PNNL-11049

UC-810

Project Technical Information

RECEIVED

MAR 28 1996

OSTI

**Detailed Design Data Package:
1.9a Measure Hydrogen Generation
During Formating; 1.10a Nitrate Salt
Reaction**

**K. D. Wiemers
M. H. Langowski
M. R. Powell**

March 1996

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

**Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute**

MASTER

**Detailed Design Data Package:
1.9a Measure Hydrogen Generation During Formating;
1.10a Nitrate Salt Reaction**

K. D. Wiemers
M. H. Langowski
M. R. Powell

March 1996

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

Pacific Northwest National Laboratory
Richland, Washington 99352

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the

Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
prices available from (615) 576-8401.

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

The document was printed on recycled paper.

TABLE OF CONTENTS

1.0 DESCRIPTION OF DATA	1.1
1.1 Simulant Composition	1.1
1.2 Test Matrix	1.2
1.3 Test Conditions	1.2
1.4 Process Profiles	1.2
1.5 Nitrate Salt and Organic Reactions - Thermal Analyses	1.4
2.0 KEY POINTS	2.1
3.0 REFERENCES	3.1
APPENDIX OF TABLES	
APPENDIX OF FIGURES	
APPENDIX A.1. SUMMARY OF BENCH-SCALE PROCEDURE FOR FORMATING	A.1.1

LIST OF TABLES

	<u>Page</u>
1.0 DESCRIPTION OF DATA	
1.1.1 Description of Table 1.1.1 Format and Derivation	T1.-1
Stock NCAW Simulant Composition As Determined By ICP-ES, ICP-MS, and XRF	T1.-2
1.1.2 Sodium Salts Added to Stock Simulant During Initial Heat Up	T1.-5
1.1.3 Waste Oxide Loading of Initial Feed Simulant	T1.-6
1.1.4 Recycle Composition - Oxides and Sources	T1.-7
1.1.5 Recycle Simulant Additions	T1.-8
1.2.1 Test Matrix	T2.-1
1.3.1 Test Variables for Redox/Rheology Control Evaluation	T3.-1
1.4.1 Key Test Events List	T4.-1
1.4.2 Peak Gas Generation Rates, mmole/min	T4.-5
1.4.3 Tabulated H ₂ Generation Rates as a Function of Time	T4.-6
1.4.4 Molar Gas Releases during Lab-Scale Formating	T4.-16
1.5 Nitrate Salt and Organic Reactions - Summary of Data	T5.-1

LIST OF FIGURES

1.0 DESCRIPTION OF DATA

1.4.1. PROCESS PROFILES

1.4.1 Test 1.1	F1.4.1.-1
1.4.2 Test 1.2	F1.4.1.-2
1.4.3 Test 1.3	F1.4.1.-3
1.4.4 Test 2.1	F1.4.1.-4
1.4.5 Test 2.2	F1.4.1.-5
1.4.6 Test 3.1	F1.4.1.-6
1.4.7 Test 3.2	F1.4.1.-7
1.4.8 Test 4.1	F1.4.1.-8
1.4.9 Test 5.1	F1.4.1.-9
1.4.10 Test 5.2	F1.4.1.-10
1.4.11 Test 6.1	F1.4.1.-11
1.4.12 Test 6.2	F1.4.1.-12
1.4.13 Test 7.1	F1.4.1.-13

1.4.2. COMPARISON PROFILES

1.4.2.1a-d Amount of Formic Acid	F1.4.2.-1a-d
1.4.2.2a-d Formic Acid Addition Rate	F1.4.2.-2a-d
1.4.2.3a-d Nitrite Concentration	F1.4.2.-3a-d
1.4.2.4a-d Reflux versus Boil-off	F1.4.2.-4a-d
1.4.2.5a-d Effect of Noble Metals	F1.4.2.-5a-d
1.4.2.6a-d Low Nitrite, High Nitrate	F1.4.2.-6a-d

1.4.3. TEMPERATURE DEPENDANCE

1.4.3.1 Test 1.1, Cool Down Profile for H ₂	F1.4.3-1
1.4.3.2 Test 6.1, Cool Down Profile for H ₂	F1.4.3-2
1.4.3.3 Test 6.2, Cool Down Profile for H ₂ during Peak Generation	F1.4.3-3
1.4.3.4 Test 6.2, Heat Up Profile for H ₂	F1.4.3-4
1.4.3.4 Test 6.2, Cool Down Profile for H ₂	F1.4.3-5
1.4.3.5 Test 1.1, Hydrogen Generation Rate Variation with Temperature	F1.4.3-6
1.4.3.6 Test 6.2, Hydrogen Generation Rate Variation with Temperature	F1.4.3-7

