace gas volume and the generation or depletion of O₂.

One of the key steps in measuring the final O₂ value is injecting a sample from the headspace gas of the test container into a gas chromatograph. The recovery of this sample as reflected by its total sample volume percent determination is a critical measurement in this procedure. The target value for this determination is 100%. Exhibit A5 in the Appendix provides a plot of the O₂ changes versus the total sample volume percent determinations for these tests. There is no obvious relationship between the total sample volume percent determination and the generation or depletion of O₂.

PROPAGATION OF MEASUREMENT UNCERTAINTIES

As evident in equation (1), the determination of r , the difference in moles of O₂ from the beginning to the end of a test, is dependent on several measurements conducted over the course of the test. One question of interest as the results of these tests are evaluated is the potential impact of the uncertainties of these measurements on the derived values for r . Propagating the measurement uncertainties or errors afflicting the terms of equation (1) into the resultant r reveals this potential impact.

The errors in experimental measurements fall into the two broad categories of bias errors and random errors. Bias is related to accuracy, the closeness of agreement between the measured value and the true value.² Randomness of a measurement is related to the precision or repeatability of the measurement. Appropriately-taken together, these two errors yield the uncertainty of the measurement. The error propagation for equation (1) conducted here follows the framework provided in reference [3]. This reference also provides a full discussion of the practice of and underlying theory for uncertainty analysis in an experimental setting. It is a linearized approach based on the use of a Taylor series expansion of equation (1).

Using the approach and terminology of [3], a 95% coverage estimate of the uncertainty in the result r , U_r , can be expressed as

$$U_r^2 = B_r^2 + (tS_r)^2 \quad (2)$$

where B_r represents the 95% confidence bound of the bias limit for r , S_r represents the estimate of the standard deviation of the random errors, and t is the two-tailed, 95% Student t value (i.e., the 97.5th percentile, with degrees of freedom equal to those associated with the estimate of S_r).

²

In the situation where bias errors are known, the corresponding measurements are frequently corrected for these biases. Some random errors may be induced into the measurement by this process, however. In addition, the durations of the biases often vary. Some bias or systematic errors may remain constant over only a few measurements while others may afflict an entire experimental study. For this study, the approach taken is to select bounding values (at a 95% confidence level) for the potential measurement biases.

The bias (B_r) and precision (S_r) errors for r are estimated by propagating the bias (B_i) and precision (S_i) errors of each measurement term i of equation (1) using a Taylor's series expansion as indicated in the following equations:

$$B_r^2 = \sum_{i=1}^J \theta_i^2 B_i^2 + 2 \sum_{i=1}^{J-1} \sum_{j=i+1}^J \theta_i \theta_j \rho_{ij} B_i B_j \quad (3)$$

and

$$(tS_r)^2 = \sum_{i=1}^J \theta_i^2 (tS_i)^2 + 2 \sum_{i=1}^{J-1} \sum_{j=i+1}^J \theta_i \theta_j \rho'_{ij} (tS_i)(tS_j) \quad (4)$$

where the summations are over the J ($=7$) terms of equation (1), which are listed in Table 2 and which contribute uncertainty to the resultant r , each $\theta_i = \frac{\partial r}{\partial i^{\text{th}} \text{ term}}$ represents the partial derivative of equation (1) with respect to the i^{th} term of that equation, each B_i represents the 95% confidence estimate of the bias for the i^{th} such term, S_i represents the standard deviation of the precision errors for this i^{th} term, the corresponding Student t value is chosen for 95% (two-tailed) confidence and reflecting the degrees of freedom associated with S_i , the ρ_{ij} expression represents the correlation between the biases for terms i and j , and the ρ'_{ij} expression represents the correlation between the random errors for terms i and j .

For the approach being used here, the degrees of freedom associated with each estimated S_i is assumed large enough to justify using $t=2$ in the analyses that follow.

Table 2 provides a list of the partial derivative of equation (1) with respect to each term of interest and provides initial estimates of the bias and precision errors for each of these terms.

Table 2: Information Associated with the Propagation of Errors

Term		Units	Partial Derivative	95% Bound for Bias, B _i (relative)	95% Bound for Bias, B _i (absolute)	1 Standard Deviation Precision, S _i (relative)	1 Standard Deviation Precision, S _i (absolute)
1	a		$\frac{-P_1 \cdot V}{R \cdot T_1}$	2%	0.004	2%	0.004
2	V	cc	$\frac{m \cdot P_2}{R \cdot T_2} - \frac{a \cdot P_1}{R \cdot T_1}$	3%	1	3%	1
3	m		$\frac{P_2 \cdot V}{R \cdot T_2}$	5%	0.01	5%	0.01
4	P ₁	torr	$\frac{-a \cdot V}{R \cdot T_1}$	1%	7	1%	7
5	P ₂	torr	$\frac{m \cdot V}{R \cdot T_2}$	1%	7	1%	7
6	T ₁	°K	$\frac{a \cdot P_1 \cdot V}{R \cdot T_1^2}$	0.33%	1	0.33%	1
7	T ₂	°K	$\frac{-m \cdot P_2 \cdot V}{R \cdot T_2^2}$	0.33%	1	0.33%	1

The estimates of the uncertainties presented in Table 2 will be the basis for deriving the uncertainties, via error propagation, for the r's resulting from these 9975 package tests.³ As indicated in this table, relative and absolute errors will be considered in this analysis for each measurement.

There is a need to understand the difference between using relative and absolute errors to represent or model these uncertainties. Let the true value for a measurement be represented by M_T. If the size of the errors afflicting M_T is affected by the size of M_T itself, then the use of relative errors would be appropriate. If the size of the errors is unaffected by the size of M_T, then the use of absolute errors is appropriate.

For example, the value of the sample volume, V, varies from a low of 14.43 cc to a high of 123.67cc over these tests. The bias, when considered as a relative 3% error, would range from 14.43 x 0.03 = 0.433 cc to 123.67 x 0.03 = 3.71 cc. The bias, when considered as an absolute error, would be a constant 1 cc. The standard deviation of the random errors afflicting V, when considered as a relative error, would range from 14.43 x 0.03 = 0.433 cc to 123.67 x 0.03 = 3.71 cc. The standard deviation would be a constant (an absolute) 1 cc when these random errors are assumed to be unaffected by the size of V.

It is not unusual for the absolute errors to dominate when M_T is at the low end of the range of its possible values while relative errors dominate when M_T is at the high end of its range. In the discussion that follows, error propagations are conducted that consider various combinations of these errors as relative or absolute, since the true models for these uncertainties are not known.

³

These estimates of bias and precision were developed during discussions of these issues and are felt to be representative of these measurement uncertainties.

Correlations among the biases and any among the random errors afflicting the measurements for any one test would be limited to the beginning and ending temperatures and the beginning and ending pressures. It is expected that such correlations would be positive in sign. Note, however, that the partial derivatives for the two pressures and those for the two temperatures are of different signs. This implies that any such correlations among these biases and/or among these random errors would tend to reduce the uncertainty of the resultant, r .

SIGNIFICANT DIFFERENCES IN MOLES OF OXYGEN

In the analyses that follow, the focus is on two primary situations. The first assumes that there are no correlations among these measurements and that the uncertainties of Table 2 are representative. In this situation, the error propagation is to be developed (i.e., the choice between each relative and absolute error model is made) to provide an upper bound on the uncertainties for the r values (at a 95% confidence level). The second situation reflects highly correlated errors between the two temperature measurements, highly correlated errors between the two pressure measurements, and uncertainties for all measurements smaller than those appearing in Table 2. The intent is to use the second situation to conduct a sensitivity analysis on the assumptions used in the first situation.

