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Radioactive NCAW Core Sample
(102-AZ-C1) and Simulant During
HWVP Feed Preparation Testing:
Letter Report**

M. H. Langowski
E. V. Morrey
J. M. Tingey
M. R. Beckett

March 1996

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest National Laboratory
Richland, Washington 99352

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SUMMARY

The Hanford Waste Vitrification Plant (HWVP) is being built for the Department of Energy (DOE) to process high-level and transuranic (TRU) waste, producing canistered glass logs for disposal in a national repository. Testing programs, using simulated waste, have been established within the HWVP project to verify process technology. A parallel testing program with actual radioactive waste is being performed to confirm the validity of using simulants in process testing.

The first feed type to be processed by HWVP, and the first to be tested on a laboratory-scale, is pretreated neutralized current acid waste (NCAW). The total inventory of NCAW is contained in two 1,000,000 gal double shell tanks designated 101-AZ and 102-AZ. Three core samples, taken from the two tanks, have been characterized and pretreated (i.e., washed). Results from the offgas characterization of the third NCAW core sample (1st core sample from 102-AZ) during HWVP feed preparation are presented in this letter report.

Waste simulants were processed so they could be compared with laboratory-scale radioactive testing of the core sample. The results of the waste simulant offgas characterization are also reported and comparisons are drawn from the data.

Two laboratory-scale radioactive HWVP feed preparation process tests were completed using the third NCAW core sample. Nine simulant tests were completed. Feed preparation process steps consisted of formic acid addition (forming), digestion, recycle waste stream addition, and second digestion. On-line offgas composition/generation rate, slurry temperature, and slurry pH measurements were collected during testing. The offgases measured included H_2 , NO_x , N_2O , NO , CO_2 , CO , and N_2 . Online total hydrocarbon analysis was performed during the forming of the core sample. In addition, two offgas grab samples were analyzed for volatile organic species. The formed core sample was also analyzed to determine NH_3 , nitrate, nitrite, ^{14}C , and ^{129}I concentrations. Finally, scanning electron microscopy was performed on the formed core sample to determine the physical/chemical form of the noble metals (i.e., Pd, Rh, and Ru).

Results indicated that slurry chemistry and offgas generation reactions were similar between the core sample and simulants. Observed offgas differences between simulant and core sample could be explained by differences in testing conditions and slurry chemical composition with the exception of H_2 . Process temperature, slurry composition, acid/base neutralization capacity of the slurry, and formic acid addition rate are crucial variables that must be controlled (i.e. differences minimized) to compare core sample and simulant offgas behavior. The reason(s) for the differences in H_2 generation is not apparent at this time. With the exception of H_2 generation, current data indicates that the simulants being used in process development work are appropriate, but require additional investigation in the critical areas of H_2 and NH_3 generation.

Tests were repeatable (offgas generation rates and amounts within 25% with the exception of

H₂). Differences observed between the hot cell and the out-of-cell simulant tests were on the same order as duplicate tests so that differences were not attributed to the test set up location.

Nitrogen and carbon mass balances showed 92% and 94% element accountability, respectively. Uncertainty in analytical and offgas measurements are possible sources of error. NH₃ generation between the core sample and simulant were comparable based on the amounts of H₂ measured (i.e., measured NH₃/measured H₂ were within 16%).

Simulant tests performed with variable concentrations of noble metals showed a correlation between total measured H₂ and noble metals. Less total H₂ was produced as the concentration of noble metals decreased. Simulant tests performed with increased amounts of carbonate showed a relative delay (i.e., when specific tests were compared) in H₂ initiation. The peak H₂ generation rate was also observed to increase with a decrease of slurry pH at the time of H₂ initiation. In addition, a decrease in slurry pH at the time of H₂ initiation was observed for the slurry with less carbonate. N₂O generation was generally more and NO_x generation was generally less, in simulants with more carbonate when compared to simulants with less carbonate.

Offgas generation profiles for the 80 ml laboratory simulant test were similar to 1500 ml laboratory simulant test (results varied within 7% for CO₂ total moles to 31% for NO_x total moles), which indicated that scale-up correlations might be possible.

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Acronyms

HEPA	High Efficiency Particulate Air
HWVP	Hanford Waste Vitrification Plant
gWO	grams of Waste Oxides
IC	Ion Chromatography
ICP-ES	Inductively Coupled Plasma-Emission Spectroscopy
NCAW	Neutralized Current Acid Waste
RPPLT	Radioactive Process/Product Laboratory Testing
R/RCE	Redox/Rheology Control Evaluation
SIPT	Slurry-Integrated Performance Testing
THC	Total Hydrocarbons
gTO	grams of Total Oxides
WFQ	waste form qualification
SRTC	Savannah River Technical Center
PNL	Pacific Northwest Laboratory
SEM	Scanning Electron Microscopy
PHTD	PNL HWVP Technology Development
DST	Double Shell Tank

1.0 Introduction

The primary objective of the Radioactive Process/Product Laboratory Testing (RPPLT) is to provide preliminary confirmation that the nonradioactive waste feed simulant recipe is adequate for addressing the testing needs of design, safety, waste form qualification (WFQ), and permitting of the Hanford Waste Vitrification Plant (HWVP). Work was authorized by the Fiscal Year (FY) 1991 and 1992 Statements of Work for Applied Technology Tasks to be Performed by PHTD in Support of the HWVP Project, WHC-SP-0638 Revision 0 and WHC-SD-HWV-SOW-002 Revision 0.

Pacific Northwest Laboratory (PNL)¹ HWVP Technology Development (PHTD) Project testing is an extension of Double-Shell Tank (DST) Characterization Program study to characterize the first core sample from Tank 102-AZ (or the third NCAW core sample). The DST study has been completed and resulted in characterization and pretreatment of the core sample and characterization of the resulting washed solids. All work was performed under the Technology Program Plan, Characterization of Core Samples from DST's 101-AZ and 102-AZ, Revision 1, June 1989. Washed solids samples and analyses from the DST Characterization Program were used to perform forming tests and characterize H₂ generation for the RPPLT task.

The information contained in this letter report specifically addresses offgas production during the forming, digestion, and recycle addition of the third Neutralized Current Acid Waste (NCAW) core sample and core simulant. Testing was conducted using a laboratory-scale version of the HWVP flowsheet.

2.0 Approach

2.1 Simulant Preparation

Waste simulants were used in laboratory-scale radioactive testing to develop and test procedures for use in the hot cell and to directly compare results with the core sample. The simulants were prepared using the method developed by Wiemers et al. (1993) to simulate the history of the waste processing. The method involves the co-precipitation of Fe, Ni, and Zr hydroxides, the precipitation of MnO₂ from KMnO₄ and Mn(NO₃)₂, the precipitation of Al(OH)₃, and the co-precipitation of minor component hydroxides in the presence of insoluble components. Precipitation and co-precipitation of hydroxides are accomplished by adding NaOH to metal nitrate solutions. Soluble components are added after the various slurries have been washed to remove nitrate and sodium. This method for NCAW preparation, or variations of it, is used to prepare simulants for the HWVP process development testing on all scales (i.e., laboratory-scale through full scale (SIPT)).

Four simulants that varied slightly in composition were used. The compositions of the simulants and core sample are reported in **Appendix A: Core Sample, Simulant, and Recycle Compositions**. Inductively Coupled Plasma-Emission Spectroscopy (ICP-ES) results for the major cations and Ion Chromatography (IC) results for the anions are

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summarized in the tables in Appendix A. The recycle waste stream simulant composition is also listed in the appendix. The recycle simulant was added to the NCAW simulant and the core sample to simulate the HWVP process flow sheet. The FY 1991 simulant was obtained from the Redox/Rheology Control Evaluation (R/RCE) cost account, or laboratory-scale testing, and was used in R/RCE FY 1991 laboratory-scale tests (Tests L3.1 and L5.2). The FY 1991 simulant was also used in RPPLT Tests S1.1 and S1.2. FY 1991 simulant matches nominal concentrations as detailed by R. A. Smith² except the noble metals' concentrations (i.e., Pd, Rh, and Ru), are 25% higher.

The second simulant, used in Tests S2.1-S2.4, closely matches the non-radioactive components of the core sample based on the analysis of the washed solids. Offgas testing of the core sample and analysis of the formed slurry resulted in revised estimates of carbonate and noble metals in the core sample washed solids. The soluble components of the second simulant were rebatched to produce a simulant with proper carbonate concentration (i.e., 151% less carbonate than in the initial simulant used in S2.1-S2.4). This second simulant was used in Test S2.5.

The noble metals concentration could not be adjusted in the initial simulant, so two additional simulants were prepared to approximate the core sample revised composition. Due to budget and time constraints, it was decided to use the already prepared Slurry Integrated Performance Testing (SIPT) NCAW simulant. The SIPT NCAW simulant was prepared to targets supplied by R. A. Smith² except it did not contain noble metals, carbonate or nitrite. RA Smith's composition varies slightly from the revised core sample analysis, and therefore significant components were adjusted to match the core sample. The simulant used in Test 2.6 had Fe, Al, nitrite, nitrate, and carbonate, matched to the revised core sample composition. Test S2.7 simulant was prepared with SIPT simulant with additions to match Fe, Al, nitrite, nitrate, carbonate, and the noble metals (Pd, Rh, and Ru) to the revised core sample composition. A simulant was not prepared with all components identical to the core sample.

The composition variables of simulants and the initial and revised core sample analysis are shown in Table 2.1.1. The L3.1 and L5.2 variables are listed for comparison purposes. The L5.2 and L3.1 were performed by R/RCE in FY 1991. Further details for these two test are reported in Wiemers et al. (1993).

2.2 Core Sample

The limited amount of washed solids (≈ 15 g WO) from the first NCAW core sample³ from Tank 102-AZ precludes a conventional test matrix. Only two duplicate runs were performed. The core sample was split into two 57.5 ml (@125 gWO/L) batches for each run. Not enough core

²Letter from R.A. Smith to J.M. Creer (1991). "Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Scale Testing-Errata Correction."

³The core sample is the third NCAW core sample but the first removed from Tank 102-AZ. The first two were removed from Tank 101-AZ.

Table 2.1.1: Composition Variables for the 1st 102-AZ Core Sample and Simulants

Component	Nominal NCAW FY 1991 Simulant ^a				
	L3.1 mole E/L (@ 125g WO/L)	L5.2 mole E/L (@ 125g WO/L)	S1.1 mole E/L (@ 125g WO/L)	S1.2 mole E/L (@ 125g WO/L)	
CO3--	1.25E-01	1.25E-01	0.00E+00	1.25E-01	
NO2-	4.35E-01	1.31E-01	4.35E-01	1.31E-01	
NO3-	1.16E-01	1.30E-01	1.30E-01	1.30E-01	
Pd	1.26E-03	1.45E-03	1.45E-03	1.45E-03	
Rh	1.04E-03	1.28E-03	1.28E-03	1.28E-03	
Ru	3.85E-07	4.79E-03	0.00E+00	4.79E-03	
Al	2.27E-01	2.27E-01	2.27E-01	2.27E-01	
Fe	4.51E-01	4.51E-01	4.51E-01	4.51E-01	

Component	Core Sample				
	Initial Analysis mole E/L (@ 125g WO/L)	Revised Analysis mole E/L (@ 125g WO/L)	S2.1-S2.4 mole E/L (@ 125g WO/L)	S2.5 mole E/L (@ 125g WO/L)	S2.6 mole E/L (@ 125g WO/L)
CO3--	2.53E-01	7.50E-02	2.53E-01	7.50E-02	7.50E-02
NO2-	2.61E-01	2.61E-01	2.61E-01	2.61E-01	2.61E-01
NO3-	1.15E-01	1.16E-01	1.15E-01	1.15E-01	1.40E-01
Pd	1.32E-03	6.15E-05	1.32E-03	1.32E-03	1.31E-04
Rh	1.09E-03	1.22E-04	1.09E-03	1.09E-03	3.42E-04
Ru	4.04E-03	1.05E-03	4.04E-03	4.04E-03	3.28E-03
Al	4.79E-01	4.79E-01	4.79E-01	4.79E-01	4.79E-01
Fe	5.66E-01	5.66E-01	5.66E-01	5.66E-01	5.66E-01

Simulant Target Values (continued)

*Wiemers et. al., 1993 from FY 1991 NCAW Simulant Target Composition based on Smith, 1991.					
S1.1, S1.2, L3.1 and L5.2	FY1991 simulant Reference Wiemers et al PHTD-C93-03.02A K899 See Appendix A.	Initial Core Sample Analysis Composition. See Appendix A. (Noble Metals 7% higher than nominal)	Initial Core Sample Analysis Composition except for carbonate. Carbonate concentration is the same as the Revised Core Sample Analysis. See Appendix A. (Noble Metals 7% higher than nominal).	SPT feed composition Smith's letter (All other components other than listed above)	See Appendix A.
S2.1-2.4					
S2.5					
S2.6-2.7					

sample was available to have the planned two 80 ml batches. Due to radiolytic damage to the container lid, the core sample was dry when received from the Tank Characterization Program. The sample was exposed to $\approx 30^{\circ}\text{C}$ ambient temperature. Deionized water was added to the core sample to process it as slurry. Characterization results of the third NCAW core sample, reported by Gray et al.⁴, provided a target composition for the simulant.