1.4.4 HYDROGEN MITIGATION

1.4.4.1a-d Test Set 6, Quenching Tests	F1.4.4.-1a-d
--	--------------

1.5. THERMOGRAMS FOR DRIED NCAW SIMULANT

1.5.1 Test 1.3, Feed Simulant, DSC	F1.5.-1
1.5.2 Test 1.3, Feed Simulant, TGA	F1.5.-2
1.5.3 Test 1.3, Feed Simulant, TGA 2	F1.5.-3
1.5.4 Test 1.3, Formated Feed Simulant, DSC	F1.5.-4
1.5.5 Test 1.3, Formated Feed Simulant, TGA 1	F1.5.-5
1.5.6 Test 1.3, Formated Feed Simulant, TGA 2	F1.5.-6
1.5.7 Test 1.3, Formated Feed Simulant plus Recycle Simulant, DSC	F1.5.-7
1.5.8 Formated Feed Simulant plus Recycle Simulant, TGA 1	F1.5.-8
1.5.9 Formated Feed Simulant plus Recycle Simulant, TGA 2	F1.5.-9
1.5.10 Test 1.1, Formated Feed Simulant plus Recycle Simulant, DSC	F1.5.-10
1.5.11 Test 1.1, Formated Feed Simulant plus Recycle Simulant, TGA 1	F1.5.-11
1.5.12 Formated Feed Simulant plus Recycle Simulant, TGA 2	F1.5.-12

2.0 KEY POINTS

2.1 Threshold for Initiation of Second Hydrogen Release	F2.-1
2.2 Process Profile: Hydrogen Peak Induction Time Dependence on Initial Nitrite Concentration	F2.-2
2.3 Hydrogen Peak Induction Time Dependence on Initial Nitrite Concentration	F2.-3
2.4 Ammonia Generation Dependence on Hydrogen Generation and Nitrate Concentration	F2.-4

DETAILED DESIGN DATA PACKAGE
PHTD Redox/Rheology Evaluation Control
Milestone 1.2.2.03.02B
December 6, 1991

The detailed design data package provides test data on gas generation rates during forming of NCAW and on nitrate salt reactions in dried SRAT/SME NCAW feeds. These issues correspond to the HWVP architectural engineer firm, Fluor Daniels, technology data needs, Item 1.9a (Hydrogen Generation) and Item 1.10a (Nitrate Salt Reactions). This work was performed in accordance with the Fiscal Year 1991 Statement of Work for Applied Technology Tasks to be Performed by Pacific Northwest Laboratory in Support of the Hanford Waste Vitrification Plant Project (Kruger 1991).

1.0 DESCRIPTION OF DATA

Tables and figures are provided for the following data needs:

- Simulant Composition
- Test Matrix
- Test Conditions
- Process Profiles
- Comparison Profiles
- Maximum Gas Generation Rates
- Total Gas Emissions
- Nitrate Salt and Organic Thermal Analyses

Brief descriptions for each table/figure are provided below. Details of the scoping tests will be provided in a subsequent report.

1.1 Simulant Composition

The feed simulant was prepared via co-precipitation of component hydroxides from nitrate solutions. A few of the minor components were added as salts other than nitrates or as oxides. The stock simulant composition is identified in Table 1.1.1. Sodium carbonate, nitrite, and nitrate were added to the stock simulant during initial heat up of the slurry. The amounts of carbonate, nitrite, and nitrate added for each test are listed in Table 1.1.2. The predicted and measured waste oxide for each feed simulant (stock simulant + salts) are compared in Table 1.1.3.

A simulated waste recycle stream was added after additions and reactions with formic acid. The recycle simulant composition and corresponding source chemicals are listed in Table 1.1.4. The amount of recycle oxides added to each test batch are listed in Table 1.1.5. Reference compositions were provided by WHC (Smith 1991).

1.2 Test Matrix

The strategy for the test matrix is discussed in the Redox/Rheology Control Evaluation FY1991 test plan (Wiemers 1991). A summary of the tests conducted for FY 91 is provided in Table 1.2.1. Each test consisted of the following steps: heat up to 95 °C, add formic acid, digest, add recycle, and concentrate. The last three steps were conducted at 100 °C (near boiling). Formic acid was added both before and after recycle addition in Test 5.1. The system was shut down (ie., cooled and sweep gas discontinued) between digestion and recycle addition. Formic acid addition was conducted with return of condensate to the reaction vessel. Digestion was conducted with boil-off (ie., no condensate return) except during test 4.1 in which the slurry was refluxed (condensate returned to the reaction vessel) for 4 hours followed by a 4hr boil-off period. With the exception of Test set 5, all tests were conducted under an argon/4.4% oxygen purge of ~ 0.3 L/min. Argon was selected to provide detection of nitrogen. Oxygen was added to provide an indicator of the nitric oxide to nitrogen dioxide conversion. Decreases in oxygen were observed, however, the oxygen was never completely depleted. ¹ Test set 5 was conducted with air to simulate the large-scale operational conditions.

1.3 Test Conditions

Conditions for each test are summarized in Table-1.3.1. The test variables were the amount of formic acid added, formic acid addition rate, initial nitrite concentration, initial nitrate concentration, digestion conditions (boil off or reflux), and noble metal presence or absence. Test set 6 was conducted to evaluate the potential of quenching the second hydrogen peak by interrupting the formic acid addition and power supply to the heating mantle.

1.4 Process Profiles

Process profiles for each test are provided in Figures 1.4.1.1-13. These profiles identify, as a function of process time, the offgas generation rate (mmole/min) for H₂, CO₂, N₂O, and NO_x, the slurry pH, volume and temperature, and the amount of formic acid added. Note that the gas compositions are measured downstream of a condenser (26-27 °C) and do not include any vapors lost to the condensate (such as

¹ Occasional monitoring of the NO/NO_x was performed during testing. The ratio varied throughout the test period and will be reported in the final report.