Table 3 provides the results for the first situation, the upper bounding case. It identifies each of the 9975 package tests, provides values for the 7 measurement terms from equation (1), evaluates the corresponding value for r , and propagates the uncertainties of the measurements into the resulting r , selecting the maximum of the relative and absolute error models for each measurement. No correlations among the biases or random errors are considered in this table.

The next to the last column of this table provides the uncertainty of the measured difference, r , in O_2 , at a 95% confidence level. This is a $\pm$ uncertainty for the derived value of r . The last column indicates the results of assessing the difference between the calculated value of r and zero in light of r 's uncertainty. Three labels are used for the rows of this last column. If the value of r is sufficiently greater than zero, the label " O_2 generated" is used for the row. If the value of r is sufficiently less than zero, the label used is " O_2 depleted." Otherwise, the label "No difference" is used for the row.

Exhibit A6 in the Appendix provides a plot of the results of Table 3 by test. It shows the upper and lower error bounds for each test plotted around zero. If the calculated value of r falls within this interval, there is no significance difference between the initial and final moles of O_2 . A plotted value about the upper limit, indicates that the final moles of O_2 is significantly greater than the initial for that test, and a plotted value below the lower limit indicates that the final O_2 moles are significantly less than the initial moles. Thus, this plot provides a graphical representation of the significance of the O_2 difference relative to the 95% uncertainty limits.

Table 3: Results of Bounding Error Propagation by Test Number

Test	a	PI	V	T1	m	P2	T2	R	r	95 % Uncertainty for r	r value relative to zero at 95 %
1	0.20946	752.2	34.11	296.6	0.188	743.2	295.7	62324.73	-0.000032	0.00003470	No difference
2	0.20946	741.9	63.86	294.7	0.179	711.8	297.2	62324.73	-0.000101	0.00006254	O ₂ Depleted
3	0.20946	740.9	30.50	299.3	0.211	741.3	295.9	62324.73	0.000005	0.00003222	No difference
4	0.20946	748.3	30.90	298.5	0.201	751.5	295.4	62324.73	-0.000007	0.00003182	No difference
5	0.20946	755.5	29.81	297.3	0.228	891.3	295.5	62324.73	0.000074	0.00004012	O ₂ Generated
6	0.20946	775.7	62.33	295.5	0.039	774.7	294.5	62324.73	-0.000447	0.00007169	O ₂ Depleted
7	0.20946	649.4	49.71	296.2	0.036	808.1	331.0	62324.73	-0.000296	0.00005145	O ₂ Depleted
8	0.20946	750.2	64.10	295.6	0.196	735.1	295.7	62324.73	-0.000046	0.00006467	No difference
9	0.20946	734.5	62.91	299.1	0.202	733.3	298.2	62324.73	-0.000018	0.00006303	No difference
10	0.20946	746.5	43.46	298.5	0.202	746.5	295.8	62324.73	-0.000010	0.00004463	No difference
11	0.20946	755.7	38.51	296.4	0.197	749.7	295.9	62324.73	-0.000022	0.00003948	No difference
12	0.20946	756.6	30.72	297.5	0.2	753.7	296.1	62324.73	-0.000012	0.00003161	No difference
13	0.20946	762.3	51.66	302.1	0.031	655.9	295.9	62324.73	-0.000381	0.00005323	O ₂ Depleted
14	0.20946	765.1	64.37	296.3	0.167	975.2	329.5	62324.73	-0.000048	0.00007500	No difference
15	0.20946	754.1	65.63	299.6	0.117	806.3	327.6	62324.73	-0.000252	0.00006695	O ₂ Depleted
16	0.20946	760.2	30.78	296.1	0.155	753.2	314.3	62324.73	-0.000082	0.00003058	O ₂ Depleted
17	0.20946	762.2	42.04	298.0	0.206	779.1	297.2	62324.73	0.000003	0.00004546	No difference
18	0.20946	760.0	30.34	298.0	0.155	1179.8	296.4	62324.73	0.000040	0.00004593	No difference
19	0.20946	751.7	52.40	298.4	0.182	744.5	297.4	62324.73	-0.000061	0.00005307	O ₂ Depleted
20	0.20946	753.4	53.82	297.6	0	1178.3	321.3	62324.73	-0.000458	0.00008059	O ₂ Depleted
21	0.20946	744.0	25.98	298.4	0.06	803.2	323.0	62324.73	-0.000155	0.00002898	O ₂ Depleted
22	0.20946	749.4	43.03	298.3	0.154	742.1	298.0	62324.73	-0.000099	0.00004357	O ₂ Depleted
23	0.20946	758.2	31.95	299.0	0.119	806.3	307.8	62324.73	-0.000112	0.00003417	O ₂ Depleted
24	0.20946	764.4	43.83	298.1	0.197	764.3	297.8	62324.73	-0.000022	0.00004545	No difference
25	0.20946	749.5	14.43	295.9	0.126	800.2	324.7	62324.73	-0.000051	0.00001633	O ₂ Depleted
26	0.20946	752.6	25.67	296.2	0.162	789.2	317.1	62324.73	-0.000053	0.00002617	O ₂ Depleted
28	0.20946	758.2	68.91	296.7	0.242	829.8	297.9	62324.73	0.000153	0.00009085	O ₂ Generated
29	0.20946	768.4	27.47	371.7	0.133	341.5	419.5	62324.73	-0.000143	0.00001726	O ₂ Depleted
30	0.20946	755.8	63.26	297.8	0.165	724.6	297.6	62324.73	-0.000132	0.00006300	O ₂ Depleted
31	0.20946	733.8	26.22	369.5	0.205	738.8	367.5	62324.73	-0.000002	0.00002169	No difference
32	0.20946	753.9	91.65	297.5	0.129	772.2	296.9	62324.73	-0.000287	0.00009684	O ₂ Depleted
33	0.20946	760.0	38.54	298.8	0.202	751.8	296.8	62324.73	-0.000013	0.00003982	No difference
34	0.20946	768.9	38.98	298.9	0.202	760.5	296.9	62324.73	-0.000013	0.00004072	No difference
35	0.20946	745.8	53.04	296.4	0.189	755.3	297.4	62324.73	-0.000040	0.00005432	No difference
36	0.20946	748.5	61.32	297.9	0.013	3843.2	324.5	62324.73	-0.000366	0.00026301	O ₂ Depleted
37	0.20946	741.6	26.49	297.4	0.2	813.1	316.1	62324.73	-0.000003	0.00002739	No difference
38	0.20946	744.9	44.90	297.4	0.141	802.2	297.9	62324.73	-0.000104	0.00004835	O ₂ Depleted
39	0.20946	752.4	46.04	297.4	0.208	758.3	297.8	62324.73	0.000000	0.00004889	No difference
40	0.20946	759.7	46.27	297.9	0.201	805.8	298.0	62324.73	0.000007	0.00005028	No difference
41	0.20946	750.0	19.25	298.2	0.199	742.32	296.4	62324.73	-0.000009	0.00001952	No difference
42	0.20946	751.6	72.90	301.3	0.197	739.1	296.9	62324.73	-0.000038	0.00007337	No difference
43	0.20946	742.4	70.24	303.0	0.209	730.8	296.9	62324.73	0.000001	0.00007241	No difference
44	0.20946	750.5	123.67	300.6	0.186	722.7	297.4	62324.73	-0.000141	0.00012212	O ₂ Depleted
45	0.20946	756.9	37.51	298.5	0.21	782.5	297.4	62324.73	0.000013	0.00004130	No difference
46	0.20946	763.9	38.12	298.9	0.211	788.3	296.9	62324.73	0.000015	0.00004253	No difference
47	0.20946	749.7	18.96	297.9	0.073	1197.3	370.0	62324.73	-0.000088	0.00002573	O ₂ Depleted
48	0.20946	752.4	71.59	297.7	0.227	1095.2	336.7	62324.73	0.000240	0.00010292	O ₂ Generated
49	0.20946	744.4	69.90	297.8	0.297	1092.7	333.9	62324.73	0.000503	0.00013241	O ₂ Generated
50	0.20946	748.8	122.76	298.2	0.189	736	298.4	62324.73	-0.000118	0.00012278	No difference
51	0.20946	755.7	18.74	298.1	0.199	753.4	298.1	62324.73	-0.000008	0.00001917	No difference
52	0.20946	762.5	45.15	298.8	0.2014	747.9	298.4	62324.73	-0.000022	0.00004616	No difference
53	0.20946	754.9	18.74	297.6	0.13	872.6	338.2	62324.73	-0.000059	0.00002052	O ₂ Depleted
54	0.20946	754.7	31.56	298.1	0.2	775.2	315.6	62324.73	-0.000020	0.00003153	No difference
55	0.20946	743.3	71.49	298.4	0.19	744.9	298.1	62324.73	-0.000054	0.00007213	No difference
56	0.20946	759.8	37.50	298.4	0.2	774.6	297.5	62324.73	-0.000008	0.00003931	No difference
57	0.20946	774.9	18.49	298.3	0.101	1048.9	300.6	62324.73	-0.000057	0.00002561	O ₂ Depleted
58	0.20946	750.0	31.27	298.8	0.00126	750.3	299.3	62324.73	-0.00000594	0.00003234	No difference
59	0.20946	742.4	59.55	298.2	0.162	1019	322.6	62324.73	-0.000009	0.00007296	No difference