The target simulant composition was revised after the forming of the core sample showed that the amount of carbonate was 3.4 times less than the initial core sample analysis. In addition, the noble metals were reanalyzed and found to be less than the initial core sample analysis. The revised core sample analysis showed 22.4 times less Pd, 9.3 times less Rh, and 3.1 times less Ru (mole element/L) than the initial core sample analysis.

The compositions of the core sample and core simulants are shown in Appendix A. As stated previously, the composition variables of simulants and the initial and revised core sample analysis are shown in Table 2.1.1.

2.3 Testing

2.3.1 Equipment

The apparatus used in forming the core sample and simulants (S1.1-S1.2, and S2.1-S.2.4) is shown in Figure 2.3.1. A slightly different apparatus was used in forming 1500 ml batch size simulants. The apparatus for the 1500 ml batch size is essentially the same, except for a few differences. The differences are listed in Table B1 in Appendix B. Offgas equipment with detection limits is shown in Table 2.3.1.1.

2.3.2 Test Descriptions

The following steps were performed for each test:

1. Monitored offgas for H_2 , CO_2 , NO_x , N_2 , O_2 , CO , and N_2O during all test phases. Monitored slurry pH and temperature during all test phases.
2. Heated slurry to 95°C . Allowed temperature to stabilize for 10 min. Added ≈ 90 wt% HCOOH at a specified rate based on batch size (Equivalent to a full-scale batch size rate of 2 gal/min). Collected condensate. Added water to keep volume constant.
3. Heated slurry to boiling ($\approx 101^{\circ}\text{C}$). Boiled for 4 h. Collected condensate. Added water to keep volume constant.
4. Added recycle waste stream simulant. Boiled for 2 h at 101°C . Added water to keep volume constant.

⁴Letter report to Westinghouse Hanford Company prepared by W. J. Gray, M. E. Peterson, R. D. Scheele, and J. M. Tingey of Pacific Northwest Laboratory, Richland, Washington (1991).

"Characterization of the First Core Sample of Neutralized Current Acid Waste from Double Shell Tank 102-AZ."

FIGURE 2.3.1 RADIOACTIVE OFFGAS MEASUREMENT SYSTEM

Table 2.3.1.1: Offgas Equipment Detection Limits

Gas	Method of Measurement	Approximate Minimum Detection Limit	Approximate Accuracy $\pm$
CO ₂	Gas Chromatograph	50 ppm	2 %
N ₂ O	Gas Chromatograph	50 ppm	2 %
NO _x	Chemiluminescent	1 ppm	7 %
H ₂	Gas Chromatograph	10 ppm	2 %
N ₂	Gas Chromatograph	100 ppm	2 %
O ₂	Gas Chromatograph	100 ppm	2 %
CO	Gas Chromatograph	200 ppm	2 %

Offgases produced during the forming, digestion, and recycle addition were collected and analyzed on one core sample to generate source term data and to support safety issues related to H₂ and NH₃ generation in the HWVP. Nearly continuous (1-min interval) measurements were made of the following components: H₂, NO, NO₂, N₂O, CO, CO₂, N₂, O₂, and total hydrocarbons. Helium was introduced into the system as a dilution gas and was measured to allow calculation of molar generation rates of each of the gases. The total amounts of NH₃, ¹⁴C, and ¹²⁹I generated during core sample tests were measured by analytical chemical methods. Ammonia was also measured for Test S2.4 (in hot cell forming of simulant). Grab samples of offgas were taken during the core sample run R1.1 when a response was observed from the flame ionization detector and analyzed by GC/MS to determine speciation of volatile organics.

Nine simulant runs and two core sample tests were performed. The tests are listed in Table 2.3.2.1. Simulant or core sample identification is tabulated along with the test description for each test. Tests L3.1 and L5.2 were run in FY 1991 by the R/RCE cost account or laboratory scale. Information is provided on L3.1 and L5.2 to facilitate comparisons between RPPLT and R/RCE testing.

Batch size, HCOOH amount and rate are shown in Table 2.3.2.2 for each test. Formic acid addition rate and amount are scaled appropriately to batch size. Batch sizes varied from 57.5 ml for the core sample tests to 1500 ml for laboratory-scale size testing. Formic acid was generally added until the H₂ generation rate was observed to peak.

3.0 Results

Offgas generation, nitrogen and carbon mass balances, N₂O/NO_x ratios, NO/NO_x generation, THC, ¹⁴C, ¹²⁹I, and volatile organic results are reported in this section for radioactive testing. Simulant data are provided where applicable. Additional information about simulant composition, mass balance calculations, acid/base neutralization capacity, carbon analytical methods, and carbon and anion concentrations are contained in Appendixes A-E.

3.1 Offgas Generation

The amount of each gas component (in moles/L of slurry @ 125 gWO/L) released for each test and process phase are shown in Table 3.1.1. The peak generation rates (in mmoles/min/L of slurry @ 125 g WO/L) for each test are shown in Table 3.1.2. The amounts have been normalized for batch size to allow for easier comparison. The reaction mechanisms theorized to account for the majority of the measured offgases are as follows (Wiemers et. al. 1993):

3.1.1 Scale Up: Tests S1.2 and L3.1

The first tests were performed to show comparisons between the radioactive laboratory-scale setup (batch size=80 ml) and the R/RCE laboratory-scale (batch size=1500 ml) simulant setup (scale-up factor of 18). Tests S1.2 and L3.1 are directly comparable on the different

Table 2.3.2.1: Simulant and Test Description for RPPLT and Other Tests

Run Number	Simulant Description	Test Description
S1.1	FY 1991 Simulant received from Redox/Rheology Control Evaluation (Laboratory-Scale)	Scale up of RPPLT to Redox/Rheology Control Evaluation (Laboratory-Scale) (80 ml batch size compared to 1500 ml)
S1.2	FY 1991 Simulant received from Redox/Rheology Control Evaluation (Laboratory-Scale)	Scale up of RPPLT to Redox/Rheology Control Evaluation (Laboratory-Scale) Test 3.1 (80 ml batch size compared to 1500 ml)
S2.1	Core Simulant with Initial Core Sample Analysis Composition	Duplicate run of Test S2.3 (80 ml batch size)
S2.2	Core Simulant with Initial Core Sample Analysis Composition	Aborted test
S2.3	Core Simulant with Initial Core Sample Analysis Composition	Simulant run out of hot cell for comparison to simulant run in hot cell (80 ml batch size)
S2.4	Core Simulant with Initial Core Sample Analysis Composition	Simulant run in hot cell for comparison to S2.3 and core sample run (80 ml batch size)
S2.5	Core Simulant with CO_3^{--} adjusted to the Revised Core Sample Analysis Composition; Noble Metals are the same as the initial core sample analysis composition	Noble Metals Comparison: Simulant with 22.4 x Pd, 9.3 x Rh, (1.5 L batch size), 3.1 x Ru as the revised core sample analysis
S2.6	SIPT Simulant with composition adjusted for Fe, Al, CO_3^{--} , NO_2^- and NO_3^- Final Core Sample Analysis Composition	Noble Metals Comparison: Simulant with 2.2 x Pd, 2.8 x Rh (1.5 L batch size), 3.1 x Ru as the revised core sample analysis (units=>mole E/L)
S2.7	SIPT Simulant with composition adjusted for Noble Metals, Fe, Al, CO_3^{--} , NO_2^- and NO_3^- Final Core Sample Analysis Composition	Simulant with the revised noble metals content for comparison to the core sample (1.5 L batch size)
R1.1	1st NCAW Core Sample from Tank 102-AZ	Formating of NCAW core sample in hot cell
R1.2	1st NCAW Core Sample from Tank 102-AZ	Duplicate run of Test R1.1 (R1.1).

Table 2.3.2.1 (continued)

Run Number	Simulant Description	Test Description
L3.1	FY 1991 simulant with nominal noble metals, Redox/Rheology Control Evaluation (R/RCE)	Test run by Laboratory-scale R/RCE FY 1991. 30% nominal nitrite case ($\text{NO}_2^- \sim 0.13$ mole/L) Provides comparison for 80 ml to 1.5 L batch size scale-up.
L5.2	FY 1991 simulant without noble metals, R/RCE	Test run by Laboratory-scale R/RCE FY 1991 (1.5 L batch size). Simulant without noble metals case. Provides comparison for core sample offgas generation (R1.1).

Table 2.3.2.2: Batch size, Formic Acid Amount, and Addition Rate for RPPLT and Other Tests

Test No.	Batch Size (ml)	Amount of 90 wt% Formic Acid Added to Slurry (ml)	Formic Acid Addition Rate (ml of 90 wt% HCOOH/min)	Amount of HCOOH Added to Slurry (moles HCOOH/L of slurry @ 125 gWO/L)	Formic Acid Addition Rate (moles HCOOH/min/ L of slurry @ 125 gWO/L)
S1.1	80	4.00	0.0348	1.17	0.0102
S1.2	80	4.82	0.0361	1.42	0.0106
S2.1	80	6.86	0.0273	2.01	0.0080
S2.2	80	Aborted test	Aborted test	Aborted test	Aborted test
S2.3	80	6.88	0.0280*	2.02	0.0082*
S2.4	80	7.08	0.0271	2.07	0.0080
S2.5	1500	98.9	0.4435	1.55	0.0069
S2.6	1500	98.8	0.4431	1.55	0.0069
S2.7	1500	98.9	0.4643	1.55	0.0073
R1.1	57.5	4.26	0.0186	1.74	0.0076
R1.2	57.5	3.31	0.0166	1.35	0.0068
L3.1	1500	66.4	0.6116	1.10	0.0096
L5.2	1500	92.5	0.5491	1.43	0.0086

* The HCOOH addition rate was delayed (slower) initially by a pump malfunction. The rate in the table is over the time interval of ~33 min to the ~280 min. The average rates over 0 to 280 min were 0.0248 ml/min and 0.0073 moles/min/L.

Table 3.1.1: Amount of Gas Components Released (moles/L of slurry @ 125 g WO/L)

Test	Gas Species	Formic Acid Addition	Digestion	Recycle	Total Gas
S1.1	H ₂	0.0046	0.0282	—	0.0328
	CO ₂	0.2536	0.1474	—	0.4010
	N ₂ O	0.0240	0.0035	—	0.0275
	NO _x	0.0647	0.0048	—	0.0695
S1.2	H ₂	0.0024	0.0162	—	0.0185
	CO ₂	0.3348	0.1160	—	0.4508
	N ₂ O	0.0508	0.0014	—	0.0522
	NO _x	0.0067	0.0005	—	0.0072
S2.1	H ₂	n/a	0.0303	n/a	n/a
	CO ₂	n/a	0.1294	n/a	n/a
	N ₂ O	n/a	0.0021	n/a	n/a
	NO _x	n/a	0.0014	n/a	n/a
S2.3	H ₂	0.0069	0.0473	0.0134	0.0677
	CO ₂	0.5052	0.1792	0.0595	0.7438
	N ₂ O	0.0907	0.0025	0.0005	0.0937
	NO _x	0.2593	0.0029	0.0005	0.0293
S2.4	H ₂	0.0053	0.0318	0.0060	0.0432
	CO ₂	0.4438	0.1429	0.0396	0.6262
	N ₂ O	0.0862	0.0013	0.0009	0.0884
	NO _x	0.0208	0.0009	0.0003	0.0220
S2.5	H ₂	0.0222	0.0613	0.0115	0.0950
	CO ₂	0.3889	0.1039	0.0303	0.5231
	N ₂ O	0.0842	0.0000	0.0003	0.0845
	NO _x	0.0503	0.0000	0.0000	0.0503
S2.6	H ₂	0.0024	0.0411	0.0399	0.0834
	CO ₂	0.2501	0.1215	0.0849	0.4565
	N ₂ O	0.0127	0.0024	0.0006	0.0158
	NO _x	0.2119	0.0016	0.0014	0.2141
S2.7	H ₂	0.0008	0.0306	0.0157	0.0471
	CO ₂	0.2193	0.0985	0.0395	0.3573
	N ₂ O	0.0091	0.0009	0.0005	0.0104
	NO _x	0.2547	0.0030	0.0010	0.2587

Table 3.1.1 (continued)

Test	Gas Species	Formic Acid Addition	Digestion	Recycle Addition	Total Gas
R1.1	H ₂	0.0007	0.0094	0.0050	0.0151
	CO ₂	0.1674	0.0653	0.0216	0.2543
	N ₂ O	0.0331	0.0003	0.0007	0.0341
	NO _x	0.0856	0.0015	0.0009	0.0880
R1.2	H ₂	0.0005	0.0087	0.0052	0.0144
	CO ₂	0.1532	0.0529	0.0264	0.2326
	N ₂ O	0.0241	0.0007	0.0007	0.0256
	NO _x	0.1178	0.0023	0.0014	0.1215
L3.1	H ₂	0.0079	0.0157	-	0.0236
	CO ₂	0.3390	0.0812	-	0.4202
	N ₂ O	0.0571	6.6E-04	-	0.0578
	NO _x	0.0050	4.2E-05	-	0.0050
L5.2	H ₂	7.24E-04	3.92E-04	-	0.0011
	CO ₂	0.2983	0.0028	-	0.3012
	N ₂ O	0.0145	6.3E-04	-	0.0151
	NO _x	0.1839	0.0092	-	0.1931

Table 3.1.2: Peak Gas Generation Rates (mmole/min/L of slurry @ 125 g WO/L)

Test	H ₂	CO ₂	N ₂ O	NO _x
S1.1	0.404	4.94	0.696	2.57
S1.2	0.318	4.51	1.555	0.203
S2.1	≈0.282	5.785	≈1.143	0.384
S2.3	0.442	5.906	1.216	0.438
S2.4	0.259	4.875	1.145	0.406
S2.5	0.540	4.583	1.020	0.640
S2.6	0.463	3.297	0.150	2.373
S2.7	0.358	3.899	0.124	3.114
R1.1	0.058	4.079	0.441	1.340
R1.2	0.111	3.594	0.329	1.696
L3.1	0.280	5.338	1.363	0.180
L5.2	<0.033	4.433	0.187	2.593

setups. Figure 3.1.1.1 shows the comparison of offgas process profiles for tests S1.2 and L3.1. The simulant used in both tests was identical and contained 30% nominal nitrite (0.131 mole NO_2^-/L) and 100% nominal carbonate (0.125 mole $\text{CO}_3^{2-}/\text{L}$). Test S1.2 was conducted with a batch size of 80 ml, and L3.1 was conducted by R/RCE laboratory-scale during fiscal year 1991 with an ≈ 1500 ml batch size.