DETAILED DESIGN DATA PACKAGE

PHTD Redox/Rheology Evaluation Control

Milestone 1.2.2.03.02B

December 11, 1991

NO_x, NH₃, and HCOOH). Corrections for time delays between gas release from the slurry and injection into the detector were included in the gas profiles. Step decreases in the slurry volume are due to sampling. Continuous decreases in slurry volume are a result of boil-off. Initial increases in slurry volume are due to formic acid addition.

Key events with regards to offgas generation measurements are summarized in Table 1.4.1. Peak gas generation rates are listed in Table 1.4.2. The hydrogen generation rates for each tests are tabulated in Table 1.4.3. Total moles of each gas released as a function of the process step are given in Table 1.4.4. Profiles of slurry components and the amount of NH₄⁺, NO₃⁻, NO₂⁻, and HCO₂⁻ measured in the condensate as a function of process phase will be reported in a subsequent document.

Comparisons of the offgas generation rates for the following test variables are provided in Figures 1.4.2.1-6:

<u>Figure</u>	<u>Variable</u>	<u>Test</u>
1.4.2.1	Amount of Formic Acid	1.1, 1.2, 1.3
1.4.2.2	Rate of Formic Acid Addition	1.3, 2.2
1.4.2.3	Amount of Nitrite	1.3, 3.1, 3.2
1.4.2.4	Reflux during Digestion	1.3, 1.4
1.4.2.5	Absence of Noble Metals	1.1, 5.2
1.4.2.6	Low Nitrite, High Nitrate	3.1, 7.1

Temperature effects on the hydrogen generation rate were measured during Tests 1.1, 6.1 and 6.2. Heat up and cool down profiles are provided in Figures 1.4.3.1-5. The measurements for Tests 1.1 and 6.1 were collected during a relatively steady-state hydrogen generation period, several hours after the second hydrogen peak was observed. These profiles are provided in Figures 1.4.3.1 and 1.4.3.2. During Test 6.2 power to the heating mantle was interrupted and the formic acid addition was discontinued during peak hydrogen generation. The cool down profile in Figure 1.4.3.3 reflects the observed behavior during this period. The slurry was then reheated followed by a second cooling after the hydrogen release reached a fairly steady state value (refer to test 6.2 process profile, Figure 1.4.12). Figures 1.4.3.4 and 1.4.3.5 reflect the behavior during these periods, respectively. The hydrogen generation rate as a function of temperature for Tests 1.1 cool down and Test 6.2 second heat up and subsequent cool down are shown in Figures 1.4.3.6 and 1.4.3.7, respectively.

1.5 Nitrate Salt and Organic Reactions

The major enthalpy and weight changes in four NCAW feed simulant samples were measured as a function of temperature. The samples analyzed represented a NCAW feed simulant (1.3-7.1), a formatted NCAW simulant (1.3-32.1), and two formatted NCAW feed simulants to which a recycle stream simulant was added (1.3-47.1 and 1.1-47.1).

For the scanning thermogravimetry (STG) and differential scanning calorimetry (DSC) measurements samples were dried to concentrate the solids and decrease the volatile components (primarily water). The samples were dried at 60 °C for ~24hrs. Weight loss varied from 80 to 84%. Approximately 10 mg samples of the dried materials were heated at a rate of 10 C/min over a temperature range of 40 to 700 °C under an air purge. The STG measures weight changes as a function of temperature. The DSC measures energy changes as a function of temperature. The thermograms are provided in Figures 1.5.1-12. The data is summarized in Table 1.5.1.

In the thermograms of these four samples two endotherms and an exotherm were observed between 50 and 550 °C. The two endotherms were observed between 50 and 130 °C, and 230 and 310 °C. The enthalpy of these two endotherms were approximately 80 and 60 J/gm, respectively. The exotherm is observed between 125 and 250 °C with an enthalpy of approximately -275 J/gm (-66 cal/gm). The exotherm was observed in all thermograms except for sample 1.3-7.1 (initial feed simulant). This suggests that formate, which is not present in sample 1.3-7.1, contributes to the observed exotherm. The weight loss associated with the exotherm is greater for samples 1.1-47.1 and 1.3-4.7, perhaps because these samples included the recycle stream which approximately doubled the nitrate loading (compare with sample 1.3-32.1). For a relative comparison, reported major enthalpy changes for a West Valley feed simulant (SF-10) ranged from -229 to -854 J/gm (Bowen 1988). The exotherm was observed in the temperature range of 240 and 600 °C. The exotherm is attributed to the combustion of sugar.

The first endotherm was not observed in the thermograms of samples 1.3-32.1 (formatted feed simulant) and 1.1-47.1 (formatted feed simulant plus recycle stream simulant). Note that $\text{Al}(\text{NO}_3)_3$, LiNO_3 , KNO_3 , and NaNO_3 all decompose between 150 and 600 °C and may have a net endothermic contribution to the total enthalpy. In the temperature range of 520 to 680 °C endothermic contributions may result from the fusion of divalent alkali-earth nitrates like $\text{Ca}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, and $\text{Ba}(\text{NO}_3)_2$. The

DETAILED DESIGN DATA PACKAGE

PHTD Redox/Rheology Evaluation Control

Milestone 1.2.2.03.02B

December 6, 1991

endothermic contributions from the enthalpy of fusion of components are expected to be small and in most cases negligible compared to the decomposition enthalpies. Several small endothermic peaks were reported by Bowan in the temperature range of 680 to 860 °C. These peaks were attributed to the formation of the eutectics or the fusion products with SiO₂ and/or B₂O₃.