Table 4 repeats the conclusions from Table 3 and adds the results from three more approaches to the error propagation for equation (1). The columns of Table 4 headed "Correlations With Uncertainties" reflects the results of an error propagation using the information of Table 2 and assuming perfect positive correlations between the biases for the two pressure measurements, between the biases for the two temperature measurements, between the random errors for the two pressure measurements, and between the random errors for the two temperature measurements. The next pair of columns shows the results from the

approach of assuming these same correlations but reducing the uncertainties of Table 2 by a factor of 2. The last pair shows the results from the error propagation assuming these same correlations and reducing the uncertainties of Table 2 by a factor of 5. For these correlated situations, the minimum of the relative and absolute error models is selected to represent each and every uncertainty term of equations (3) and (4) involved in the error propagation.

Table 4: Comparisons Among The Error Propagation Approaches

Test	r	Bounding Situation		Perfectly Correlated Situation		Correlated With Uncertainties Reduced by a Factor of 2		Correlated With Uncertainties Reduced by a Factor of 5	
		95%	r value	95%	r value	95%	r value	95%	r value
		Uncertainty for r	relative to zero at 95%	Uncertainty for r	relative to zero at 95%	Uncertainty for r	relative to zero at 95%	Uncertainty for r	relative to zero at 95%
1	-0.000032	0.00003470	No difference	0.00003139	O2 Depleted	0.00001569	O2 Depleted	0.00000628	O2 Depleted
2	-0.000101	0.00006254	O2 Depleted	0.00005424	O2 Depleted	0.00002712	O2 Depleted	0.00001085	O2 Depleted
3	0.000005	0.00003222	No difference	0.00002935	No difference	0.00001468	No difference	0.00000587	No difference
4	-0.000007	0.00003182	No difference	0.00003017	No difference	0.00001509	No difference	0.00000603	O2 Depleted
5	0.000074	0.00004012	O2 Generated	0.00003407	O2 Generated	0.00001704	O2 Generated	0.00000681	O2 Generated
6	-0.000447	0.00007169	O2 Depleted	0.00003197	O2 Depleted	0.00001598	O2 Depleted	0.00000639	O2 Depleted
7	-0.000296	0.00005145	O2 Depleted	0.00002306	O2 Depleted	0.00001153	O2 Depleted	0.00000461	O2 Depleted
8	-0.000046	0.00006467	No difference	0.00006046	No difference	0.00003023	O2 Depleted	0.00001209	O2 Depleted
9	-0.000018	0.00006303	No difference	0.00005957	No difference	0.00002978	No difference	0.00001191	O2 Depleted
10	-0.000010	0.00004463	No difference	0.00004214	No difference	0.00002107	No difference	0.00000843	O2 Depleted
11	-0.000022	0.00003948	No difference	0.00003708	No difference	0.00001854	O2 Depleted	0.00000742	O2 Depleted
12	-0.000012	0.00003161	No difference	0.00003006	No difference	0.00001503	No difference	0.00000601	O2 Depleted
13	-0.000381	0.00005323	O2 Depleted	0.00002698	O2 Depleted	0.00001349	O2 Depleted	0.00000540	O2 Depleted
14	-0.000048	0.00007500	No difference	0.00006116	No difference	0.00003058	O2 Depleted	0.00001223	O2 Depleted
15	-0.000252	0.00006695	O2 Depleted	0.00004227	O2 Depleted	0.00002114	O2 Depleted	0.00000845	O2 Depleted
16	-0.000082	0.00003058	O2 Depleted	0.00002399	O2 Depleted	0.00001200	O2 Depleted	0.00000480	O2 Depleted
17	0.000003	0.00004546	No difference	0.00004217	No difference	0.00002108	No difference	0.00000843	No difference
18	0.000040	0.00004593	No difference	0.00003499	O2 Generated	0.00001750	O2 Generated	0.00000700	O2 Generated
19	-0.000061	0.00005307	O2 Depleted	0.00004669	O2 Depleted	0.00002334	O2 Depleted	0.00000934	O2 Depleted
20	-0.000458	0.00008059	O2 Depleted	0.00002909	O2 Depleted	0.00001454	O2 Depleted	0.00000582	O2 Depleted
21	-0.000155	0.00002898	O2 Depleted	0.00001593	O2 Depleted	0.00000797	O2 Depleted	0.00000319	O2 Depleted
22	-0.000099	0.00004357	O2 Depleted	0.00003370	O2 Depleted	0.00001685	O2 Depleted	0.00000674	O2 Depleted
23	-0.000112	0.00003417	O2 Depleted	0.00002258	O2 Depleted	0.00001129	O2 Depleted	0.00000452	O2 Depleted
24	-0.000022	0.00004545	No difference	0.00004266	No difference	0.00002133	O2 Depleted	0.00000853	O2 Depleted
25	-0.000051	0.00001633	O2 Depleted	0.00001018	O2 Depleted	0.00000509	O2 Depleted	0.00000204	O2 Depleted
26	-0.000053	0.00002617	O2 Depleted	0.00002098	O2 Depleted	0.00001049	O2 Depleted	0.00000420	O2 Depleted
28	0.000153	0.00009085	O2 Generated	0.00007288	O2 Generated	0.00003644	O2 Generated	0.00001458	O2 Generated
29	-0.000143	0.00001726	O2 Depleted	0.00001366	O2 Depleted	0.00000683	O2 Depleted	0.00000273	O2 Depleted
30	-0.000132	0.00006300	O2 Depleted	0.00005112	O2 Depleted	0.00002556	O2 Depleted	0.00001022	O2 Depleted
31	-0.000002	0.00002169	No difference	0.00002024	No difference	0.00001012	No difference	0.00000405	No difference
32	-0.000287	0.00009684	O2 Depleted	0.00006468	O2 Depleted	0.00003234	O2 Depleted	0.00001294	O2 Depleted
33	-0.000013	0.00003982	No difference	0.00003755	No difference	0.00001878	No difference	0.00000751	O2 Depleted
34	-0.000013	0.00004072	No difference	0.00003838	No difference	0.00001919	No difference	0.00000768	O2 Depleted
35	-0.000040	0.00005432	No difference	0.00004931	No difference	0.00002466	O2 Depleted	0.00000986	O2 Depleted
36	-0.000366	0.00026301	O2 Depleted	0.00003163	O2 Depleted	0.00001582	O2 Depleted	0.00000633	O2 Depleted
37	-0.000003	0.00002739	No difference	0.00002605	No difference	0.00001302	No difference	0.00000521	No difference
38	-0.000104	0.00004835	O2 Depleted	0.00003480	O2 Depleted	0.00001740	O2 Depleted	0.00000696	O2 Depleted
39	0.000000	0.00004889	No difference	0.00004501	No difference	0.00002251	No difference	0.00000900	No difference