As shown in Figure 3.1.1.1, Table 3.1.1 and Table 3.1.2, the peak gas generation rates and total gas components released compare very well between scales (results varied within 7% for CO_2 total moles to 31% for NO_x total moles). This is consistent with results from Savannah River Technical Center (SRTC), which reported agreement between scales (scale-up factor $>10^4$), between hot cell and laboratory tests, and between radioactive and simulant waste (Ha et al. 1992). These results combined with SRTC's indicate that laboratory-scale results could be scaled up to predict plant scale to support safety, design, etc. Further study on the scale-up of data is being performed by Merz and Ryan⁵ and will include RPPLT data from this report.

3.1.2 Duplicate Simulant Runs: Test S2.1 and S2.3

Two identical runs were performed on the radioactive laboratory-scale setup to establish reproducibility. The offgas profiles for the identical tests, S2.1 and S2.3, are shown in Figure 3.1.2.1. Total mole values were not available for Test S2.1 due to problems with the offgas equipment that resulted in the loss of data during formic acid and recycle additions. The digestion phase data were available, except for an ≈ 20 minute portion that was estimated for H_2 and CO_2 gases, to produce the values in Table 3.1.1. The curves were such that estimation was possible (See Figure 3.1.2.1). Some agreement exists between total moles produced during digestion for Tests S2.1 and S2.3. Peak generation rates for Tests S2.1 and S2.3 agreed within 6% for N_2O and CO_2 . The NO_x peak generation rates differed by $\approx 12\%$. The S2.3 peak H_2 generation rate was 1.6 times higher than the rate observed in S2.1. However, the peak generation rate may be slightly higher than shown in Table 3.1.1 for test S2.1 because the data lost over the 20 min interval may contain the H_2 peak generation rate.

To better compare the data, the amounts of gas produced were determined over approximately the same time interval for tests S2.1, S2.3, and S2.4 (See Table 3.1.2). The time interval consisted of time to destroy the carbonate phase plus 45 min. This time interval was chosen based on the availability of data from S2.1. Hydrogen data was not available for Test S2.1. The agreement between Tests S2.1 and S2.3 for CO_2 and N_2O gases is within 11%; NO_x data is within 25%; H_2 is within 33.3%. Based on these results and the peak generation rates the repeatability between identical tests is reasonable (i.e.,

⁵D. Merz and J. L. Ryan. 1993. Redox/Offgas Summary Report, PHTD-C93-3.02L. To be published.

Figure 3.1.1.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests S1.2 and L3.1

Test # S2.1 (Normalized to a 1 Liter Batch @ 125 g TO/L)

Test # S2.3 (Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure 3.1.2.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests S2.1 and L2.3

offgas generation rates and amounts are within 10 to 25% with the exception of H₂).

Table 3.1.2.1: Amount of Offgas Produced During Carbonate Destruction Phase Plus 45 minutes for Tests S2.1, S2.3, and S2.4

Test	Gas Species	Amount of Gas Produced During Carbonate Destruction Phase + 45 min (moles/L)
S2.1	H ₂	n/a
	CO ₂	0.3600
	N ₂ O	0.0584
	NO _x	0.0147
	Integration Time Interval	0 to 191 min
S2.3	H ₂	0.0022
	CO ₂	0.3539
	N ₂ O	0.0658
	NO _x	0.0192
	Integration Time Interval	0 to 201 min
S2.4	H ₂	0.0033
	CO ₂	0.3584
	N ₂ O	0.0705
	NO _x	0.0161
	Integration Time Interval	0 to 222 min

3.1.3 Tests Run Out of Hot Cell and In Hot Cell: Tests S2.3 and S2.4

Tests S2.3 and S2.4 are directly comparable tests between the laboratory setup and the hot cell setup. Test S2.4 was performed with simulant to test the apparatus for the core sample forming. It was also necessary to verify that hot cell testing did not influence the data. The hot cell test offgas generation rates and total moles generally compared to S2.3. Peak and total component values were within $\pm 25\%$, with the exception of H₂ (~36% difference in total moles and 41.4% difference in peak generation). **Figure 3.1.3.1** shows the comparison between Tests S2.3 and S2.4 offgas process profiles. S2.4 pH data is not shown in the figure due to a malfunction in the pH probe during testing.

In Table 3.1.2.1, comparing Tests S2.4, S2.3, and S2.1 (Note: S2.1 and S2.3 are identical runs) offgas profiles over the time interval shown shows better agreement. The results of S2.4 are bracketed by the results from the two duplicate runs S2.1 and S2.3

Figure 3.1.3.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests S2.3 and S2.4

for CO_2 and NO_x . Values of N_2O for S2.4 and S2.3 are within 7%. From these results, it was concluded that the observed offgas differences between the in-cell and out-of-cell tests were not significant and were on the same order as the differences observed when tests were repeated (i.e., Tests S2.1 and S2.3).

3.1.4 Core Sample, Duplicate Runs: Tests R1.1 and R1.2

The core sample was divided into two 57.5 ml batches to perform duplicate runs R1.1 and R1.2. Originally, the batch size was to have been 80 ml but less sample was available when the core sample was received. Offgas results of CO_2 from forming the core sample showed much less carbonate ($0.075 \text{ mole CO}_3^{2-}/\text{L @ } 125 \text{ gWO/L of slurry}$) present than indicated in the initial core sample analysis ($0.253 \text{ mole CO}_3^{2-}/\text{L @ } 125 \text{ gWO/L of slurry}$). Carbonate destruction is characterized by the large initial CO_2 peak as seen in Figure 3.1.4.1. A rough estimate of carbonate concentration can be obtained by integrating this peak. Integration results for CO_2 /carbonate are shown in Appendix E. The amount of HCOOH added to R1.2 was less than R1.1 in order to maintain the proper redox when the melter feed batches were combined for vitrification.

Some NaNO_3 , CsNO_3 , and NaNO_2 were added to specified target amounts⁶ in the core sample before it was divided into two batches for processing. Additions of nitrate, nitrite, and cesium were per test plan⁷ instructions. The effects of these components are significant in forming and vitrification. Prior to the HWVP, NaNO_2 and CsNO_3 will be added to some or all of the feeds to help prevent corrosion and recover cesium. Some NaNO_2 and CsNO_3 were added to the core sample to simulate this addition. Addition of NaNO_3 was performed to adjust the nitrate concentration to nominal nitrate concentration. This action can be justified by the fact that nitrate concentrations in the cesium recovery stream are estimated to be higher than stoichiometric CsNO_3 .

Total offgas values compared within 8.5% for H_2 and CO_2 ; N_2O and NO_x values compared within 27.6%. More NO_x and less N_2O were produced in R1.2 than R1.1. The pH dropped faster in R1.2 than in R1.1. The HNO_2 disproportionation reaction is favored as the pH decreases (Wiemers et al. 1993 and Smith et.al. 1993). Thus, more NO is produced as the pH decreases. The higher amounts of NO_x observed while processing of R1.2 might be attributed to the faster decrease in pH. It is possible that R1.1 had a slightly higher

⁶0.116 moles NO_3^-/L of slurry @ 125 gWO/L (nominal, Smith 1991²)

5.32E-03 moles Cs/L of slurry @ 125 gWO/L (nominal, Smith 1991²)

0.261 moles NO_2^-/L of slurry @ 125 gWO/L (60% nominal, Smith 1991²)

⁷1992. "Test Plan, Laboratory-Scale Testing of the First Core Sample from Tank 102-AZ." PHTD-C92-05.05A. Prepared by Pacific Northwest Laboratory, Richland, Washington.

Figure 3.1.4.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests R1.1 and R1.2

amount of carbonate as a result of a nonhomogeneous division of the core samples. In Figure 3.1.4.1, the large carbonate peak characteristic of carbonate destruction appears slightly larger than the peak in R1.2. This lends evidence that more carbonate is present in R1.1. The R1.1 core sample would have experienced a slightly greater slurry buffering effect due to the carbonate.

Peak generation rates were within 12% to 47.7% for all offgases. Hydrogen generation did not form a sharp peak characteristic of simulant work (Wiemers et al. 1993) in test R1.1. Instead, a gentle rise was observed during digestion. The slower rise in H₂ generation is more characteristic of non-noble metal simulants (Wiemers et al. 1993 and Langowski et al. 1993). It is not known under what conditions the slower rise in H₂ generation is favorable except under zero concentration of noble metals. Test R1.2 exhibited a sharper peak during digestion. This peak resulted after the slurry volume decreased to a low amount through the evaporation of water. It is believed that some of the core sample may have dried out around the sides of the vessel and was superheated, causing a peak in H₂ generation. In a related but different series of offgas testing, H₂ was observed to be generated at ≈200°C from heating dried solids (formed slurry with frit).⁸

The higher generation rates for CO₂ and N₂O, 4.08 and 0.44 mmoles/min/L (Table 3.2.1), observed in Test R1.1 may be attributed to the presence of more carbonate, leading to slurry buffering conditions more favorable to the production of N₂O. The proposed slurry chemistry reaction for N₂O production is as follows:

The production of N₂O by this reaction also produces CO₂ so that increased N₂O production is accompanied by an increase in CO₂ production. This is shown in Figure 3.1.4.1. The NO_x peak generation rate in R1.2 is approximately 21% higher than in R1.1. The faster pH drop may have resulted in more NO produced by disproportionation, leading to a higher peak generation rate.

A significant amount of CO₂ was still being produced after nitrite destruction. More CO₂ is observed than can be accounted for by the destruction of formic acid by the following reaction:

The proposed slurry reaction for NH₃ production shows four moles of CO₂ produced for every mole of nitrate consumed by reaction with formic acid. This reaction is shown

⁸Personnel communication with E.V. Morrey and P.A. Smith. Results from testing conducted by P.A. Smith and J. Vienna.

below:

The CO_2 generation observed after 200 min in test R1.1 is consistent with the production of NH_3 and the proposed slurry reaction. The amount of NH_3 produced during the processing of runs R1.1 and R1.2 was 0.152 g NH_3/L of slurry or 1.02 mmoles NH_3 . A rough integration of R1.1 and R1.2 from 200 to 600 min gives an estimated 1.15 mmoles of NH_3 . Ammonia results are discussed further in section 3.5.

3.1.5 Core Sample Compared to Simulant with Noble Metals: Tests R1.1 and S2.7

It should be noted that the simulant used in Test S2.7 was not identical to the core sample (see Table A2 in the Appendix A for compositional differences). Carbonate, nitrite, nitrate, Pd, Rh, Ru, Fe and Al were matched (in Test S2.7 simulant) to the core sample to provide a more representative simulant. These components were either major components or thought to be important in slurry chemistry reactions. The effect of the compositional differences is unknown.

Figure 3.1.5.1 shows the comparison of offgas process profiles for Tests R1.1 and S2.7. About three times more H_2 and NO_x were generated during S2.7 than R1.1. Approximately 1.4 times more CO_2 was generated during S2.7 than R1.1.

Due to data acquisition software problems, pH measurements are not available for S2.7. However, S2.6, which had a simulant composition very similar to S2.7 (except for noble metals concentrations), exhibited a similar offgas process profile (See Figure 3.1.5.2). It is reasonable to assume that the pH profile for S2.6 resembles S2.7. In S2.6, the pH dropped more rapidly than the core sample run R1.1. More NO_x and less N_2O was produced during both S2.6 and S2.7 than R1.1. This might be attributed to the more rapid drop in pH, which may favor NO_x production by increasing the proportion of $\text{NO}_2^- \Rightarrow \text{HNO}_2$.

H.D. Smith et al. (1993) reported that H_2 and NH_3 amounts appeared to be less in a simulant test when organics were added. Smith suggested that the organics might be suppressing the H_2 and or NH_3 generation by deactivating catalysts in some way. The core sample contains unknown organic species while S2.7 simulant contains a small amount of oxalate but no other organics. It is possible that the unknown organics in the core sample suppressed the H_2 in the same way as observed by Smith. The total moles of CO_2 generation could be affected by a lower H_2 and NH_3 generation as well since the proposed reaction for NH_3 generation shows 4 moles of CO_2 are generated for every 1 mole of NH_3 ,

Test # R1.1

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Test # S2.7

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure 3.1.5.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests R1.1 and S2.7

Figure 3.1.5.2: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests S2.7, S2.6, and S2.5

and the proposed reaction for H_2 generation shows 2 moles of CO_2 generated for every 1 mole of H_2 .