Henken tests were conducted on each of the samples at temperatures of 380, 450, and 550 °C. Between 15 and 21 mg of sample was placed in a small test tube. The test tube was placed into a preheated, temperature controlled block. Indications of an explosion by visual observation were made over a 20 minute period. No explosions were observed in the Henken tests run on these samples.

2.0 KEY POINTS

The reported findings are based on a limited number of tests and test variables. Replicate tests should be conducted to ensure repeatability of data if conditions required to obtain results are prototypic of plant operation. The operational and compositional envelope to which the key points apply are defined below. A summary description of the bench-scale test procedure is provided in Appendix A.

Feed simulant composition:	NCAW FY1991, refer to Table 1.1.1
Recycle simulant composition:	refer to Table 1.1.4
Amount of formic acid:	27 to 74 ml 86.7wt% HCOOH/L slurry
Formic acid addition rate:	2 to 8 gpm (plant scale equivalent)
Formic acid addition location:	Below slurry surface
Nitrite concentration:	0.13 to 0.45 moles NO ₂ /L slurry
Nitrate concentration:	0.13 to 0.40 moles NO ₃ /L slurry
Carbonate concentration:	0.13 moles CO ₃ ²⁻ /L slurry
Forming Temperature:	95 °C
Digestion/concentration temperature:	100 °C (boiling not observed)
Test duration:	~ 10 hours
Sweep Gas:	Argon/4% O ₂ (air for Test set 5)
Initial Slurry Volume:	1.5L
Reaction Vessel:	2L

The key points are:

- The hydrogen generation profile is depicted by a small first release and sometimes a significantly larger second release. The first peak hydrogen generation rate was <0.05 mmoles H₂/min-L (125 gWO/L). The second peak hydrogen generation rate ranged from 0.21 to 0.75 mmoles H₂/min-L (125 gWO/L).
- Under the conditions tested, the data indicates that the ratio of formic acid added to initial nitrite must satisfy a threshold value to initiate a second hydrogen release at relatively high rates. A bounding area defining this threshold in terms of the amount of formic acid added to initiate a large second

DETAILED DESIGN DATA PACKAGE

PHTD Redox/Rheology Evaluation Control

Milestone 1.2.2.03.02B

December 6, 1991

hydrogen release and the initial amount of nitrite present is shown in Figure 2.1.² Redox data indicate that the quantity of formic acid required will increase in proportion to the nitrate content of the feeds. This information suggests that the highest hydrogen generation case may be a feed containing low nitrite and high nitrate concentrations. The dependence of hydrogen generation on such variables as noble metal concentration, temperature, complexing agents, upper bound nitrate concentrations and pH (ie., CO_3^{2-} , OH^-) have not been fully investigated for HWVP feeds.

- Under the conditions tested, the hydrogen generation rate profile and peak height for the second hydrogen release appears to be quite sensitive to the point at which formic acid addition is interrupted. A 20-fold increase (compare Tests 1.3 and 6.1) in peak hydrogen generation rates was observed over a time interval of less than 10 minutes. This observation is presently unexplained. Other factors to which hydrogen generation is extremely sensitive such as minor differences in experimental noble metal concentration and temperature may also have contributed to the observed differences in peak hydrogen generation rate. Selected tests should be repeated to verify the observed phenomena if these scenarios and the conditions required to implement them are found to be applicable to plant operations. The effect of other process and composition variables should also be evaluated.
- The amount of ammonia measured (slurry + condensate) was related to the amount of hydrogen measured and initial nitrate concentration (Figure 2.4). The correlation to nitrate is based on two data points and requires verification. Ammonia was previously detected qualitatively in feed simulant containing only nitrate (no nitrite addition) (Wiemers 1990).
- An exothermic reaction in dried formatted NCAW simulant was observed in the temperature range of 125 to 250 °C with an enthalpy of ~275J/gm. The data strongly suggests the exotherm to be a result of formate and nitrate present in the sample.

²Note that within the variable range tested, the "induction time" (defined as the time from beginning of formic acid addition to initiation of the second hydrogen release) increases with increase in the initial amount of nitrite present (Figures 2.2 and 2.3). The induction time appears also to decrease with increase in formic acid addition rate. Note difference in induction time between test 3.1 (0.57 ml/min) and test 7.1 (0.48 ml/min) (refer to Figure 1.4.2.6).

DETAILED DESIGN DATA PACKAGE
PHTD Redox/Rheology Evaluation Control
Milestone 1.2.2.03.02B
December 6, 1991

3.0 REFERENCES

Bowan, B.W., V. Jain, T. Vansickle, and P. McGinnis. 1988. The Thermal Analysis of SF-10 Feed - Part I - The Major Enthalpy Changes Between 25 and 1000C. OG:88:0224. West Valley Nuclear Services, West Valley, New York.

Gibbons, R. N. January 1991. Transmittal of Fluor Daniel Technology Needs Data Sheets. Letter to R. B. Morson, HWVP, FRF-1155/9100129.