40	0.000007	0.00005028	No difference	0.00004764	No difference	0.00002382	No difference	0.00000953	No difference
41	-0.000009	0.00001952	No difference	0.00001849	No difference	0.00000924	No difference	0.00000370	O2 Depleted
42	-0.000038	0.00007337	No difference	0.00006895	No difference	0.00003447	O2 Depleted	0.00001379	O2 Depleted
43	0.000001	0.00007241	No difference	0.00006652	No difference	0.00003326	No difference	0.00001330	No difference
44	-0.000141	0.00012212	O2 Depleted	0.00010926	O2 Depleted	0.00005463	O2 Depleted	0.00002185	O2 Depleted
45	0.000013	0.00004130	No difference	0.00003771	No difference	0.00001885	No difference	0.00000754	O2 Generated
46	0.000015	0.00004253	No difference	0.00003865	No difference	0.00001933	No difference	0.00000773	O2 Generated
47	-0.000088	0.00002573	O2 Depleted	0.00001215	O2 Depleted	0.00000607	O2 Depleted	0.00000243	O2 Depleted
48	0.000240	0.00010292	O2 Generated	0.00008658	O2 Generated	0.00004329	O2 Generated	0.00001732	O2 Generated
49	0.000503	0.00013241	O2 Generated	0.00008592	O2 Generated	0.00004296	O2 Generated	0.00001718	O2 Generated
50	-0.000118	0.00012278	No difference	0.00011134	O2 Depleted	0.00005567	O2 Depleted	0.00002227	O2 Depleted
51	-0.000008	0.00001917	No difference	0.00001815	No difference	0.00000907	No difference	0.00000363	O2 Depleted
52	-0.000022	0.00004616	No difference	0.00004361	No difference	0.00002181	No difference	0.00000872	O2 Depleted
53	-0.000059	0.00002052	O2 Depleted	0.00001369	O2 Depleted	0.00000685	O2 Depleted	0.00000274	O2 Depleted
54	-0.000020	0.00003153	No difference	0.00002994	No difference	0.00001497	O2 Depleted	0.00000599	O2 Depleted
55	-0.000054	0.00007213	No difference	0.00006578	No difference	0.00003289	O2 Depleted	0.00001316	O2 Depleted
56	-0.000008	0.00003931	No difference	0.00003739	No difference	0.00001870	No difference	0.00000748	O2 Depleted
57	-0.000057	0.00002561	O2 Depleted	0.00001397	O2 Depleted	0.00000698	O2 Depleted	0.00000279	O2 Depleted
58	-0.0000594	0.00003138	No difference	0.00003015	No difference	0.00001508	No difference	0.00000603	No difference
59	-0.000009	0.00007296	No difference	0.00005799	No difference	0.00002900	No difference	0.00001160	No difference

Table 5 summarizes the results from the various approaches to propagating the errors of Table 2 into equation (1). This table identifies those tests (by number) that reveal an O₂ change significantly nonzero (at the 95% confidence level). The average of the uncertainties across all of the tests is also provided for each situation.

Table 5: Summary Information from Error Propagations

Description of Propagation Approach	Tests showing an increased O ₂ level	Tests showing a decreased O ₂ level	Average Uncertainty in O ₂ Change (moles)
Bounding Case Using Maximum of Relative versus Absolute Errors	5, 28, 48, 49	2, 6, 7, 13, 15, 16, 19-23, 25, 26, 29, 30, 32, 36, 38, 44, 47, 53, 57	0.00005541
Correlated Errors Using Minimum of Relative versus Absolute Errors	5, 18, 28, 48, 49	1, 2, 6, 7, 13, 15, 16, 19-23, 25, 26, 29, 30, 32, 36, 38, 44, 47, 50, 53, 57	0.00004151
Correlated Errors Using Minimum of Relative versus Absolute Errors with Initial Uncertainties Reduced by a Factor of 2	5, 18, 28, 48, 49	1, 2, 6-8, 11, 13-16, 19-26, 29, 30, 32, 35, 36, 38, 42, 44, 47, 50, 53-55, 57	0.00002075
Correlated Errors Using Minimum of Relative versus Absolute Errors with Initial Uncertainties Reduced by a Factor of 5	5, 18, 28, 45, 46, 48, 49	1, 2, 4, 6-16, 19-26, 29, 30, 32-36, 38, 41, 42, 44, 47, 50-57	0.00000830

In comparing the test conditions indicated in Table A2 to the anticipated operational window for the 9975 package, several of the tests are deemed unrepresentative of the operational conditions or are considered to have led to questionable outcomes. The tests deemed unrepresentative include 29, 35, 40, 46, and 52 (due to under injection of the sample in the gas chromatography measurement), 5 and 18 (due to excessive moisture), and 28, 35, 42, 43, 48, and 49 (due to the samples not having sand, slag, and crucible, SS&C, components).

Exhibit A7 in the Appendix provides a plot the O₂ changes for those remaining tests that are considered to be representative of the 9975-package operational conditions. Also, shown on this plot are the corresponding upper uncertainty limits for these oxygen differences. This plot shows that none of these tests have O₂ changes indicating significant (at the 95% confidence level) increases in oxygen.

The average O₂ change for these tests is -0.00009 moles, and the average uncertainties corresponding to the error propagation approaches of Table 5 range from a high of 0.000053 moles to a low of 0.0000094 moles. Expressed as relative uncertainties, these high and low values are 59% and 10%, respectively.

Exhibit A8 in the Appendix provides a plot of the initial versus final moles of oxygen for these tests. A paired t-test for these data (assuming that these test results are representative of --- i.e., a random sample from --- the intended operational window for the 9975) is also provided in this exhibit. This statistical test reveals that the null hypothesis of a zero mean difference between the initial

and final moles of oxygen (final - initial) for these experiments is strongly rejected (the probability of obtaining these results by chance alone is 1 in 100,000 if there is no difference in the quantity of O_2) in favor of the hypothesis that the mean oxygen difference is less than zero; i.e., in favor of the hypothesis that on average oxygen is depleted for these tests.