Peak generation rates were 6.2 times higher for H_2 and 2.3 times higher for NO_x . A fairly sharp H_2 peak was observed in Test S2.7 compared to a gradual rise in H_2 observed in R1.1. NO_x and N_2O also decreased sharply in S2.7. In R1.1, N_2O and NO_x decreased more slowly. The shape of the CO_2 peaks and the CO_2 generation rate were fairly similar in both tests. N_2O peak generation rates was 3.6 times higher in test R1.1 than test S2.7. A greater proportion of N_2O was generated during test R1.1.

3.1.6 Core Sample Compared to Simulant without Noble Metals: Tests R1.1 and L5.2

In comparing test R1.1 and L5.2, note that the core sample had approximately 40% less nitrite and carbonate than L5.2 (FY 1991 R/RCE simulant). The start of N_2O and NO_x generation occurred at $pH=4.6$ in both R1.1 and L5.2. Hydrogen generation was significantly less for test L5.2 compared to R1.1. A plot comparison is shown in Figure 3.1.6.1. The L5.2 simulant contained no noble metals. Very little H_2 generation is observed in the absence of noble metals (Wiemers et al. 1993).

The N_2O and NO_x generation curves appear quite similar. Both show a gradual decrease before a slow rise in H_2 generation. The generation of offgases in the core sample show characteristics of a non-noble metal simulant rather than a noble metal simulant. Characteristics of a noble metal feed include the following (Wiemers et al. 1993): the N_2O and NO_x releases start around a pH of 7.5 compared to 4.0 - 5.0 pH for non-noble metals feed; a distinct H_2 peak is observed shortly following decline of the N_2O/NO_x peaks; N_2O/NO_x peaks decrease suddenly compared to a gradual decline for non-noble metals feed; and levels of CO_2 and H_2 decline slowly throughout digestion and recycle. Test R1.1 exhibits all the characteristics of a non-noble metal feed except for two: 1) considerable H_2 and CO_2 concentrations exist during digestion and recycle and 2) the N_2O/NO_x ratio is higher than expected for nominal non-noble metal feeds (≈ 0.39 versus ≈ 0.08). These observations indicate a possible condition in the core sample that yielded the noble metals less active catalytically.

3.1.7 Comparison of Simulants with Different Noble Metal Concentrations: Tests S2.7, S2.6, and S2.5

Tests S2.7, S2.6, and S2.5 were run with different amounts of noble metals. The S2.5 test had a concentration that was 7% higher than nominal noble metals⁹. S2.6 had 10.7%

⁹Nominal simulant concentrations of noble metals @ 125 g WO/L of slurry are as follows: 1.23E-03 mole Pd/L, 1.02E-03 mole Rh/L, and 3.77E-03 mole Ru/L.²

Figure 3.1.6.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests R1.1 and L5.2

nominal Pd, 33.5% nominal Rh, and 87% nominal Ru. Test S2.7 had 5% nominal Pd, 12% nominal Rh and 27.9% nominal Ru. Tests S2.6 and S2.7 simulant were prepared using SIPT2 simulant, which is a full scale feed preparation simulant. Tests S2.6 and S2.7 had about twice the Cu concentration as S2.5. Total moles of H₂, CO₂, and N₂O decreased in Tests S2.5, S2.6, and S2.7 with the decrease in noble metals (See Table 3.1.1). Table 3.1.7.1 shows a comparison of selected results for Tests S2.5, S2.6, and S2.7. The time to initiate the H₂ generation increased with a decrease in noble metals. The peak H₂ generation rate, total measured moles of H₂ and N₂O/NO_x decrease with a decrease in noble metals concentrations.

Table: 3.1.7.1: Peak Hydrogen Generation Rates, Total Measured Moles of H₂ and N₂O/NO_x Ratios for Tests S2.5, S2.6, and S2.7

Test Name and % Nominal Noble Metals	Time to H ₂ Generation Peak (min)	H ₂ Peak Height (mmoles/min /L of slurry)	Total H ₂ (moles/L of slurry)	N ₂ O/NO _x ratio
Test S2.5 107% Pd 107% Rh 107% Ru	249	0.540	0.0950	1.680
Test S2.6 11% Pd 33% Rh 87% Ru	265	0.463	0.0834	0.074
Test S2.7 5% Pd 12% Rh 28% Ru	296	0.358	0.0471	0.040

Carbonate concentrations were the same for all three tests at 0.075 moles CO₃²⁻/L. However the pH decreased at a slower rate in Test S2.5. The pH data acquisition system did not record the pH during S2.7, but the offgas process profile shown in Figure 3.1.5.2 appeared to be very similar to S2.6. It is reasonable to assume in this case that the S2.6 pH profile would be similar to the S2.7 pH profile. The Test S2.5 simulant was slightly different in composition from S2.6 and S2.7 because it was not made with SIPT feed. See Appendix A for composition details. The pH variation may be due to the difference in composition and/or preparation method.

The S2.5 profile is very similar to profiles seen by (Wiemers et al. 1993) in tests conducted with noble metals. A small initial H₂ peak is observed followed by a larger

spike. The N_2O generation is also larger than the NO_x generation. Significantly more N_2O was generated during S2.5 than S2.6 and S2.7. This may be due to the slower decrease in pH which appears to favor N_2O generation or due to the smaller Cu concentration. Recent work by King¹⁰ shows that in the presence of Cu, but no noble metals, the production of N_2O is suppressed for a simple system of water, $NaNO_2$, and $HCOOH$. The larger Cu concentrations in S2.6 and S2.7 simulants could have suppressed N_2O generation ($3.93E-03$ mole Cu/L @ 125 gWO/L $\Rightarrow$ S2.6 and S2.7, $2.21E-03$ mole Cu/L @ 125 gWO/L $\Rightarrow$ S2.5).

In Tests S2.6 and S2.7, no initial H_2 peak is observed. The H_2 present is observed to peak moderately sharply and then increase slowly over time. Note that the larger increase observed after the H_2 spike in Test S2.6 is due to poor temperature control. Hydrogen generation is sensitive to temperature. After recycle addition, the temperature rapidly shot past $100^\circ C$, causing significant H_2 spikes.

3.1.8 Comparison of Simulants with Different Carbonate Concentrations

Two sets of tests were conducted with different carbonate concentrations. Test set one includes Tests S1.1 and S1.2. Test set two is comprised of Tests S2.3 and S2.5. The two sets are not directly comparable because noble metal concentrations are different.

3.1.8.1 0% Carbonate and 100% Nominal Carbonate: Tests S1.1 and S1.2

Figure 3.1.8.1.1 shows the comparison between Tests S1.1 and S1.2. Test S1.1 simulant contained 30% nominal nitrite (≈ 0.13 moles nitrite/L of slurry) and 0% nominal carbonate. Test S1.2 simulant contained 30% nominal nitrite and 100% nominal carbonate (≈ 0.125 moles carbonate/L of slurry). Refer to Table 2.1.1 for slurry composition variables. Slurry volume data was not available for S1.1.

In Figure 3.1.8.1.1, the initial carbonate spike is much greater in S1.2 than S1.1 due to the higher concentration of carbonate available for destruction in Test S1.2. Consequently, a significant buffering of the pH occurs in Test 1.2. Strong evidence for the pH dependence of the N_2O/NO_x ratio is offered in the process profiles of Test S1.2 and S1.1. The N_2O/NO_x ratio is 0.396 in Test S1.1 but increases to 7.250 in Test S1.2 (See Table 3.1.8.1.1). A significant increase in N_2O is observed in Test S1.2, which has 100% nominal carbonate when compared to Test S1.1 without carbonate. About 1.9 times more N_2O was produced in S1.2 than S1.1. There was 9.7 times more NO_x produced during S1.1 than during S1.2.

¹⁰June 8, 1993. "Recent Studies on the Treatment of Alkaline Nuclear Wastes with Formic Acid for Vitrification Plants." Presentation made to Pacific Northwest Laboratory by Dr. Bruce King, Univ. of Georgia.

Figure 3.8.1a.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests S1.1 and S1.2

These results are similar to the test conducted by H.D. Smith et al.(1993) in which simulants were spiked with NaOH and formated. A significant increase in the amount of N_2O was observed in the tests spiked with hydroxide when compared with tests without the hydroxide addition. The alkalinity of a simulant/slurry has a significant effect on the generation of N_2O and NO_x , whether caused by carbonate or hydroxide additions.

The acid/base neutralization capacity (see Appendix F) may thus play an important role in the generation of N_2O and NO_x . The role of noble metals is less clear. The comparison of Tests S1.1 and S1.2 may indicate that noble metals are not as important as the acid/base neutralization capacity in the production of N_2O and NO_x . The N_2O/NO_x ratio decreased from 7.3 to 0.4 for Tests S1.1 and S1.2 when noble metals were held constant and the carbonate was decreased from 100% nominal to 0% nominal. A test should be performed with no noble metals and 200% nominal carbonate to see if N_2O can be significantly produced without the presence of noble metals. It may be that both noble metals and carbonate/hydroxide concentrations need to be at certain limits to generate significant N_2O .

Table 3.1.8.1.1 shows the peak H_2 generation rates, the total measured H_2 , the H_2 initiation time, and the pH for Tests S1.1 and S1.2. Note that the initiation time and pH are for the H_2 peak which contains the maximum generation rate for the test. The initiation time was observed to increase with the carbonate concentration. The H_2 peak

Table 3.1.8.1.1: Peak H_2 Generation Rates, Total Measured Moles of H_2 , Slurry pH at H_2 Initiation, and N_2O/NO_x Ratios for Tests S1.1 and S1.2

Test Name and % Nominal Carbonate	Time to H_2 Generation Peak (min)	H_2 Peak Maximum Generation Rate (mmoles/m in/L of slurry)	Total H_2 (moles/L of slurry)	Slurry pH at time of H_2 Initiation	N_2O/NO_x ratio
Test S1.1 0%	94	0.404	0.0328	4.3	0.396
Test S1.2 100%	121	0.318	0.0185	5.25	7.250

generation rate and total measured H_2 showed a decrease with an increase in carbonate. The pH profile was more acid for the slurry with less carbonate concentration. The pH

decreases faster when acid (i.e., H^+) is not consumed by reaction with carbonate. The slurry pH at H_2 initiation was higher for the 100% nominal carbonate containing slurry. The peak H_2 generation rate appears to be larger the lower the slurry pH. This may be because as the pH decreases less $HCOOH$ disassociates to H^+ and $HCOO^-$ ($pK_a=3.74$). Thus more $HCOOH$ is available to form H_2 and CO_2 at lower pHs. The total moles of H_2 may increase with a decrease in carbonate simply because more time is available to generate H_2 . This extra time exists because the peak initiates sooner and because the peak generation rate is higher.

3.1.8.2 60% Nominal Carbonate and 211% Nominal Carbonate: Tests S2.5 and S2.3

The process profiles for Tests S2.5 and S2.3 are shown in Figure 3.1.8.2.1. Test S2.3 contained 211% nominal carbonate (≈ 0.253 moles of carbonate/L of slurry) and a noble metal concentration of the initial core sample analysis (See Table 2.1.1). Test S2.5 was run with 60% nominal carbonate (≈ 0.075 moles of carbonate/L of slurry) and noble metal concentration of the initial core sample analysis.

The N_2O/NO_x ratio was 3.2 in test S2.3 and 1.7 in test S2.5. There was 10% more N_2O generated during S2.3 than S2.5. There was 1.7 times more NO_x generated during S2.5 than S2.3. The observed trends are similar to the trends observed in S1.1 and S1.2. More NO_x is generated by the lower carbonate concentration simulant, and more N_2O is generated by the higher carbonate concentration simulant. Tests S1.1, S1.2, S2.3, and S2.5 are not directly comparable because S1.1 and S1.2 contain different noble metals and nitrite concentrations than S2.3 and S2.5. A larger change in NO_x and N_2O was observed between tests S1.1 and S1.2 (difference of 0.125 moles CO_3^{2-}/L) when compared with the change observed between tests S2.3 and S2.5 (difference of 0.178 moles CO_3^{2-}/L). The increase in total measured N_2O between tests S2.3 and S2.5 is 0.006 moles which is less than the increase observed between S1.2 and S1.1 of 0.024. The increase in N_2O may have been less between S2.3 and S2.5 because the limit for total moles of N_2O (produced during each test) may have been reached and therefore could not increase any further.

Similar trends were observed for the initiation and generation of H_2 between Tests S2.3 and S2.5 and Tests S1.1 and S1.2. The initiation time was observed to increase with the carbonate concentration. The H_2 peak generation rate and total measured H_2 showed a decrease with an increase in carbonate. The pH profile was more acid for the slurry with less carbonate concentration. Table 3.1.8.2.1 illustrates the observed trends. Also, as seen in the comparison between S1.1 and S1.2, the pH of H_2 initiation is lower in the slurry with less carbonate, and the peak generation rate is higher when tests S2.5 and S2.3 are compared.