Kruger, O. L. February 1991. Fiscal Year 1991 Statement of Work for Applied Technology Tasks to be Performed by Pacific Northwest Laboratory in Support of the Hanford Waste Vitrification Plant Project. WHC-SP-0638. Prepared for the U.S. Department of Energy Office of Environmental Restoration and Waste Management by Westinghouse Hanford Company, Richland, WA.

Smith, R.A. January 1991. Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing -- Errata Correction. Letter to J. M. Creer. #9150151.

Wiemers, K.D. June 1990. The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment. HWVP-90-1.2.2.03.03A. Richland, WA.

Wiemers, K.D. March 1991. Test Plan for Evaluation of Neutralized Current Acid Waste (NCAW) Reductant Requirements, Offgas Productivity and Feed Preparation Reactions. HWVP-91-1.2.2.03.02A. PNL HWVP Technology Development Program, Richland, WA.

DETAILED DESIGN DATA PACKAGE
PHTD Redox/Rheology Evaluation Control
Milestone 1.2.2.03.02B
December 6, 1991

TABLES

TABLE 1.1.1. Description of Table 1.1.1 Format and Derivation

- 1) Analytical values were received in g E/L. These values were converted to mole E/L
- 2) The mole E/L values were placed in column 5.
- 3) Target values for elements which were not analyzed were added to column 5 and substitutions were made for analytical values which were suspect. The resulting column gives the best estimate of stock simulant composition.
- 4) The mole E/L column was used to calculate g oxide/L values in column 6.
- 6) A second g oxide/L column was prepared with the nominal sodium value substituted. This column is not shown.
- 7) Wt% was calculated by the normalization of the second g ox/L and the subsequent multiplication by a factor of 100.
- 8) These wt% values for the feed simulant are shown in column 3. The wt% column includes the target sodium.
- 9) Column 2 is the reference feed composition (Smith, 1991).
- 10) Column 3 shows the values for the NCAW Feed Simulant. These values are taken from the PHTD Test Plan (Wiemers, 1991) for the Redox/Rheology Control Evaluation.
These values are slightly different from the reference feed composition due to substitutions and deletions for radioactive and toxic components.
- 11) Definitions: *Stock Simulant- Feed without additives. NO₃⁻ is at nominal concentration in the stock simulant. NO₃⁻ is present from the co-precipitation of nitrates which is part of the stock simulant preparation procedure.
*Feed Simulant- Feed which contains additives (ie. NaNO₂ and Na₂CO₃. NaNO₃ was added only if the nitrate level was to be increased above nominal.)
*Nominal Feed Simulant- Feed which contains additives in nominal concentrations. Nominal concentrations for additives in this case are the target feed compositions for the anion portions of the additives (NO₂⁻, NO₃⁻ and CO₃⁻⁻).
*E=element

TABLE 1.1.1. Stock NCAW Simulant Composition As Determined By ICP-ES, ICP-MS, and XRF

1	2	3	4	5	6
	NCAW SRAT Ref Feed* FY91 Rev.	NCAW** TARGET-Nominal Feed Simulant*3	NCAW Nominal Feed Simulant*3 Analyt Val and Sub.	NCAW Stock Simulant*4 Analyt Val and Sub.	NCAW Stock Simulant*4 Analyt Val and Sub.
Oxide (O)	wt%(feed oxide)	wt%(feed oxide)	wt%(feed oxide)	mole % of feed	g oxide/l
Ag2O	1.20E-01	1.22E-01	1.26E-01	1.35E-03	1.56E-01
Al2O3	9.04E+00	9.25E+00	9.08E+00	2.22E-01	1.13E+01
Am2O3	7.22E-02				
As2O3	4.25E-05				
B2O3	5.75E-03	5.86E-03	5.87E-03	2.10E-4 sub tar	7.31E-03
BaO	1.76E-01	1.79E-01	1.85E-01	1.50E-03	2.30E-01
BeO	1.01E-01				
Br					
CaO	7.91E-01	8.06E-01	6.44E-01	1.43E-02	8.02E-01
CoO	3.02E+00	3.08E+00	2.84E+00	2.76E-02	3.54E+00
CeO2	6.05E-01	6.56E-01	4.88E-01	3.53E-03	6.08E-01
Co2O3					
Cr2O3	2.62E-01	2.67E-01	2.74E-01	4.49E-03	3.41E-01
Cs2O	6.05E-01	6.12E-01	7.29E-02	6.45E-04	9.09E-02
CuO	2.45E-01	2.50E-01	2.46E-01	3.83E-03	3.05E-01
Dy2O3	1.04E-04				
Er2O3	3.08E-06				
Eu2O3	2.02E-02				
F	9.70E-02	9.90E-02	9.94E-02	6.52E-3 sub tar	1.24E-01
Fe2O3	2.82E+01	2.88E+01	2.82E+01	4.40E-01	3.51E+01
Gd2O3	3.70E-03				
GeO2	1.57E-04	1.56E-04			
HgO					
HfO2O3	5.32E-06				
I	4.50E-06	4.60E-06	4.61E-06	4.53E-8 sub tar	5.75E-06
In2O3					
K2O	1.96E-01	2.00E-01	2.01E-01	5.32E-3 sub tar	2.51E-01
La2O3	6.53E-01	6.67E-01	6.69E-01	5.12E-3 sub tar	8.34E-01
Li2O	1.84E-04	7.23E-05	7.26E-05		
MgO	2.02E-01	3.72E-01	3.49E-01	1.08E-02	4.35E-01
MnO2	2.14E+00	2.19E+00	2.24E+00	3.21E-02	2.79E+00
MoO3	5.59E-01	5.70E-01	5.22E-01	4.52E-03	6.51E-01
Na2O	2.14E+01	2.19E+01	2.19E+01	2.17E-01	6.72E+00
Nb2O3	1.01E-02	1.03E-02	9.78E-03	1.04E-04	1.22E-02
Nd2O3	5.78E-01	3.56E+00	3.57E+00	2.64E-2 sub tar	4.44E+00
NiO	2.30E+00	2.35E+00	2.27E+00	3.78E-02	2.82E+00
NpO2					
P2O5	8.72E-01	8.87E-01	8.89E-01	1.56E-2 sub tar	1.11E+00
PbO2	7.00E-01	7.15E-01	7.30E-01	3.80E-03	9.09E-01
PdO##	1.20E-01	1.23E-01	1.16E-01	1.18E-03	1.44E-01
Pm2O3	4.60E-02				
Pr2O3	1.53E-01	1.56E-01	1.56E-01	1.18E-3 sub tar	1.95E-01
PuO2	6.00E-02				
Rb2O3	5.75E-02	5.87E-02	6.78E-03	7.72E-05	8.45E-03