CONCLUSIONS

A review of the oxygen data from the gas generation tests supporting the 9975 SARP has been conducted including the development of an error propagation of the measurement uncertainties into the equation for the change in moles of O_2 . This analysis revealed tests with significant (at a 95% confidence level) differences between their beginning and ending moles of O_2 based upon the measurement and analytical uncertainties assumed in this report.

REFERENCES

- [1] Livingston, Ronald R., Gas Generation Test Support for Revision of 9975 SARP: Task Technical and Quality Assurance Plan," WSRC-RP-99-00164, February 18, 1999.
- [2] SAS Institute, JMP® Statistics and Graphics Guide, Version 3 of JMP, SAS Institute Inc., Cary, NC, 1995.
- [3] Coleman, Hugh W. and W. Glenn Steele, Jr., Experimentation and Uncertainty Analysis for Engineers, John Wiley & Sons, Inc., New York, 1989.

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APPENDIX:

TABLES AND EXHIBITS

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Table A1: Test Measurements by Test Number⁴

Test	Volume (cc)	Initial Pressure (torr)	Initial Temperature (°K)	Initial Total moles	Estimate Initial N ₂ moles	Estimate Initial O ₂ moles	Final Pressure (torr)	Final Temperature (°C)	Final Temperature (°K)	Final Total moles	%H ₂	%O ₂	%N ₂	Final H ₂ moles	Final O ₂ moles	Final N ₂ moles	Δ O ₂ moles (final-initial)
1	34.11	752.2	296.6	1.388E-03	1.084E-03	2.907E-04	743.2	22.7	295.7	1.376E-03	0.55	18.80	84.00	7.566E-06	2.586E-04	1.155E-03	-3.212E-05
2	63.86	741.9	294.7	2.579E-03	2.014E-03	5.403E-04	711.8	24.2	297.2	2.454E-03	0.00	17.90	84.50	0.000E+00	4.393E-04	2.074E-03	-1.010E-04
3	30.50	740.9	299.3	1.211E-03	9.459E-04	2.537E-04	741.3	22.9	295.9	1.226E-03	0.00	21.10	82.30	0.000E+00	2.587E-04	1.009E-03	4.942E-06
4	30.90	748.3	298.5	1.243E-03	9.705E-04	2.603E-04	751.5	22.4	295.4	1.261E-03	0.00	20.10	82.50	0.000E+00	2.535E-04	1.041E-03	-6.814E-06
5	29.81	755.5	297.3	1.215E-03	9.491E-04	2.546E-04	891.3	22.5	295.5	1.443E-03	10.80	22.80	61.70	1.558E-04	3.289E-04	8.901E-04	7.434E-05
6	62.33	775.7	295.5	2.625E-03	2.050E-03	5.499E-04	774.7	21.5	294.5	2.631E-03	4.20	3.90	81.60	1.105E-04	1.026E-04	2.147E-03	-4.473E-04
7	49.71	649.4	296.2	1.749E-03	1.365E-03	3.663E-04	808.1	105.5	331.0	1.947E-03	3.70	3.60	87.00	7.206E-05	7.011E-05	1.694E-04	-2.962E-04
8	64.10	750.2	295.6	2.610E-03	2.038E-03	5.467E-04	735.1	22.7	295.7	2.557E-03	0.05	19.60	86.00	1.278E-06	5.011E-04	2.199E-03	-4.560E-05
9	62.91	734.5	299.1	2.479E-03	1.936E-03	5.192E-04	733.3	25.2	298.2	2.482E-03	0.08	20.20	85.10	1.986E-06	5.014E-04	2.112E-03	-1.780E-05
10	43.46	746.5	298.5	1.744E-03	1.362E-03	3.653E-04	746.5	22.8	295.8	1.760E-03	0.62	20.20	83.80	1.091E-05	3.555E-04	1.694E-04	-9.794E-06
11	38.51	755.7	296.4	1.575E-03	1.230E-03	3.300E-04	749.7	22.9	295.9	1.566E-03	0.26	19.70	88.10	4.070E-06	3.084E-04	1.379E-03	-2.157E-05
12	30.72	756.6	297.5	1.254E-03	9.788E-04	2.626E-04	753.7	23.1	296.1	1.255E-03	0.54	20.00	84.80	6.775E-06	2.509E-04	1.064E-03	-1.164E-05
13	51.66	762.3	302.1	2.092E-03	1.633E-03	4.381E-04	655.9	22.9	295.9	1.837E-03	6.19	3.10	90.80	1.137E-04	5.696E-05	1.668E-03	-3.811E-04
14	64.37	765.1	296.3	2.667E-03	2.082E-03	5.586E-04	975.2	97.8	329.5	3.057E-03	0.89	16.70	80.00	2.721E-05	5.105E-04	2.446E-03	-4.809E-05
15	65.63	754.1	299.6	2.651E-03	2.070E-03	5.552E-04	806.3	111.7	327.6	2.592E-03	0.00	11.70	82.60	0.000E+00	3.032E-04	2.141E-03	-2.520E-04
16	30.78	760.2	296.1	1.268E-03	9.901E-04	2.656E-04	753.2	109.2	314.3	1.184E-03	0.22	15.50	78.20	2.604E-06	1.835E-04	1.475E-03	-8.211E-05
17	42.04	762.2	298.0	1.725E-03	1.347E-03	3.614E-04	779.1	24.2	297.2	1.768E-03	1.64	20.60	79.60	2.900E-05	3.643E-04	1.408E-03	2.889E-06
18	30.34	760.0	298.0	1.242E-03	9.694E-04	2.600E-04	1179.8	23.4	296.4	1.938E-03	24.15	15.50	53.10	4.680E-04	3.003E-04	1.029E-03	4.029E-05
19	52.40	751.7	298.4	2.118E-03	1.654E-03	4.436E-04	744.5	24.4	297.4	2.105E-03	0.00	18.20	83.80	0.000E+00	3.831E-04	1.764E-03	-6.057E-05
20	53.82	753.4	297.6	2.186E-03	1.707E-03	4.579E-04	1178.3	25.1	321.3	3.167E-03	80.00	0.00	23.60	2.534E-03	0.000E+00	7.474E-04	-4.579E-04
21	25.98	744.0	298.4	1.039E-03	8.115E-04	2.177E-04	803.2	94.7	323.0	1.037E-03	2.60	6.00	95.60	2.695E-05	6.220E-05	9.910E-04	-1.555E-04
22	43.03	749.4	298.3	1.734E-03	1.354E-03	3.633E-04	742.1	25	298.0	1.719E-03	0.13	15.40	86.30	2.235E-06	2.648E-04	1.484E-03	-9.853E-05
23	31.95	758.2	299.0	1.300E-03	1.015E-03	2.723E-04	806.3	96.9	307.8	1.343E-03	1.60	11.90	88.60	2.149E-05	1.598E-04	1.190E-03	-1.125E-04
24	43.83	764.4	298.1	1.803E-03	1.408E-03	3.777E-04	764.3	24.8	297.8	1.805E-03	5.00	19.70	76.60	9.024E-05	3.556E-04	1.383E-03	-2.216E-05
25	14.43	749.5	295.9	5.865E-04	4.579E-04	1.228E-04	800.2	92.6	324.7	5.705E-04	2.17	12.60	82.70	1.238E-05	7.189E-05	4.718E-04	-5.095E-05
26	25.67	752.6	296.2	1.047E-03	8.172E-04	2.192E-04	789.2	94.4	317.1	1.025E-03	1.19	16.20	79.40	1.220E-05	1.661E-04	8.140E-04	-5.312E-05
28	68.91	758.2	296.7	2.825E-03	2.206E-03	5.918E-04	829.8	24.9	297.9	3.080E-03	1.82	24.20	68.20	5.605E-05	7.453E-04	2.100E-03	1.535E-04
29	27.47	768.4	371.7	9.112E-04	7.115E-04	1.909E-04	341.5	99.3	419.5	3.588E-04	0.46	13.30	85.80	1.650E-06	4.772E-05	3.078E-04	-1.431E-04
30	63.26	755.8	297.8	2.576E-03	2.011E-03	5.396E-04	724.6	24.6	297.6	2.471E-03	1.27	16.50	75.80	3.139E-05	4.078E-04	1.873E-03	-1.318E-04
31	26.22	733.8	369.5	8.355E-04	6.524E-04	1.750E-04	738.8	94.5	367.5	8.457E-04	0.03	20.50	76.00	2.537E-07	1.734E-04	6.428E-04	-1.621E-06
32	91.65	753.9	297.5	3.726E-03	2.910E-03	7.805E-04	772.2	23.9	296.9	3.825E-03	8.13	12.90	78.50	3.109E-04	4.934E-04	3.002E-03	-2.872E-04
33	38.54	760.0	298.8	1.573E-03	1.228E-03	3.294E-04	751.8	23.8	296.8	1.566E-03	1.60	20.20	76.40	2.506E-05	3.164E-04	1.197E-03	-1.304E-05
34	38.98	768.9	298.9	1.609E-03	1.256E-03	3.370E-04	760.5	23.9	296.9	1.602E-03	0.20	20.20	76.90	3.204E-06	3.236E-04	1.232E-03	-1.339E-05
35	53.04	745.8	296.4	2.141E-03	1.672E-03	4.485E-04	755.3	24.4	297.4	2.161E-03	0.00	18.90	55.20	0.000E+00	4.085E-04	1.193E-03	-4.003E-05
36	61.32	748.5	297.9	2.472E-03	1.930E-03	5.178E-04	3843.2	106.3	324.5	1.165E-02	74.70	1.30	17.90	8.703E-03	1.515E-04	2.086E-03	-3.663E-04
37	26.49	741.6	297.4	1.060E-03	8.276E-04	2.220E-04	813.1	106.1	316.1	1.093E-03	0.40	20.00	64.20	4.373E-06	2.187E-04	7.019E-04	-3.334E-06
38	44.90	744.9	297.4	1.804E-03	1.409E-03	3.780E-04	802.2	24.9	297.9	1.940E-03	7.40	14.10	77.70	1.436E-04	2.735E-04	1.507E-03	-1.044E-04
39	46.04	752.4	297.4	1.869E-03	1.459E-03	3.915E-04	758.3	24.8	297.8	1.881E-03	6.50	20.80	72.10	1.223E-04	3.913E-04	1.356E-03	-2.066E-07
40	46.27	759.7	297.9	1.893E-03	1.478E-03	3.966E-04	805.8	25.0	298.0	2.007E-03	3.00	20.10	54.40	6.022E-05	4.035E-04	1.092E-03	6.940E-06
41	19.25	750.0	298.2	7.769E-04	6.066E-04	1.627E-04	742.32	23.4	296.4	7.736E-04	0.70	19.90	81.20	5.415E-06	1.539E-04	6.282E-04	-8.780E-06
42	72.90	751.6	301.3	2.918E-03	2.278E-03	6.112E-04	739.1	23.9	296.9	2.912E-03	0.10	19.70	80.00	2.912E-06	5.736E-04	2.330E-03	-3.754E-05
43	70.24	742.4	303.0	2.761E-03	2.156E-03	5.784E-04	730.8	23.9	296.9	2.774E-03	0.00	20.90	79.30	0.000E+00	5.798E-04	2.205E-03	1.384E-06
44	123.67	750.5	300.6	4.954E-03	3.868E-03	1.038E-03	722.7	24.4	297.4	4.822E-03	0.20	18.60	82.40	9.644E-06	8.969E-04	3.973E-03	-1.408E-04
45	37.51	756.9	298.5	1.526E-03	1.192E-03	3.196E-04	782.5	24.4	297.4	1.583E-03	2.30	21.00	76.80	3.642E-05	3.325E-04	1.216E-03	1.289E-05