Figure 3.8.1b.1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Tests S2.5 and S2.3

Table 3.1.8.2.1: Peak Hydrogen Generation Rates, Total Measured Moles of H_2 , Slurry pH at H_2 Initiation, and N_2O/NO_x Ratios for Tests S2.5 and S2.3

Test Name and % Nominal Carbonate	Time to H_2 Generation Peak (min)	H_2 Peak Maximum Generation Rate (mmoles/m in/L of slurry)	Total H_2 (moles/L of slurry)	Slurry pH at time of H_2 Initiation	N_2O/NO_x ratio
Test S2.5 60%	154	0.540	0.0950	4.5	1.680
Test S2.3 211%	233	0.442	0.0677	5.3	3.198

3.2 Mass Balances for Core Sample Runs R1.1 and R1.2

Mass balances were performed for combined tests R1.1 and R1.2. It was necessary to do this because the slurry samples from each run were combined in the hot cell and analyzed together in duplicate. Two mass balances were performed; one for carbon and one for nitrogen. Calculations are shown in Appendix B.

3.2.1 Nitrogen Mass Balance

The nitrogen mass balance is summarized in Table 3.2.1.1. The initial nitrogen value of $6.22E-02$ moles was determined from the initial core sample concentrations for nitrite and nitrate and nitrate from recycle waste stream simulant. The final core sample nitrogen was determined by adding the contributions from the following: nitrate, nitrite, and NH_3 in the slurry; nitrate, nitrite, and NH_3 in the condensate; N_2O and NO_x in the offgas; NH_3 recovered from the drierite in a scrubber solution. Ninety-two percent of the nitrogen was accounted for in the mass balance. This result is acceptable as well as consistent with results from mass balances from R/RCE (Smith et al. 1993) and SIPT (Langowski et al. 1993). Possible sources of uncertainty include 5% uncertainty in the analytical measurements and 5% in the offgas numbers.

3.2.2 Carbon Mass Balance

A carbon balance was possible because acceptable results were obtained from the hot persulfate method for determining total carbon, total inorganic carbon and total organic

Table 3.2.1.1: Nitrogen Mass Balance for Tests R1.1 and R1.2

Initial Nitrogen (moles) [From Nitrite and Nitrate in NCAW Core Sample and Recycle]	6.22E-02 (Initial Total Nitrogen)
Final Nitrogen in Slurry (moles) [From Nitrate, Nitrite, and NH ₃]	3.69E-02
Offgas Nitrogen (moles) [From N ₂ O, NO _x , and NH ₃ trapped by Drierite]	1.89E-02
Condensate Nitrogen (moles) [From Nitrate, Nitrite, and NH ₃]	1.12E-03
ΣSum of Final Nitrogen Components (moles)	5.69E-02 (Final Total Nitrogen)
% Nitrogen Accounted for by Mass Balance	92%

Table 3.2.2.1: Carbon Mass Balance for Tests R1.1 and R1.2

Initial Slurry Carbon (moles) [From CO ₃ ²⁻ , Organic Carbon, HCOOH Added]	2.06E-01 (Initial Total Carbon)
Offgas Carbon (moles) [From CO ₂]	2.80E-02
Final Carbon in the Slurry (moles) [From Total Carbon Measurement by Hot Persulfate Method]	1.20E-01
Condensate Carbon (moles) [From Total Carbon Measurement by Hot Persulfate Method]	4.61E-02
ΣSum of Final Carbon Components (moles)	1.94E-01 (Final Total Carbon)
% Carbon Accounted for by Mass Balance	94%

carbon of the formed core sample (See Appendix D for the results of a study on carbon analysis methods). A summary of the carbon mass balance is shown in Table 3.2.2.1. The initial carbon was calculated from the carbonate and organic carbons concentrations in the initial slurry and recycle (See Appendix A), and the amount of HCOOH added to the core sample during forming. Final slurry carbon was determined by adding the contributions of the CO₂ from the offgas, total carbon measurement of the slurry, and the total carbon from the condensate. Ninety-four percent of the carbon was accounted for in

the mass balance. This result is very good. Possible sources of uncertainty include 5% uncertainty in the analytical measurements and 5% in the offgas numbers. Possible sources of carbon in the condensate may be organics which were steam stripped or carbonate formed from CO₂ offgas passing through the condensate. The Total Carbon/ Total Organic Carbon/Total Inorganic Carbon (TC/TOC/TIC) analysis indicated that 99% to 100% of the carbon detected in the core sample condensates was organic (See Appendix C). Therefore, very little of the carbon in the core sample condensates may result from carbonate.

Offgas grab samples analyzed by Gas Chromatograph/Mass Spectrometer (GC/MS) showed the presence of a small amount of organics in the core sample offgas. This lends some evidence to the possibility of steam stripping. See Appendix C for specific quantities and types of organics.

3.3 N₂O/NO_x Ratios, NO/NO_x Generation and Total Hydrocarbon Analysis

3.3.1 N₂O/NO_x Ratios

The N₂O/NO_x ratios are reported in Table 3.3.1.1. Tests S1.1, S2.6, S2.7 R1.1, R1.2, and L5.2 all have N₂O/NO_x ratios < 1. Lower than nominal concentrations of noble metals and/or carbonate were characteristic of each one of these tests. Since carbonate tends to buffer the slurry pH (by consuming H⁺) during formic acid addition, the pH is expected to drop faster when less carbonate is present. The formation of nitrous acid from nitrite is pH dependent according to the following reaction:

$$\log([\text{HNO}_2]/[\text{NO}_2^-]) = 3.35 - \text{pH} \quad (7)$$

As the pH becomes more acid more nitrite forms nitrous acid. Consequently, nitrous acid disproportionates to form NO according to the reaction:

In addition, N₂O and NO can be formed from the chemical reaction of nitrite with formic acid according to the following:

It is predicted that more NO is formed from the disproportionation reaction as the pH drops below 5. Less nitrite is then available for reaction with formic acid to form N₂O.

Recent work by King¹¹ showed that in the presence of Cu but no noble metals, the

Table 3.3.1.1: N₂O/NO_x Ratios; Nitrite; pH and Formic Acid Amounts at the Initiation of N₂O and NO_x Generation

Test No.	Nitrite (moles /L)	N ₂ O (moles /L)	NO _x (moles /L)	N ₂ O/NO _x	pH (NO _x initiation)	pH (N ₂ O initiation)	HCOOH (mole/L) NO _x initiation	HCOOH (mole/L) N ₂ O initiation
S1.1	0.131	0.028	0.070	0.396	5.9	5.3	0.37	0.40
S1.2	0.131	0.052	0.007	7.250	6.75	6.75	0.70	0.70
S2.1	0.261	n/a	n/a	n/a	8.5	8.5	0.80	0.80
S2.2	A	B	O	R	T	E	D	T
S2.3	0.261	0.094	0.029	3.198	8.5	8.5	0.62	0.62
S2.4	0.261	0.088	0.022	4.018	7.8	7.8	1.06	1.06
S2.5	0.261	0.085	0.050	1.680	7.3	7.3	0.33	0.33
S2.6	0.261	0.016	0.214	0.074	7.4	4.6	0.12	0.37
S2.7	0.261	0.010	0.259	0.040	n/a	n/a	0.05	0.37
R1.1	0.261	0.034	0.088	0.388	5	4.6	0.5	0.55
R1.2	0.261	0.026	0.121	0.211	5.05	4.6	0.30	0.37
L3.1	0.131	0.058	0.005	11.6	7.3	8.5	0.25	0.13
L5.2	0.435	0.015	0.193	0.078	5.3	4.05	0.43	0.65

production of N₂O is suppressed for a simple system of water, NaNO₂, and HCOOH. This may account for the differences seen between Test S2.6 and S2.7, which had N₂O/NO_x <1 when compared with S2.5 (N₂O/NO_x = 1.7). The S2.5 simulant contained 2 and 5.5 times more noble metals than S2.6 and S2.7, respectively. Tests S2.5, S2.6 and S2.7 had equal amounts of carbonate, but S2.6 and S2.7 had 1.8 times more of Cu. In S2.5, 5.4 and 8.1 times more N₂O was measured when compared to S2.6 and S2.7, respectively. The combination of more noble metals and less Cu in test S2.5 may be responsible for the larger amount of measured N₂O and the larger N₂O/NO_x ratio of 1.7. The same reasoning applies to tests L5.2, R1.1 and R1.2. Test L5.2 had no noble metals, only nominal Cu concentrations (3.93E-3 mole Cu/L) and nominal carbonate (0.125 mole carbonate/L). R1.1 and R1.2 had low noble metals (6.15E-05 mole/Pd/L, 1.22E-04 mole Rh/L, and 1.05E-03 mole Ru/L) and low carbonate (0.074 mole carbonate/L). The lower

¹¹June 8, 1993. "Recent Studies on the Treatment of Alkaline Nuclear Wastes with Formic Acid for Vitrification Plants." Presentation made to Pacific Northwest Laboratory by Dr. Bruce King, Univ. of Georgia.

concentrations of noble metals (L5.2, R1.1, and R1.2), the presence of Cu (L5.2, R1.1, and R1.2), and the lower concentration of carbonate (R1.1 and R1.2) may account for the $\text{N}_2\text{O}/\text{NO}_x$ ratios of <1 .

Test S1.1 had no carbonate while Test S1.2 had nominal carbonate (0.125 mole $\text{CO}_3^{2-}/\text{L}$). The concentrations of noble metals and Cu were identical for both tests. Test S1.1 had $\text{N}_2\text{O}/\text{NO}_x <1$ while S1.2 had $\text{N}_2\text{O}/\text{NO}_x \approx 7.3$. The pH was seen to drop more quickly in S1.1 due to the absence of carbonate. The faster pH drop is likely to have favored the disproportionation of nitrite to NO in test S1.1. Test S1.2 is identical to L3.1 except for batch size (80 ml:1500 ml). Ratios of $\text{N}_2\text{O}/\text{NO}_x$ are comparable for L3.1 and S1.2, 11.6 and 7.3 respectively.

Duplicate runs R1.1 and R1.2 show comparable $\text{N}_2\text{O}/\text{NO}_x$ ratios of approximately 0.38 and 0.2, respectively. Test S2.4, was a duplicate of S2.1 and S2.3, except that the test was conducted in the hot cell, showed a comparable ratio of 4.0 with S2.3 ($\text{N}_2\text{O}/\text{NO}_x \approx 3.3$).

3.3.2 NO/NO_x generation

The carrier gas for all RPPLT tests was 99.7% Ar and 0.3% He. No O_2 was available for the reaction:

(8)

The NO/NO_x analyzer was periodically switched to read NO. Figure 3.3.2.1 shows the offgas generation of NO and NO_x for test R1.2. The points are NO generation while the line is the NO_x generation. The points lie on the curve showing that little or no NO₂ was produced during testing. Similar results were observed for all other RPPLT tests.

3.3.3 Total Hydrocarbons Analysis

The total hydrocarbons (THC) present in the offgas stream were monitored by the flame ionization detector during Tests R1.1 and R1.2 (core sample). Figure 3.3.3.1 shows the THC and NO_x generation as a function of time. A maximum concentration of less than 6 ppm of THC was observed in test R1.2. A maximum concentration of approximately 15 ppm THC was observed during Test R1.1. The flame ionization detector was observed to respond to NO_x generation such that NO_x generation was an interference. Correction of the THC data for NO_x generation was not attempted because the uncorrected THC data showed very little THC present, other than NO_x interference. In addition, several different organic species were present (see section 3.4.1), making it impossible to accurately extrapolate data to estimate total amounts of organic species released during the test.

Test # R1.2

Figure 3.3.2.1: NO and NO_x Generation for Test R1.2

Test # R1.2

Figure 3.3.3.1: Total Hydrocarbons and NO_x Generation for Test R1.2

3.4 Volatile Organic and Radiochemical Analyses

3.4.1 R1.1 (Core Sample) Volatile Organics in the Offgas

Two offgas grab samples were removed when the flame ionization detector indicated that hydrocarbons were present in the offgas during R1.1. The grab samples were subsequently analyzed by the GC/MS. Results are reported in Table 3.4.1.1. The

Table 3.4.1.1: Test R1.1 Volatile Organic Analysis Results (Core Sample Run)

Sample No.	Concentration (ppm unless otherwise indicated)	Organic Type	Time Sample Removed from Offgas
R1.1-Sample #1	6.7 20 1.3 1.86 2.5 ng/ml 0.6 3.5 ng/ml 1.5 ng/ml	Acetone *Nitrous Acid, methyl ester *2-Methyl-1-Propene *Nitrogen oxide (NO ₂) *Unknown *Cyclotrisiloxane *Unknown Siloxane *Unknown Siloxane	86 min
R1.1-Sample #2	6.3 20 1.3 3.0 ng/ml 0.6 0.35 2.39 1.48 3.5 ng/ml	Acetone *Nitrous Acid, methyl ester *2-Methyl-1-Propene *Unknown *Chloromethoxymethane *Silane, methoxytrimethyl *Nitrogen oxide (NO ₂) *Cyclotrisiloxane, hexamethyl *Unknown (Siloxane?)	100 min

*GC/MS was not calibrated for these compounds. Results are qualitative.

volatile organic samples were removed at 86 and 100 min after the start of forming. As stated above, NO_x interfered with the THC peak. Since it was not known, at the time, that a NO_x interference existed, samples were removed during NO_x generation interference and not necessarily during THC generation.