TABLE 1.1.1. Stock NCAW Simulant Composition As Determined By ICP-ES, ICP-MS, and XRF

1	2	3	4	5	6
	NCAW SRAT Ref Feed* FY91 Rev.	NCAW** TARGET-Nominal Feed Simulant*3 wt%(feed oxide)	NCAW Nominal Feed Simulant*3 Analyt Val and Sub. wt%(feed oxide)	NCAW Stock Simulant*4 Analyt Val and Sub. mole E/L of feed	NCAW Stock Simulant*4 Analyt Val and Sub. g oxide/L
Oxide (O)	wt%(feed oxide)	wt%(feed oxide)	wt%(feed oxide)		
Rh2O3##	1.04E-01	1.06E-01	1.08E-01	1.06E-03	1.35E-01
Ru2O3##	3.80E-01	3.87E-01	4.91E-01	4.87E-03	6.12E-01
SO3	6.55E-01	6.69E-01	6.68E-01	1.04E-02	
Sb2O3	5.88E-03	5.95E-03	5.98E-03	5.11E-05	7.45E-03
SeO2	1.59E-02	1.61E-02	1.48E-02	1.66E-04	1.84E-02
SiO2	4.03E+00	4.11E+00	5.88E+00	1.22E-01	7.33E+00
Sm2O3	7.50E-02	7.72E-02	7.75E-02	5.54E-5 sub tar	9.66E-02
SnO	1.08E-02	1.08E-02	1.08E-02	9.99E-5 sub tar	1.35E-02
SnO	1.19E-01	1.21E-01	4.56E-02	5.48E-04	5.68E-02
Ta2O5	3.33E-03	3.39E-03	3.40E-03	1.95E-5 sub tar	4.24E-03
Tb2O3	2.26E-04				
Tc2O7	1.52E-01				
TeO2	1.07E-01	1.01E-01	8.78E-02	6.85E-04	1.09E-01
ThO2					
TiO2	6.52E-01	6.66E-01	4.71E-01	7.34E-03	5.86E-01
Tm2O3	1.68E-10				
U3O8	4.74E+00				
Y2O3	7.99E-02	8.17E-02	7.93E-02	8.75E-04	9.18E-02
ZnO	3.34E-01	3.41E-01	3.30E-01	5.05E-03	4.11E-01
ZrO2	1.51E+01	1.54E+01	1.58E+01	1.60E-01	1.97E+01
sum	9.96E+01	9.97E+01	1.04E+02		
	Nominal NCAW Feed Simulant mole E/L	Comments			
Na2C2O4	6.95E-03	target value (nominal)			
NO3-	1.33E-01	IC measured value of stock NCAW simulant. This is the actual value and it is slightly higher than target (nominal).			
NO2-	4.35E-01	target value (nominal)			
CO3--	1.25E-01	target value (nominal)			
SO3-	1.02E-02	target value (nominal)			
Cl-	1.06E-02	target value (nominal)			
Na	8.64E-01	target value (nominal). Na will vary if NO2 and NO3 are changed per test conditions. Note: NO2- source NaNO2, NO3- source (test 7.1) NaNO3, and CO3- source Na2CO3			

* Smith, R.A. 1991.

**Wiemers, K.D. 1991 HWVP Cost Account 1.2.2.03.02-Redox/Rheology Control Evaluation Test Plan

*3 Nominal feed simulant consists of the stock simulant plus additives NaNO2 and Na2CO3 in nominal concentrations.

*4 NCAW stock simulant does not contain Na2CO3 and NaNO2. These two compounds were added prior to each test to 1.5L aliquots. See Tables 1.2 and 4.

Values for the rare earth elements are target values. Analytical Values for the rare earths were suspect.

The analytical values shown in the stock simulant columns for sodium (mole E/L and g ox/L) do not include NaNO2 or Na2CO3 which were added prior to each test. The target value for sodium was used to calculate wt% in the nominal NCAW simulant column. The analyzed value for Na is 0.5% from the nominal target when Na2CO3 and NaNO2 are taken into account.