⁴ Test 27 was unsuccessful due to equipment failure.

Table A1: Test Measurements by Test Number (continued)

Test	Volume (cc)	Initial Pressure (torr)	Initial Temperature (°K)	Initial Total moles	Estimate Initial N ₂ moles	Estimate Initial O ₂ moles	Final Pressure (torr)	Final Temperature (°C)	Final Temperature (°K)	Final Total moles	%H ₂	%O ₂	%N ₂	Final H ₂ moles	Final O ₂ moles	Final N ₂ moles	Δ O ₂ moles (final-initial)
46	38.12	763.9	298.9	1.563E-03	1.221E-03	3.274E-04	788.3	23.9	296.9	1.624E-03	1.20	21.10	62.10	1.949E-05	3.427E-04	1.009E-03	1.524E-05
47	18.96	749.7	297.9	7.654E-04	5.977E-04	1.603E-04	1197.3	97	370.0	9.842E-04	3.40	7.30	81.80	3.346E-05	7.185E-05	8.051E-04	-8.847E-05
48	71.59	752.4	297.7	2.903E-03	2.267E-03	6.081E-04	1095.2	63.7	336.7	3.736E-03	0.00	22.70	74.00	0.000E+00	8.480E-04	2.765E-03	2.399E-04
49	69.90	744.4	297.8	2.804E-03	2.189E-03	5.872E-04	1092.7	60.9	333.9	3.670E-03	1.50	29.70	66.40	5.506E-05	1.090E-03	2.437E-03	5.029E-04
50	122.76	748.8	298.2	4.946E-03	3.862E-03	1.036E-03	736	25.4	298.4	4.858E-03	0.40	18.90	79.20	1.943E-05	9.182E-04	3.848E-03	-1.178E-04
51	18.74	755.7	298.1	7.623E-04	5.952E-04	1.597E-04	753.4	25.1	298.1	7.599E-04	1.50	19.90	73.40	1.140E-05	1.512E-04	5.578E-04	-8.435E-06
52	45.15	762.5	298.8	1.848E-03	1.443E-03	3.872E-04	747.9	25.4	298.4	1.815E-03	0.55	20.14	78.36	9.985E-06	3.656E-04	1.423E-03	-2.154E-05
53	18.74	754.9	297.6	7.627E-04	5.956E-04	1.598E-04	872.6	65.2	338.2	7.758E-04	1.32	13.00	85.00	1.024E-05	1.009E-04	6.594E-04	-5.891E-05
54	31.56	754.7	298.1	1.282E-03	1.001E-03	2.686E-04	775.2	42.6	315.6	1.244E-03	0.00	20.00	74.00	0.000E+00	2.488E-04	9.205E-04	-1.977E-05
55	71.49	743.3	298.4	2.857E-03	2.231E-03	5.985E-04	744.9	25.1	298.1	2.866E-03	0.36	19.00	84.00	1.032E-05	5.446E-04	2.408E-03	-5.389E-05
56	37.50	759.8	298.4	1.532E-03	1.196E-03	3.209E-04	774.6	24.5	297.5	1.567E-03	0.25	20.00	84.00	3.917E-06	3.133E-04	1.316E-03	-7.580E-06
57	18.49	774.9	298.3	7.707E-04	6.018E-04	1.614E-04	1048.9	27.6	300.6	1.035E-03	1.80	10.10	81.50	1.863E-05	1.046E-04	8.437E-04	-5.687E-05
58	31.27	750.0	298.8	1.259E-03	9.83E-04	2.64E-04	750.3	26.3	299.3	1.258E-03	0.00	20.50	78.10	0.000E+00	2.58E-04	9.82E-04	-5.945E-06
59	59.55	742.4	298.2	2.379E-03	1.857E-03	4.983E-04	1019	49.6	322.6	3.018E-03	0.70	16.20	81.60	2.113E-05	4.890E-04	2.463E-03	-9.281E-06