Results indicated that acetone was present in the offgas. It is not known at this time what reactions were responsible for producing acetone in the offgas. The GC/MS was calibrated for a limited amount of hydrocarbons. The starred compounds, reported in Table 3.4.1.1, were components that the GC/MS was not calibrated to analyze but were observed during the analysis. Results of starred compound are qualitative. The siloxanes observed in both samples have been observed in other core sample analyses and are believed to be impurities resulting from the use of silicone grease in the core sampling process.

3.4.2 Carbon-14 and Iodine-129

The offgas was run through a scrubber consisting of NaOH/Na₂CO₃ to remove and collect C¹⁴ and I¹²⁹. Carbon-14 and Iodine-129 measurement were made on the condensates, slurry, and scrubber solution from core sample runs R1.1 and R1.2. The scrubber solution samples and slurry samples were combined for R1.1 and R1.2 runs and then analyzed. The condensate samples were separately analyzed for each run. The results are shown in Table 3.4.2.1.

Table 3.4.2.1: Carbon-14 and Iodine-129 Analytical Results for the First Core Sample from Tank 102-AZ

Test Identification	¹⁴ C (Ci/L of slurry @125gWO/L	¹²⁹ I (Ci/L of slurry @125gWO/L
R1.1 Condensate	8.5E-07	<3.4E-11
R1.2 Condensate	1.3E-07	<3.1E-11
R1.1 & 1.2 Slurry (Formatted)	<1.1E-07	<5.4E-09
R1.1 & 1.2 Slurry (Formatted-duplicate)	6.2E-07	<7.5E-09
NaOH/Na ₂ CO ₃ Scrubber Solution (R1.1 & R1.2)	2.9E-08	<1.4E-12
Total Amount of ¹⁴ C and ¹²⁹ I per L of slurry @ 125 gWO/L (R1.1 & R1.2)	1.63E-06	<6.5E-09
R1.1 & R1.2 (Unformatted)	2.4E-07	<3.4E-08
Material Balance (% change)	680%	-----

Carbon-14 numbers are not significant. The total amount of ^{14}C observed was $1.5 \mu\text{Ci/L}$ of slurry. Iodine-129 values were below the detection limit and therefore, the data was inconclusive. Based on the data it appears that ^{14}C was not volatilized past the condensate in significant quantities. However, it should be noted that the data are from one core sample and should not be used to conclude that ^{14}C and ^{129}I are not present in significant quantities in Tank 102-AZ.

More analyses be performed on subsequent core samples to verify these results.

3.4.3 HEPA Filters

High Efficiency Particulate Air (HEPA) filters were obtained and archived per test plan direction. Analysis of HEPA filters, however, was not part of the scope of work. Further discussion and funding is required if analysis of HEPA filters from core sample forming is desired.

3.5 Ammonia Results from R1.1, R1.2 and S2.4

The NH_3 results are shown in Table 3.5.1 in g/L of slurry @ 125 g WO/L. Test S2.4 and the core sample runs are not directly comparable because noble metals and carbonate concentrations differ significantly (Table 2.1.1).

Table 3.5.1: Ammonia Concentrations Generated During Process Tests S2.4, R1.1 and R1.2

Test and Sample Identification (After Formating)	NH_3 (g/L of slurry @ 125 g WO/L)	Average
S2.4 Condensate	3.7E-01	
S2.4 Slurry	<4.1E-03	
S2.4 Drierite	1.25E-05	
R1.1 Condensate	3.97E-03	
R1.2 Condensate	2.06E-03	3.02E-03
R1.1 & R1.2 Slurry	1.44E-01	
R1.1 & R1.2 Slurry (duplicate)	1.53E-01	1.49E-01
R1.1 Drierite	<1.74E-05	
R1.2 Drierite	3.48E-05	2.61E-05
Total (S2.4)	3.7E-01	
Total Amount of NH_3 per L of slurry @ 125 gWO/L (R1.1 & R1.2)		1.52E-01

The trends, however, can be explained, and valuable information can still be obtained. The proposed slurry chemistry reaction for NH_3 production is as follows:

Approximately 2.5 times more NH_3 was observed during the forming and digestion of S2.4 than during R1.1 and R1.2. Test S2.4 had more noble metals than R1.1 and R1.2.¹² About 2.9 times more H_2 was measured during S2.4 than R1.1 and R1.2. One and one-half to 1.7 times more HCOOH was added to S2.4 than R1.1 and R1.2. The trend indicated by Wiemers et al. (1993) showed NH_3 to increase with measured H_2 . The data from R1.1 & R1.2, and S2.4 showed a similar trend of the NH_3 increasing with measured H_2 . However, the total NH_3 produced in tests R1.1&R1.2 and S2.4 was less than predicted by Wiemers et al. (1993). The predicted amount for our system (i.e., 0.116 moles of NO_3^-/L) is 0.72 moles $\text{NH}_3/\text{mole H}_2$. The measured amount for R1.1 and R1.2 was 0.60 moles $\text{NH}_3/\text{mole H}_2$ and for S2.4 was 0.51 moles $\text{NH}_3/\text{mole H}_2$.

As stated previously recent results by H. D. Smith et. al. (1993) indicated that the presence of organics might suppress H_2 and NH_3 by deactivating the catalysts in some way. This might account for the less than predicted amounts of H_2 and NH_3 in R1.1 & R1.2 which contained organic constituents. Most of the NH_3 generated during S2.4 was measured in the condensate. The slurry pH at the end of S2.4 was ≈ 6.6 . It is possible that some NH_3 was lost to the offgas system during testing, that prior to analysis NH_3 might have been lost from the condensate, or that the recovery of NH_3 from the drierite was not 100% efficient. This would result in lower NH_3 numbers.

Most of the NH_3 from the forming of the core sample was measured in the slurry. This may be a consequence of the lower pH experience by R1.1 and R1.2 ($\text{pH} \approx 4.6$) which would trap NH_3 as NH_4^+ .

3.6 Characterization of the Noble Metals (Pd, Rh, and Ru) in the Core Sample and Simulant by Scanning Electron Microscopy

Noble metals are thought to be the catalysts in the generation of H_2 . The noble metals were not detectable in the FY 1991 R/RCE unformatted simulant by Scanning Electron Microscopy (SEM) analysis. However, SEM analysis of the formatted simulant¹³ indicated

¹²Test S2.4 simulant was prepared to the initial core sample analysis composition which indicated a significantly greater amount of noble metals than the final core sample analysis.

¹³Analysis was performed for the R/RCE and was related in a personal communication from K. D. Wiemers, 1993.

the presence of metallic Ag with the noble metals (Pd, Rh, and Ru) mixed in.

A SEM analysis of the core sample also identified metallic Ag particles, but the noble metals were not detectable. This is consistent with the fact that very little H_2 evolved when the core sample was formatted. However, sample concentrations may have been below the noble metals detection limits of the SEM. It is also possible that the noble metals were not present in the sample examined by the SEM (i.e., due to inhomogeneity in the core sample) or that the noble metals were in a form not readily detectable by the SEM (e.g. in solution).

4.0 Conclusions and Recommendations

Slurry chemistry and offgas generation reactions were similar between the core sample and simulants during formic acid addition, digestion, and recycle addition test phases. Observed offgas differences between the core sample and simulants can be explained for all offgases except H_2 . No simulant showed the precise H_2 generation behavior of the core sample.

The amount of H_2 observed when of the core sample was processed was ≈ 3.1 times less than observed during simulant processing. It is possible that the presence of organics in the core sample may deactivate the catalysts in some way, resulting in less H_2 production than is observed in simulants. Other potential causes of the difference in H_2 production may be 1) the form of noble metals in the core sample versus the form in the simulant, 2) possible inaccuracies in the core sample noble metals analysis, and 3) the effects of inadvertently drying the core sample before processing.

Core sample offgas data are based on a limited amount of tests and test variables. Additional core sample testing should be performed to better predict and explain the H_2 behavior of the actual waste. Since it is probable that the core samples vary in composition additional testing would help to ensure that the data are repeatable.

Process temperature, slurry composition, acid/base neutralization capacity of the slurry, and formic acid addition rate are conditions that can affect the offgas gas generation rate of both the core sample and simulants. It is crucial that these variables are controlled so that the differences are minimized so that simulants and core samples can be compared.

Test results were repeatable (offgas generation rates and amount within 25%, with the exception of H_2). Differences observed between the hot cell and the out-of-cell simulant tests were on the same order as duplicate tests so that differences were not attributed to the test set-up location.

Simulant tests performed with variable noble metals showed a decrease in total moles of H_2 produced with a decrease in noble metals concentration. A decrease was also observed in the N_2O/NO_x ratio and H_2 peak height with a decrease in noble metals concentration.

Simulant tests performed with variable amounts of slurry carbonate concentrations showed that significant H_2 generation was delayed until sufficient $HCOOH$ was added to neutralize the additional carbonate. The generation of N_2O was generally more and NO_x generation was generally less in simulants containing more carbonate. The pH at which H_2 was observed to initiate was lower, and the peak H_2 generation rate was higher in simulants with less carbonate.

Volatile organic analysis showed the presence of acetone, nitrous acid, methyl ester, 2-methyl-1-propene, nitrogen oxide, chloromethoxymethane and miscellaneous siloxanes in the offgas stream. The siloxanes were attributed to grease used in core sampling from the tank. NO_x was shown to interfere with the flame ionization detector such that grab samples were removed during peak NO_x generation not necessarily peak total hydrocarbon generation times.

Radiolytic analysis results for ^{14}C and ^{129}I did not show significant amounts present in the core sample or in the offgas. Based on the data it appears that ^{14}C was not volatilized past the condensate in significant quantities. The analysis was performed on one core sample and should not be used to extrapolate to all core samples. Analysis should be repeated on subsequent core samples.

The amount of NH_3 produced during the forming of the core sample was 0.152 g NH_3/L . This number is expected to increase if more H_2 is produced by the core during forming. A 0.37 g NH_3/L quantity was detected in a simulant. The ratios of measured $\text{NH}_3/\text{measured H}_2$ were 0.61 and 0.51 respectively for the core sample and simulant.

No NO_2 was produced during testing. Therefore, NO and NO_x generation are synonymous. Since the carrier gas contained only He and Ar, O_2 was not available for reaction with NO to produce NO_2 .

$\text{N}_2\text{O}/\text{NO}_x$ ratio was < 1 for the core sample testing. Simulant testing showed a variation in the $\text{N}_2\text{O}/\text{NO}_x$ ratio of <1 to 7.3. A high acid/base neutralization capacity (e.g. increased slurry carbonate concentration) and the presence of noble metals appeared to be favorable to the generation of N_2O .

The mass balance for nitrogen for the core sample showed 92% closure. Uncertainties in the analytical and offgas measurements are possible sources of error.

The mass balance for carbon showed 94% closure. Uncertainties in the analytical and offgas measurement are possible sources of error. The hot persulfate method for carbon determination in slurries gave much better results than the furnace method. It is recommended that the hot persulfate method should be used for determining carbon in simulants. The hot persulfate method has been used primarily for radioactive samples and though cold samples could be run, the cost was prohibitive. A nonradioactive analytical hot persulfate measurement system is scheduled to be available in FY 1994 if enough funding is available.

5.0 References

B. C. Ha, D. M. Ferrara, N. E. Bibler. 1992, "Hydrogen Production During Processing of Radioactive Sludge Containing Noble Metals." In Proceedings of The International Topical Meetings on NUCLEAR AND HAZARDOUS WASTE MANAGEMENT SPECTRUM '92, Sponsored by American Nuclear Society, U.S. DOE and Atomic Energy Society of Japan, Boise Idaho, Vol. 2, p. 961.

M. H. Langowski and J. R. Gaskill. 1993. Detail Design Data Package. Item 3.4a - NOx Generation in the SRAT during Formating and Digestion. PHTD-K1017 (3.4a). Prepared by Pacific Northwest Laboratory, Richland, Washington.

H. D. Smith, K. D. Wiemers, M. H. Langowski, M. R. Powell, D. E. Larson. 1993. Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal 1992: Evaluation of Offgas Generation and Ammonia Formation, PHTD-C93-03.02B. Prepared by the Pacific Northwest Laboratory. Richland, WA.

K. D. Wiemers, M. H. Langowski, M. R. Powell, D. E. Larson. 1993. Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal 1991: Evaluation of Offgas Generation. Reductant Requirements and Thermal Stability, PHTD-93-K899, Rev. 0. Prepared by the Pacific Northwest Laboratory. Richland, WA.