Target values for Ta, Sn, and B also were used because analyses were suspect. Ge, Li, F, I were not analyzed. Target values used.

**TABLE 1.1.1. Stock NCAW Simulant Composition As Determined By
ICP-ES, ICP-MS, and XR (cont)**

The noble metal concentrations were added in 15% excess addition Pd and a 24% excess of Ru and Rh due to a calculation error. Measurements from XRF, however, showed only Ru to be high. Stock solution concentrations are presently being reconfirmed.

Note: Weight% is independent of volume but in order to use g oxide/g total oxide values(wt%) to prepare slurries it is helpful to note that wt% is equivalent to 100 g WO/L when a volume of 1L is chosen as a basis.

The gWO/L value for the stock batch was not determined (ie. ignition loss method). The initial g WO/L values for each test feed simulant, however, were determined. See Waste Oxide Loading of Initial Feed Simulant table.

Measurements taken after digestion and at the end of each test will be reported in a subsequent document.

TABLE 1.1.2.**Sodium Salts Added to Stock Simulant During Initial Heat Up**

Test No.	NaNO ₃ (mol/L)	NaNO ₂ (mol/L)	Na ₂ CO ₃ (mol/L)
1.1	Note 1	0.43	0.12
1.2	Note 1	0.44	0.13
1.3	Note 1	0.45	0.13
2.1	Note 1	0.43	0.12
2.2	Note 1	0.44	0.13
3.1	Note 1	0.13	0.13
3.2	Note 1	0.27	0.13
4.1	Note 1	0.43	0.12
5.1	Note 2	0.43	0.12
5.2	Note 3	0.45	0.13
6.1	Note 1	0.44	0.13
6.2	Note 1	0.45	0.13
7.1	0.27 Note 4	0.13	0.12

Notes

1 NaNO₃ not added to stock simulant.

Stock simulant (with noble metals) contained the nominal nitrate concentration, 0.13 mol/L.

2 Non-noble metal stock simulant concentrated to 140 gWO/L contained 0.14 mol NO₃-/L.

3 Non-noble metal stock simulant at 125 gWO/L contained 0.12 mol NO₃-/L.

4 This is the quantity(concentration) of NaNO₃ added to the stock simulant for test 7.1.

The total NO₃- concentration for test 7.1 includes the NaNO₃ added plus

NO₃- which was present in the stock simulant.

For Test 7.1---> Total NO₃- = 0.27 mol/L + 0.13 mol/L = 0.40 mol/L

TABLE 1.1.3.**Waste Oxide Loading of Initial Feed Simulant**

Test No.	Target* g WO/L	Measured** g WO/L
1.1	125	119
1.2	125	131
1.3	125	120
2.1	125	118
2.2	125	124
3.1	116	113
3.2	120	117
4.1	125	121
5.1***	140	~140
5.2	125	127
6.1	125	N/A
6.2	125	N/A
7.1	124	123

Notes

* Target values vary between tests due to changes in NaNO₂ and NaNO₃ additions. See Table 1.2. For example, the nominal target for Na₂O is 26.8 g oxide/L. Na₂O dropped to 17.5 g oxide/L for test 3.1 which was a low nitrite run.

Target values for each test were calculated by taking the reference feed target of 125g WO/L (provided by WHC) and adjusting for Na sources.

Target values are provided for comparison purposes.

** These values were determined by "loss on ignition method".

The weight loss after calcining at 1150 C for 0.5 hr was used to determine the g WO/L.

Samples represent feed simulant (stock simulant + sodium salt additives).

*** This test was performed at an initial concentration of 140 g WO/L to simulate the Slurry Integrated Performance Test condition.

7-11

WHC, 1991

...The target concentration for the recycle slurry is 60 g oxid/L of recycle.

...Actual composition was not measured.

1) To convert from column 2 to 3:
g recycle oxidant/g SHA1 oxide* g SHA1 oxidant/g recycle oxidant*60 g total recycle oxidant/g recycle
The volume 260ml of recycle is approximately what was added during PHD testing. It follows that the source amounts are fairly representative of the composition added to the vessel.

Note: The recycle slurry was added on the basis of the gram waste oxides present in the vessel at the end of digestion. The gram waste oxides were determined by subtracting the waste oxides contained in slurry samples (which were removed during formic acid addition and digestion) from the initial gram waste oxides.

(Initial gram waste oxides-1.5L of slurry*125gSOW/L of slurry-187.5gWO)