Table A2: Description of 9975 Test by Test Number⁵

Run #	Description	Time (days)	Container Volume	Grams PuO ₂	Bulk Weight(g)	Measured Volume	Temp (°C)	Run #	Sample #	H ₂ (vol%)	O ₂ (vol%)	N ₂ (vol%)	CO ₂ (vol%)	N ₂ O (vol%)	CO (vol%)	sum (vol%)
2/20/99 Start -- Set 1																
1	PuO ₂ + RF MgO sand & crucible	8.83	25cc	9.59	37.83	34.11	ambient	1	3-123637	0.55	18.8	84	0	0	0	103.35
2	PuO ₂ + calcined CaO + Ca(OH) ₂	8.92	50cc	8.85	35.80	63.86	ambient	2	3-123636	0.00	17.9	84.5	0	0	0	102.40
3	PuO ₂ Stored over dessicant	9.65	5cc	7.65	7.65	30.50	ambient	3	3-123635	0.00	21.1	82.3	0.05	0	0	103.45
4	PuO ₂ stored in 76%RH humidior	9.71	5cc	8.54	8.54	30.90	ambient	4	3-123634	0.00	20.1	82.5	0.16	0	0	102.76
5	PuO ₂ - 10% H ₂ O added	6.66	5cc	7.57	7.57	29.81	ambient	5	3-123633	10.80	22.8	61.7	0.1	0	0	95.40
6	Standard Gas	3.73	50cc	0.00	0.00	62.33	ambient	6	3-123638	4.20	3.9	81.6	1.8	0.5	1.2	93.20
3/1/99 Start -- Set 2																
7	Standard Gas + Heat	6.31	50cc	0.00	0.00	49.71	90	7	3-123639	3.70	3.6	87	NR	NR	4.06	98.36
8	#2 stored at 100% RH	6.14	50cc	7.73	31.30	64.10	ambient	8	3-123640	0.05	19.6	86	0.1	0	0	105.75
9	PuO ₂ + 30g CaF ₂	6.83	50cc	9.83	39.85	62.91	ambient	9	3-123641	0.08	20.2	85.1	0.09	0.02	0	105.49
10	PuO ₂ +Ca(OH) ₂ & MgO Crucible	5.75	25cc	7.90	15.80	43.46	ambient	10	3-123642	0.62	20.2	83.8	0.06	0	0	104.68
11	#1 stored at 100%RH	6.12	25cc	9.32	36.76	38.51	ambient	11	3-123643	0.26	19.7	88.1	0.05	0.04	4.28	112.43
12	PuO ₂ stored at 100%RH	6.82	5cc	9.52	9.52	30.72	ambient	12	3-123644	0.54	20	84.8	0.12	0.12	0	105.58
3/8/99 Start -- Set 3																
13	44g of RF SS&C sample H6	7.88	50cc	15.50	43.84	51.66	ambient	13	3-123645	6.19	3.1	90.8	0.03	1.6	0	101.72
14	#9 heated	7.88	50cc	9.83	39.85	64.37	90	14	3-123646	0.89	16.7	80	5.2	0.25	0	103.04
15	#8 heated	8.16	50cc	7.73	31.30	65.63	90	15	3-123647	0.00	11.7	82.6	0	0	0	94.30
16	PuO ₂ stored at 100%RH + Heat	7.77	5cc	7.26	7.26	30.78	90	16	3-123648	0.22	15.5	78.2	0.48	0.04	0	94.44
17	Pu Cake (no added moisture)	7.61	25cc	32.01	35.66	42.04	ambient	17	3-123649	1.64	20.6	79.6	0.06	0.05	0	101.95
18	#5 mixed with 2g Ca metal	7.56	5cc	4.88	6.93	30.34	ambient	18	3-123650	24.15	15.5	53.1	0.03	0	0	92.78
3/17/99 Start-- Set 4																
19	CaF ₂ at RT repeat #14 and #9	6.8	50cc	9.83	39.85	52.40	ambient	19	3-123651	0.00	18.2	83.8	0.37	0.08	0	102.45
20	#13 heated	6.8	50cc	15.50	43.84	53.82	90	20	3-123652	80.00	0	23.6	0	0	0	103.60
21	#10 heated	6.81	10cc	7.50	15.00	25.98	90	21	3-123653	2.60	6	95.6	0.16	0.2	0	104.56
22	PuO ₂ +MgO 1:1 ratio	6.81	25cc	9.73	19.45	43.03	ambient	22	3-123654	0.13	15.4	86.3	0.09	0.11	0	102.03
23	#11 heated	6.78	10cc	4.66	20.00	31.95	90	23	3-123655	1.60	11.9	88.6	0.22	0.17	0	102.49
24	PuO ₂ + Mg(OH) ₂	6.79	25cc	7.26	17.26	43.83	ambient	24	3-123656	5.00	19.7	76.6	0.03	0.09	0	101.42
3/26/99 Start-- Set 5																
25	PuO ₂ + MgO with lo water	10.11	10cc	6.60	25.00	14.43	90	25	3-123658	2.17	12.6	82.7	<.1	<.1	<.1	97.47
26	PuO ₂ + MgO with med water	9.74	10cc	6.24	23.43	25.67	90	26	3-123659	1.19	16.2	79.4	<.1	<.1	<.1	96.79
4/6/99 Start-- Set 6																
30	RFETS H2	7.69	50cc	8.18	43.10	63.26	ambient	30	3-125514	1.27	16.5	75.8	<.1	<.1	<.1	93.57
31	PuO ₂ +MgO w/ hi water+heat	8.83	10cc	#REF!	23.09	26.22	90C	31	3-125515	0.03	20.5	76	<.1	<.1	<.1	96.53
32	RFETS H7	7.71	100cc	6.77	14.60	91.65	ambient	32	3-125516	8.13	12.9	78.5	<.1	<.1	<.1	99.53
33	#18 repeated	7.71	10cc	4.65	6.60	38.54	ambient	33	3-125517	1.6	20.2	76.4	<.1	<.1	<.1	98.20
34	RFETS H8	7.69	10cc	8.49	10.80	38.98	ambient	34	3-125518	0.2	20.2	76.9	<.1	<.1	<.1	97.30
4/16/99 Start -- Set 7																
36	RFETS Sample H2	5.61	50cc	8.18	43.10	61.32	90	36	3-125520	74.70	1.3	17.9	0.02	<.1	<.1	93.92
37	#31 repeated	5.66	10cc	6.15	23.09	26.49	90	37	3-125521	0.40	20	64.2	0.03	0.02	<.1	84.65
38	PuO ₂ + 5% H ₂ O	5.69	25cc	9.66	10.29	44.90	ambient	38	3-125522	7.40	14.1	77.7	0.08	0.04	<.1	99.32
4/23/99 Start -- Set 8																
41	PuO ₂ +100%RH -2weeks	5.6	10cc	10.08	10.08	19.25	ambient	41	3-125525	0.7	19.9	81.2	NR	NR	<.1	101.80
44	PuCake + no treatment like #17	5.77	100cc	27.65	30.80	123.67	ambient	44	3-125528	0.2	18.6	82.4	0.32	<.1	<.1	101.52
45	PuO ₂ + 2.5% water	5.77	10cc	12.17	12.50	37.51	ambient	45	3-125529	2.3	21	76.8	<.1	<.1	<.1	100.10
46	PuO ₂ + 2.5% water	5.84	10cc	9.83	10.32	38.12	ambient	46	3-125530	1.2	21.1	62.1	<.1	<.1	<.1	84.40