APPENDIX A

Core Sample, Simulant, and Recycle Compositions

Table A1: Initial Core Sample, Simulant Target, Simulant Measured, and FY 1991 Simulant Compositions

Component	102-AZ-C1 Initial Analysis Core #1 (125 gWO/L) moles E/L of feed	102-AZ-C1 Simulant Target Values (125 gWO/L) moles E/L of feed*	102-AZ-C1 Simulant Measured Values (125 gWO/L) moles E/L of feed*	FY 1991 Simulant Target Values (125 gWO/L) moles E/L of feed**
Ag	1.56E-03	1.56E-03	1.36E-03	1.32E-03
Al	4.79E-01	4.79E-01	4.59E-01	2.27E-01
As	< 1.89E-03		NA	NA
B	< 1.99E-02	1.99E-02	1.22E-02	2.10E-04
Ba	1.01E-03	1.01E-03	9.18E-04	1.46E-03
Be	4.67E-04		NA	NA
Ca	2.00E-02	2.00E-02	1.88E-02	1.80E-02
Cd	3.26E-02	3.26E-02	3.16E-02	3.00E-02
Ce	1.82E-03	1.82E-03	NM	4.77E-03
Co	< 1.69E-02		NA	NA
Cr	7.11E-03	7.11E-03	6.70E-03	4.39E-03
Cs	5.32E-03	5.32E-03	NM	5.43E-03
Cu	2.21E-03	2.21E-03	1.99E-03	3.93E-03
Dy	6.95E-05		NA	NA
Fe	5.66E-01	5.66E-01	5.48E-01	4.51E-01
K	< 2.18E-02		NA	5.32E-03
La	7.96E-03	7.96E-03	NM	5.12E-03
Li	< 7.84E-03		NA	6.05E-06
Mg	9.67E-03	1.01E-02	5.37E-03	1.15E-02
Mn	1.28E-02	1.28E-02	1.19E-02	3.15E-02
Mo	< 3.47E-04		NA	4.95E-03
Na	7.59E-01	1.04E+00	NM	variable
Nb	NM		NA	1.10E-04
Nd	5.86E-03	1.82E-02	NM	2.64E-02
Ni	3.59E-02	3.59E-02	3.37E-02	3.93E-02
P (IC)	3.34E-02	3.34E-02	2.70E-02	1.56E-02
Pb	1.77E-03	1.77E-03	1.63E-03	3.74E-03
Pd	1.32E-03	1.32E-03	NM	variable
Pr	NM		NA	1.18E-03
Rb	NM		NA	variable
Re	1.89E-04		NA	NA
Rh	1.09E-03	1.09E-03	NM	variable
Ru	4.04E-03	4.04E-03	NM	variable
Sb	< 3.77E-03		NA	5.11E-05
Se	< 2.48E-03		NA	1.82E-04
Si	4.22E-02	4.22E-02	7.83E-03	8.56E-02
Sm	NM		NA	5.44E-04
Sn	NM		NA	9.99E-05
Sr	8.94E-04	8.94E-04	8.54E-04	1.48E-03
Ta	NM		NA	1.92E-05
Tb	1.35E-03	1.35E-03	NM	7.94E-04
Th	< 9.93E-04		NA	NA
Ti	5.16E-04	5.16E-04	NM	1.04E-02
Tl	< 9.93E-03		NA	NA
U	1.23E-02		NA	NA
Y	NM		NA	9.04E-04
V	3.67E-04		NA	NA
Zn	1.02E-03	1.02E-03	9.90E-04	5.24E-03
Zr	5.87E-02	5.87E-02	1.05E-02	1.56E-01
F	4.28E-03	4.28E-03	NM	6.52E-03
Cl	6.06E-04	6.06E-04	1.62E-03	1.06E-02
NO2	2.60E-01	2.61E-01	2.38E-01	variable
NO3	1.15E-01	1.16E-01	NM	1.30E-01
PO4	2.24E-03	2.25E-03	2.70E-02	1.56E-02
SO4	7.25E-03	7.28E-03	7.44E-03	1.04E-02
TIC	2.52E-01	2.53E-01	3.00E-01	variable
TOC (IC)	8.94E-02	8.97E-02	9.00E-02	1.39E-02

* Composition of simulant used in S2.1-S2.4. S2.5 used the same composition simulant except the carbonate concentration value was 0.075 mole/L.

** Composition of simulant used in S1.1, S1.2, L3.1, and L5.2. Variable amounts are defined in the Composition Variables for the 1st 102-AZ Core Sample and Simulants table in the Approach section.

NA = Not Added

NM = Not Measured

Table A2: Revised Core Sample and Simulant Compositions

Component	102-AZ-C1 Core #1 Revised Analysis (125 gWO/L) moles E/L feed	S2.6 Simulant Target Values (125 gWO/L) mole E/L	S2.6 Simulant Measured Values (125 gWO/L) mole E/L	S2.7 Simulant Target Values (125 gWO/L) mole E/L	S2.7 Simulant Measured Values (125 gWO/L) mole E/L
Ag	1.56E-03	1.32E-03	1.53E-03	1.32E-03	1.23E-03
Al	4.79E-01	4.79E-01	4.35E-01	4.79E-01	4.58E-01
As		NA	NA	NA	NA
B		2.10E-04	7.81E-02	2.10E-04	2.61E-02
Ba	1.01E-03	1.46E-03	1.26E-03	1.46E-03	1.26E-03
Be	4.67E-04	NA	NA	NA	NA
Ca	2.00E-02	1.80E-02	1.70E-02	1.80E-02	1.55E-02
Cd	3.26E-02	3.00E-02	2.93E-02	3.00E-02	2.74E-02
Ce	1.82E-03	4.77E-03	NM	4.77E-03	NM
Co		NA	NA	NA	NA
Cr	7.11E-03	4.39E-03	4.39E-03	4.39E-03	3.91E-03
Cs	5.32E-03	5.43E-03	NM	5.43E-03	NM
Cu	2.21E-03	3.93E-03	3.78E-03	3.93E-03	3.51E-03
Dy	6.95E-05	NA	NA	NA	NA
Fe	5.66E-01	5.66E-01	5.37E-01	5.66E-01	6.04E-01
K		5.32E-03	<dl	5.32E-03	<dl
La	7.96E-03	5.12E-03	NM	5.12E-03	NM
Li		6.05E-06	<dl	6.05E-06	<dl
Mg	9.67E-03	1.15E-02	1.42E-02	1.15E-02	1.18E-02
Mn	1.28E-02	3.15E-02	3.19E-02	3.15E-02	2.97E-02
Mo		4.95E-03	3.80E-03	4.95E-03	3.24E-03
Na	7.59E-01	7.59E-01	5.79E-01	7.59E-01	4.96E-01
Nb		1.10E-04	NM	1.10E-04	NM
Nd	5.86E-03	2.64E-02	NM	2.64E-02	NM
Ni	3.59E-02	3.93E-02	3.68E-02	3.93E-02	3.30E-02
P	3.34E-02	1.56E-02	5.08E-03	1.56E-02	6.08E-03
Pb	1.77E-03	3.74E-03	3.48E-03	3.74E-03	3.08E-03
Pd	6.15E-05	6.15E-05	NM	6.15E-05	NM
Pr		1.18E-03	NM	1.18E-03	NM
Rb		6.70E-04	NM	6.70E-04	NM
Re	1.89E-04	NA	NA	NA	NA
Rh	1.22E-04	1.22E-04	NM	1.22E-04	NM
Ru	1.05E-03	1.05E-03	NM	1.05E-03	NM
Sb		5.11E-05	<dl	5.11E-05	<dl
Se		1.82E-04	<dl	1.82E-04	<dl
Si	4.22E-02	8.56E-02	1.54E-02	8.56E-02	2.91E-02
Sm		5.44E-04	NM	5.44E-04	NM
Sn		9.99E-05	NM	9.99E-05	NM
Sr	8.94E-04	1.46E-03	1.44E-03	1.46E-03	1.35E-03
Ta		1.92E-05	NM	1.92E-05	NM
Te	1.35E-03	7.94E-04	NM	7.94E-04	NM
Th		NA	NA	NA	NA
Ti	5.16E-04	1.04E-02	9.41E-04	1.04E-02	6.56E-04
Tl		NA	NA	NA	NA
U	1.23E-02	NA	NA	NA	NA
Y		9.04E-04	NM	9.04E-04	NM
V	3.67E-04	NA	NA	NA	NA
Zn	1.02E-03	5.24E-03	2.74E-03	5.24E-03	3.71E-03
Zr	5.87E-02	1.56E-01	1.15E-01	1.56E-01	1.06E-01
F	4.28E-03	6.52E-03	NM	6.52E-03	NM
Cl	6.08E-04	1.06E-02	1.16E-02	1.06E-02	9.72E-03
NO2	2.61E-01	2.61E-01	2.83E-01	2.61E-01	2.68E-01
NO3	1.16E-01	1.16E-01	1.40E-01	1.16E-01	1.38E-01
PO4	2.25E-03	1.56E-02	NM	1.56E-02	NM
SO3	7.28E-03	1.04E-02	1.00E-02	1.04E-02	8.72E-03
TIC	7.50E-02	7.50E-02	NM	7.50E-02	NM
TOC	8.97E-02	1.39E-02	3.81E-03	1.39E-02	3.21E-03

NA = Not Added

NM = Not Measured

Table A3: Recycle Simulant Composition

Reference and Target Oxides in Recycle Simulant			Sources of Recycle Simulant for NCAW Slurry Simulant***		
Oxide	Reference* g Recycle Oxide per g Oxide in SRAT Slurry	Target Value** g Recycle Oxide per L of Recycle Simulant	Source	←-----target value-----→ g Source per 1 L of Recycle Simulant	
				g Source per 1 L of NCAW Slurry#	
CdO	0.004	2.01	CdO	2.01	0.50
MnO ₂	0.0012	0.60	KMnO ₄	1.10	0.27
Na ₂ O	0.05	25.17	NaOH	24.50	6.08
P ₂ O ₅	0.004	2.01	Na ₃ PO ₄	4.65	1.15
NO ₃ -	0.08	40.27	HNO ₃	40.92	10.16
Cl-	0.00008	0.04	NaCl	0.07	0.02
TOC	0.0027	1.36	Na ₂ C ₂ O ₄	7.59	1.88
Diatomaceous Earth	0.04	20.13	Diatomaceous Earth	20.13	5.00
Zeolite (IE-96)	0.02	10.07	Zeolite (IE-96)	10.07	2.50
sum of nonvolatiles	0.1192	60	sum	111.04	27.57

*Smith 1991

**The target concentration for the recycle slurry is 60 g oxide/L of recycle. Actual composition was not measured.

To convert from column 2 to 3: (g recycle oxide)/(sum of nonvolatiles) x (60 g total recycle oxide/L of recycle)

*** Approximately 0.19 moles of HCOOH/L of recycle simulant was added to recycle simulant before it was added to the NCAW simulant

#1L of NCAW slurry is @ 125 g WO/L of NCAW slurry. The approximate amount of recycle simulant necessary

for addition to 1 L of NCAW simulant is 250 ml of recycle simulant (@ 60 g recycle oxide/L of recycle simulant).

Note: The recycle slurry was added on the basis of the gram waste oxides present in the vessel at the end of digestion.

The amount of gram waste oxides was determined by subtracting the waste oxides contained in slurry samples (samples were removed during formic acid addition and digestion) from the initial gram waste oxides (initial gram waste oxides=1.5L of slurry x 125 gWO/L of slurry=187.5 gWO).

APPENDIX B

Mass Balance Calculations and Related Test Data

Table B1: Formating Equipment/Test Condition Differences Between Radioactive, FY 1991 tests, and S2.5-S2.7 Scales

	Radioactive Scale R1.1-R1.2 S2.1-S2.4 S1.1-S1.2	FY 1991 R/RCE L3.1 and L5.2	S2.5-S2.7
Batch Size	80 ml (simulants) 57.5 ml (core)	1500 ml	1500 ml
Sweep Gas Dilution Gas	0.3% He in Ar 0.3% He in Ar	4.4% O ₂ in Ar 4.39% CH ₄ in Ar	0.3% He in Ar 0.3% He in Ar.
Total Carrier Gas Flow Rate	1.5 L gas/L of slurry (simulant) 2.1 L gas/L of slurry (core)	0.6 L gas/L of slurry	1.3 L gas/L of slurry
Materials of Construction: Vessel/Lid Condensers Gas Lines	glass/stain. steel stainless steel stainless steel	glass/glass glass tygon	glass/glass glass tygon
Vessel Geometry: Head Space/Slurry Volume Ratio	1.09 simulant 1.93 core	0.33 simulant	0.33 simulant
Slurry Surface Area/Slurry Volume Ratio	0.35 cm ⁻¹ simulant 0.49 cm ⁻¹ core	0.17 cm ⁻¹ simulant	0.17 cm ⁻¹ simulant
HEPA Filtration	Yes (S2.4, R1.1, and R1.2)	No	No
Drierite	Yes	No	Yes
Vessel Pressure	6-15.5 in. of H ₂ O (simulant) 2 in. of H ₂ O (core)	5-10 in. of H ₂ O	6-13 in. of H ₂ O
Stirrer	Magnetic stir bar	Motor (agitated by propeller/rod)	Motor (agitated by propeller/rod)
Analyzers	Two GCs Chemiluminescence (NO/NO _x) Flame Ionization Detector	GC Chemiluminescence (NO/NO _x) IR Detectors	GC Chemiluminescence (NO/NO _x)

Table B2: Nitrogen Mass Balance Calculations

Initial NO3- (mole/L) 1.16E-01	Initial NO2- (mole/L) 2.61E-01	Recycle N (moles) 1.88E-02	Initial Slurry N (moles) 6.22E-02	
Final Slurry	Final NO3- (mole)	Final NO2- (mole)	NH3 (moles)	Final Slurry N (moles)
R1.1 & R1.2	3.35E-02	2.27E-03	1.09E-03	3.68E-02
R1.1 & R1.2(dup)	3.35E-02	2.31E-03	1.16E-03	3.69E-02
Average	3.35E-02	2.29E-03	1.13E-03	3.69E-02
Offgas	NOx (mole/L)	N2O (moles/L)	NH3 Drierite (moles/L)	N (moles)
R1.1	8.80E-02	3.41E-02	1.03E-06	8.98E-03
R1.2	1.22E-01	2.56E-02	2.05E-06	9.93E-03
			sum	1.89E-02
Condensate	NO3- (mole)	NO2- (mole)	NH3 (mole)	N (moles)
R1.1	4.68E-04	1.77E-04	1.34E-05	6.59E-04
R1.2	2.98E-04	1.61E-04	7.67E-06	4.65E-04
			sum	1.12E-03
			total	5.69E-02