⁵ Samples 28, 29, 35, 40, 42, 43, 48 and 49 contained materials that do not conform to the content description of SS&C residues.

4/29/99 Start -- Set 9

4/29/99 Start -- Set 9

Table A2: Descriptions of Tests by Test Number (continued)

Run #	Description	Time (days)	Container Volume	Grams PuO ₂	Bulk Weight(g)	Measured Volume	Temp (°C)	Run #	Sample #	H ₂ (vol%)	O ₂ (vol%)	N ₂ (vol%)	CO ₂ (vol%)	N ₂ O (vol%)	CO (vol%)	sum (vol%)
2/20/99 Start -- Set 1																
47	PuO ₂ +2.5% H ₂ O+Heat	6.77	10cc	12.17	12.50	18.96	90	47	3-125531	3.4	7.3	81.8	<0.1	<0.1	<0.1	92.50
50	PuCake - replicate 1	6.76	100cc	27.34	30.46	122.76	ambient	50	3-125534	0.4	18.9	79.2	<0.1	<0.1	<0.1	98.50
51	#41 repeated	6.76	10cc	10.08	10.08	37.11	ambient	51	3-125535	1.5	19.9	73.4	<0.1	<0.1	<0.1	94.80
52	PuCake - replicate #2	6.77	25cc	14.98	16.69	45.15	ambient	52	3-125536	0.55	20.14	78.36	<0.1	0.05	<0.1	99.10
5/18/99 Start -- Set 10																
53	#51 heated	7.95	10cc	10.08	10.08	18.74	90	53	3-127169	1.32	13	85	<0.1	<0.1	<0.1	99.32
54	Blank+Heat	7.95	10cc	0.00	0.00	31.56	90	54	3-127170	0	20	74	<0.1	<0.1	<0.1	94.00
55	PuO ₂ +13mg H ₂ O	7.95	50cc	12.57	12.70	71.49	ambient	55	3-127171	0.36	19	84	<0.1	<0.1	<0.1	103.36
56	PuO ₂ +15mg H ₂ O	7.95	10cc	10.42	10.57	37.50	ambient	56	3-127172	0.25	20	84	<0.1	<0.1	<0.1	104.25
5/26/99 Start -- Set 11																
57	PuO ₂ +15mg H ₂ O	7.75	10cc	10.42	10.57	18.49	90	57	3-127173	1.8	10.1	81.5	<0.1	<0.1	<0.1	93.40
58	Blank	8	10cc	0.00	0.00	31.27	ambient	58	3-127174	0	20.5	78.1	<0.1	<0.1	<0.1	98.60
59	PuO ₂ +13mg H ₂ O	7.78	50cc	12.57	12.70	59.55	90	59	3-127175	0.7	16.2	81.6	2.8	0.31	<0.1	101.61

Exhibit A1: A Plot of the Initial versus Final O₂ by Test Number

Exhibit A2: A Plot of the Change in O_2 (Delta O_2) by Test Number

(Symbols used to identify tests as defined by the categories of Table 1)

Exhibit A3: A Plot of the Change in O₂ (Delta O₂) by Type Group

Means and Std Deviations

Level	Number	Mean	Std Dev	Excluding Heated Tests		
				Number	Mean	Std Dev
Other	39	-0.00006	0.000176			
Pu Cake	4	-0.00007	0.000071			
PuO2	4	-0.00003	0.000036	3	-0.00001	0.000002
PuO2+CaO	3	-0.00013	0.000107	2	-0.00007	0.000039
PuO2+CaF	3	-0.00004	0.000022			
PuO2+MgO	5	-0.00005	0.000035	4	-0.00004	0.000015

Exhibit A4: A Plot of the Change in O₂ (Delta O₂) by Headspace Volume (cc)

Symbols are shaded to designate the categories of Table 1 (i.e., they are shaded as in Exhibit A3).

Exhibit A5: A Plot of the Change in O₂ (Delta O₂) by Total Sample Volume Percent delta O₂ (M)

Symbols are shaded to designate the categories of Table 1 (i.e., they are shaded as in Exhibit A3).

Exhibit A6: A Plot of the Change in O_2 (Delta O_2) by Test Number with Bounding Uncertainties

Bold symbols are used to designate statistically significant (at the 95% confidence level) test results.

Exhibit A7: A Plot of the Change in O_2 (ΔO_2) by Test Number
with Bounding Uncertainties for Representative Tests

Exhibit A8: A Plot of the Initial Versus Final Moles of Oxygen for Representative Tests

≡ Paired t-Test

Paired t-Test

final O2 (M) - initial O2 (M)

Mean Difference	-0.00009	Prob > t	0.0000080
Std Error	0.000018	Prob > t	0.9999960
t-Ratio	-5.0429	Prob < t	0.0000040
DF	45		

Symbols are shaded to designate the categories of Table 1 (i.e., they are shaded as in Exhibit A3).

Distribution List:

WSRC-TR-99-00223

Chuck Armitage, 703-F
Mark Schinitz, 703-F
Clint Wolfe, 773-A
Don Green, 773-A
Bill Shingler, 703-F
Dan Wood, 704-F
Allen Blancett, 773-A
Tami Cappeletti, 773-A
Bob Maher, 703-A
Sue King, 773-54A
Ed Claxton, 704-F
Tim Hasty, 235-F
Dave Poss, 707-C
Martha Ebra, 773-42A
Joel Williams, 707-F
Jim Schornhorst, 992-3W
John Marra, 704-T
Major Thompson, 773-A
Jeff Schaade, 703-F
Lee Hyder, 773-A, C-109
Ned Bibler, 773-A
Tom Walters, 773-A
Alice Murray, 773-A
Steve Hensel, 773-42A
Chip McClard, 703-F
Frank Graham, 773-A
Paul Korinko, 773-A
Tommy Edwards, 773-42A
Danny Prince, 773-41A
Doug Wilhelm, 773-A
Joel Jones, 730-A
John Young, 773-A
Paul Blanton, 773-54A
Neal Askew, 773-A
Ed Moore, 773-41A
Richard Balzer, 773-43A
Charles Keilers, 719-14A
Susan Wood, 773-A
Todd Wright, 773-A
Paul Deason, 773-A
ATS File
CTS File