Initial N (moles)	6.22E-02
Final N (moles)	5.69E-02
% N	91.52

Analytical and Test Information*

	Initial Slurry	Final slurry	Recycle
Volume (ml) R1.1&R1.2	115	110	29
Density (g/ml)		1.119	
g WO/L	125	146	60
WO	14.38	16.12	1.74
Analytical			
	Initial Slurry	1st samp Final Slurry	2nd samp Final Slurry
Nitrate (mole/L)	0.116	2.60E-01	2.60E-01
NO3-(g/g sample)		1.68E-02	1.68E-02
Conversion Factor (g/g samp=>g)		123.51	
Nitrite (mole/L)	0.261	1.76E-02	1.79E-02
NO2-(g/g sample)		8.45E-04	8.60E-04
NH3(mole/L)		8.45E-03	9.02E-03
NH3 (mg/Kg sample)		150	160
Condensate			
	Condensate R1.1	Condensate R1.2	Drierite
Amount (ml)	326	296	20
Nitrate (mole)	4.68E-04	2.96E-04	
NO3- (µg/ml)	89	62	N/A
Nitrite (mole)	1.77E-04	1.61E-04	
NO2- (µg/ml) <25	25	25	
NH3 (mole)	1.34E-05	6.98E-06	1.18E-07
NH3 (mg/L)	0.7	0.4	0.1

*Data generated from formic acid addition, digestion, and recycle addition of the third NCAW core sample (R1.1 and R1.2)

Table B3: Carbon Mass Balance Calculations

<u>Slurry</u>	Initial Slurry	Final slurry	Recycle
Volume (ml) R1.1&R1.2	115	110	28.8
Density (g/ml)		1.119	
g WO/L	125	146	60
WO	14.38	16.10	1.73
<u>Condensate</u>			
	Condensate R1.1	Condensate R1.2	
Amount (ml)	326	296	

Initial Inorganic Carbon (mole/L)	Initial Organic Carbon (mole/L)	Recycle Carbon (mole)	HCOOH Added (moles)	Initial Carbon
7.50E-02	8.97E-02	3.26E-03	1.83E-01	2.06E-01
<u>Final Carbon</u>		Offgas CO2 (mole/L@125)	Offgas C (moles)	
	R1.1	2.54E-01	1.46E-02	
	R1.2	2.33E-01	1.34E-02	
	sum		2.80E-02	
	Total C in slurry (g)		(moles)	
	R1.1&R1.2 (slurry)	1.52E+00	1.26E-01	
	R1.1&R1.2 (slurry)	1.36E+00	1.13E-01	
	Average		1.20E-01	
	Total C in condensate (g)		(moles)	
	R1.1 (condensate)	3.19E-01	2.66E-02	
	R1.2 (condensate)	2.34E-01	1.95E-02	
	sum		4.61E-02	
	total		1.94E-01	

Initial C (moles)	2.06E-01
Final C (moles)	1.94E-01
% C Mass Balance	94.30

Conversion Factor (g/g samp->g)	123.40	
<u>Analytical Data*</u>	1st sample	2nd sample
Total C (g/g sample)	1.23E-02	1.10E-02
Total C (g)	1.52E+00	1.36E+00
Total C (moles)	1.26E-01	1.13E-01
Total C (g/L)	13.20	11.80
TOC (g/L)	13.09	11.70
TIC	0.08	0.08
<u>Condensate</u>	R1.1	R1.2
Total C (µg/ml)	980	790
Total C (g)	3.19E-01	2.34E-01
Total C (moles)	2.66E-02	1.95E-02
Total C (g/L)	5.56	4.07

*Data generated from formic acid addition, digestion, and recycle addition of the third NCAW core sample (R1.1 and R1.2)

Table B4: General Test Information

Test No.	Batch Size (ml)	Condensate collected during testing (ml)	Water Added to slurry during test (ml)	Amount of Recycle Added to Slurry during test (ml)
S1.1. (Trial Run)	80	108 (digestion cut short)	101	Not Added
S1.2	80	203	188	Not Added
S2.1	80	407	387	20
S2.2	80	Aborted test	Aborted test	
S2.3	80	314	291	20
S2.4	80	160	123	20
S2.5	1500	988	256	375
S2.6	1500	1043	345	355
S2.7	1500	1069	343	378
R1.1	57.5	326	311	14.5
R1.2	57.5	296	261	14.5

Table B5: Ammonia Raw Data

Sample	Concentration of NH ₃	Amount of Slurry or Condensate
R1.1 & R1.2 - Formated Slurry	150 mg/kg @ 146gWO/L	0.110 L ($\rho=1.119$ g/ml)
R1.1 & R1.2 - Formated Slurry (duplicate)	160 mg/kg @ 146 gWO/L	0.110 L ($\rho=1.119$ g/ml)
R1.1 - Condensate	0.7 mg/L	0.326 L
R1.2 - Condensate	0.4 mg/L	0.296 L
R1.1 - Drierite	< 0.05 mg/L	0.02 L
R1.2 - Drierite	0.1 mg/L	0.02 L
S2.4 - Formate Slurry	< 4.7 mg/kg @ 159 g WO/L	0.0704 L($\rho=1.11$ g/ml)
S2.4 - Condensate	185 mg/L	0.16 L
S2.4 - Drierite	0.05 mg/L	0.02 L

APPENDIX C

Carbon, Anions, and Related Test Data

Table C1: Measured Total Carbon, Total Inorganic Carbon and Total Organic Carbon for Tests S2.4, R1.1 and R1.2

Test Identification	Total Carbon (g/L of slurry @ 125 g WO/L)	Organic Carbon (g/L of slurry @ 125 g WO/L)	Inorganic Carbon (g/L of slurry @ 125 g WO/L)
S2.4 Condensate	0.26	0.02	0.24
R1.1 Condensate	5.56	5.56	<0.28
R1.2 Condensate	4.07	4.07	<0.26
R1.1 & R1.2 Slurry (Formated)	13.20	13.09	0.08
R1.1 & R1.2 Slurry (Formated)	11.80	11.70	0.08

Table C2: Ion Chromatography Analytical Results for Tests S2.4, R1.1, and R1.2 (g/L of slurry @125 gWO/L)

Test ID	F ⁻	Cl ⁻	NO ₂ ⁻	Br ⁻	NO ₃ ⁻	PO ₄ ³⁻	SO ₄ ²⁻
S2.4-Cond	N/A	N/A	1.0E-02	<5.0E-4	4.6E-03	<1.0E-3	1.8E-3
R1.1-Cond	N/A	N/A	N/A	N/A	5.0E-01	<2.8E-02	1.7E-02
R1.2-Cond	N/A	N/A	N/A	N/A	3.2E-01	<2.6E-02	<1.3E-02
R1.1&R1.2 FORM Slurry	N/A	N/A	9.1E-01	<2.5E-01	1.8E01	<5.0E-02	2.2E-01
R1.1&R1.2 FORM Slurry (duplicate)	N/A	N/A	9.2E-01	<2.5E-01	1.8E01	<5.0E-02	2.0E-01

APPENDIX D

**Carbon Analyses Methods: Results from Hot Persulfate and Furnace
Methods for the Determination of Total Carbon, Total Inorganic Carbon and
Total Organic Carbon**

APPENDIX D

Carbon Analyses Methods: Results from Hot Persulfate and Furnace Methods for the Determination of Total Carbon, Total Inorganic Carbon and Total Organic Carbon

Two simulants, one with carbonate and nitrite and one without, were analyzed by the hot persulfate and furnace methods by Baldwin.¹⁴ The hot persulfate method analyzes the TIC by acid and the TOC by hot persulfate. The furnace method analyzes for TOC by heating the sample to 600°C. The TC is then analyzed by heating the sample to 1000°C. The difference is the TIC.

The samples were spiked with glucose and CaCO₃. Spike recovery by the hot persulfate method was 95 to 95%. The hot persulfate method appears to work well for the analyses of TC, TIC, and TOC in NCAW simulant.

The results from the furnace method did not make sense. The TC was higher than the TOC indicating that some matrix effect was causing the inorganic carbon to decompose at the lower temperature of 600°C. The furnace method for carbon determination did not appear to produce acceptable results for the analysis of NCAW simulant. This is consistent with the results reported by (Wiemers et al. 1993)¹⁵.

¹⁴TOC/TIC/TC Results for 102AZ-C1-HWVP-FOR-ANL. February 11, 1993 memo from D. L. Baldwin to J. M. Tingey.

¹⁵K. D. Wiemers, M. H. Langowski, M. R. Powell, D. E. Larson. 1993. Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal 1991: Evaluation of Offgas Generation, Reductant Requirements and Thermal Stability, PHTD-93-K899, Rev. 0. Prepared by the Pacific Northwest Laboratory. Richland, WA.

APPENDIX E

Integration Results of CO₂ Peaks to Estimate Slurry Carbonate

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Integration Results of CO₂ Peaks to Estimate Slurry Carbonate

(1)

The carbonate destruction reaction (eq 1) is the first phase of the reactions and is represented by the first large CO₂ peak (clearly seen for tests R1.1 and 5.2, Figure 3.1.6). Integrations of the peaks during this phase are shown in Table E1 and compare stoichiometrically (to within 3 to 30% using eq. 1) to known amounts of CO₃²⁻ in the simulants. The amount of CO₂ released from the core sample (Test R1.1) during this phase indicates that the amount of CO₃²⁻ in the core sample was actually about 1/3 of the initial core sample analysis.

Table E1: Simulant Target Carbonate Concentrations and Results from the Integration of the CO₂ Offgas Peaks

Test No.	Simulant Target Carbonate Concentration (mole CO ₃ ²⁻ /L of slurry @ 125 gWO/L	Integration of CO ₂ Peak Representing Carbonate Destruction Phase (mole CO ₃ ²⁻ /L of slurry @ 125 gWO/L
S1.2	0.125	0.272 (Interference present from N ₂ O. CO ₂ is a product of N ₂ O generation)
S2.3	0.253	0.234
S2.4	0.253	0.240
R1.1		0.075
L5.2	0.125	0.124

APPENDIX F

Acid/Base Neutralization Capacity Results

APPENDIX F

Acid/Base Neutralization Capacity Results

The acid/neutralization capacity results are summarized in mequivalents/kg of slurry in Table F1. Note that for S2.1 to S2.4 the mequivalents/kg required to reach a pH of 10 is a factor of 10 higher than S2.6 and R1.1. Tests S2.1 to S2.4 contained 202% of the nominal carbonate concentration (0.253 moles $\text{CO}_3^{2-}/\text{L}$) based in the initial core sample analysis. Test S2.6 contained 60% of the nominal carbonate concentration (0.075 moles $\text{CO}_3^{2-}/\text{L}$). Test R1.1 was estimated to contain 60% nominal carbonate based on the integration of the CO_2 offgas peak generated while the core sample was formed. Tests R1.1 and S2.6 agree fairly well at pH=10 and pH=9. Some deviation occurs at pH=7 and pH=4. While Test S2.6 simulant was titrated, the titrator was allowed to reach equilibrium at pH=7 and pH=4 for about 15 min at each pH. The mequivalents/kg are estimated to be about 10 mequivalents/kg high at pH=4 due to the buffering capacity of the slurry S2.6. Test S2.6 contains more noble metals than R1.1 and 0.24 mole NO_3^-/L more nitrate. This might have affected the acid/base capacity.

Two laboratories, Lab 1 and Lab 2, titrated the simulants with similar results showing the repeatability of this analytical technique.

Table F1: Acid/Base Neutralization Capacity: mequivalents of Acid Required to Reach pH 10, 9, 7, and 4

Test No.	mequiv/ kg of slurry Required to Titrate to pH=10	mequiv/ kg of slurry Required to Titrate to pH=9	mequiv/ kg of slurry Required to Titrate to pH=7	mequiv/ kg of slurry Required to Titrate to pH=4
S2.1-S2.4 (Lab 1)	215	341	500	822
S2.1-S2.4 (Lab 2)	220	320	420	800
S2.6 (Lab 1)	20	59	120	339
R1.1 (Lab 2)	20	55	95	290

APPENDIX G

Offgas Profiles

Test # S1.1

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G1: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test S1.1

Test # S1.2

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G2: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test S1.2

Test # S2.1

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G3: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test S2.1

Test # S2.3

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G4: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test S2.3

Test # S2.4

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G5: Offgas, Temperature, HCOOH Addition, and Volume Process Profiles for Test S2.4

Test # S2.5

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G6: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test S2.5

Test # S2.6

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G7: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test S2.6

Test # S2.7

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G8: Offgas, Temperature, HCOOH Addition, and Volume Process Profiles for Test S2.7

Test # R1.1

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G9: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test R1.1

Test # R1.2

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G10: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test R1.2

G.11

Test # 3.1

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G11: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test L3.1

Test # 5.2

(Normalized to a 1 Liter Batch @ 125 g TO/L)

Figure G12: Offgas, pH, Temperature, HCOOH Addition, and Volume Process Profiles for Test L5.2