TABLE 1.1.5. Recycle Simulant Additions

Oxide	g recy ox per ^a g ox in SRAT feed	g recy ox per ^a L of recycle	Test 1.1	Test 1.2	Test 1.3	Test 2.1	Test 2.2	Test 3.1	Test 3.2	Test 4.1	Test 5.1	Test 7.1
			g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm	g recy ox added to NCAW slm
CaO	0.004	2.01	0.60	0.59	0.58	0.51	0.58	0.51	0.48	0.55	0.67	0.52
MnO2	0.0012	0.60	0.18	0.18	0.17	0.15	0.17	0.15	0.14	0.16	0.20	0.18
Na2O	0.05	25.17	7.48	7.35	6.99	6.34	7.05	6.34	5.97	6.82	8.39	6.51
P2O5	0.004	2.01	0.60	0.59	0.58	0.51	0.58	0.51	0.48	0.55	0.67	0.52
NO3-	0.08	40.27	11.97	11.78	11.18	10.14	11.29	10.14	9.58	10.91	13.42	10.41
Cl-	0.00008	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
TOC	0.0027	1.38	0.40	0.40	0.38	0.34	0.38	0.34	0.32	0.37	0.45	0.35
Diatomaceous Earth	0.04	20.13	5.99	5.88	5.59	5.07	5.64	5.07	4.78	5.45	6.71	5.21
Zeolite (IE-96)	0.02	10.07	2.99	2.94	2.80	2.53	2.82	2.53	2.39	2.73	3.35	2.60
sum of oxides	0.12	60.00	17.84	17.52	16.66	15.11	16.82	15.11	14.24	16.25	19.99	15.52

^aWHC, 1991

^aNote: The recycle slurry was prepared in a 60 g recycle oxides/L of recycle concentration.

1) To convert from column 2 to 3:

g recycle oxide/g SRAT oxide * g SRAT oxide/total g recycle oxide * 60 g total recycle oxide/L of recycle

2) To determine the data for column 4-13:

ml of recycle added to test * 1L/1000ml * g recycle oxide/L of recycle

3) See Table 4 for ml of recycle added to each test.

TABLE 1.2.1. Test Matrix

<u>Test Variable</u>	<u>Test</u>	<u>Description of Test Conditions</u>
Amount of Formic Acid	1.1	Excessive amount of formic acid added (74 ml 87wt% HCOOH/L 125 gWO/L slurry).
	1.2	Minimum amount of formic acid added (27 ml 87wt% HCOOH/L 125 gWO/L)
	1.3	Baseline amount of formic acid added (49 ml 87wt% HCOOH/L 125 gWO/L)
Formic Acid Add Rate	2.1	Addition rate 4X nominal (max. 2 ml/min, equivalent to 8 gpm)
	2.2	Addition rate 2X nominal (.99 ml/min, equivalent to 4 gpm)
Amount of Nitrite	3.1	Amount of nitrite 30% nominal (0.13 mole NO ₂ -/L 125 gWO/L)
	3.2	Amount of nitrite 60% nominal (0.27 mole NO ₂ -/L 125 gWO/L)
Reflux during Digestion	4.1	Extended digestion period: 4 hours under reflux and 4 hours with concentration.
Noble Metals Absent	5.1	Conducted for Slurry Integrated Performance Testing. Formic acid was added before and after recycle addition. Limited data available at this time.
	5.2	Excessive amount of formic acid added (68 ml 80wt% HCOOH/L 125 gWO/L) in absence of noble metals.
Hydrogen Quenching	6.1	Formic acid addition discontinued at onset of hydrogen spike.
	6.2	Formic acid addition and power supply to heating mantle discontinued at onset of hydrogen spike.
Amount of Nitrate/Nitrite	7.1	Amount of nitrate 3X nominal (0.40 moles NO ₃ -/L 125 gWO/L) Amount of nitrite 30% nominal (0.13 moles NO ₂ -/L 125 gWO/L)

TABLE 1.3.1. Test Variables for Redox/Rheology Control Evaluation

Test No.	<-----Target----->			<-----Target----->			<-----Target----->			Initial Waste Oxide Loading gWO/L	Initial Density g/ml	Contains Noble Metals
	NO3- Loading in Initial feed simulant*			NO2- Loading in Initial feed simulant**			CO3- Loading in Initial feed simulant **					
	(mol)	(mol/L)	(g/L)	(mol)	(mol/L)	(g/L)	(mol)	(mol/L)	(g/L)			
1.1	0.20	0.13	8.23	0.65	0.43	19.60	0.19	0.12	7.36	125	1.08	yes
1.2	0.20	0.13	8.23	0.65	0.44	20.13	0.19	0.13	7.56	125	1.08	yes
1.3	0.19	0.13	8.23	0.65	0.45	20.54	0.19	0.13	7.72	125	1.08	yes
2.1	0.20	0.13	8.23	0.65	0.43	19.86	0.19	0.12	7.46	125	1.08	yes
2.2	0.20	0.13	8.23	0.65	0.44	20.26	0.19	0.13	7.61	125	1.08	yes
3.1	0.20	0.13	8.23	0.20	0.13	6.10	0.19	0.13	7.51	125	1.08	yes
3.2	0.20	0.13	8.23	0.40	0.27	12.23	0.19	0.13	7.56	125	1.08	yes
4.1	0.20	0.13	8.23	0.65	0.43	19.73	0.19	0.12	7.41	125	1.08	yes
5.1	0.23	0.14	8.56	0.73	0.43	19.87	0.21	0.12	7.50	140	1.1***	no
5.2	0.18	0.12	7.64	0.65	0.45	20.54	0.19	0.13	7.72	125	1.1	no
6.1	0.20	0.13	8.23	0.65	0.44	20.13	0.19	0.13	7.56	125	1.08	yes
6.2	0.19	0.13	8.23	0.65	0.45	20.68	0.19	0.13	7.77	125	1.08	yes
7.1	0.61	0.40	24.82	0.20	0.13	6.07	0.19	0.12	7.39	125	1.08	yes

*TEST 5.1 and 5.2 NO3- values are derived from ARF SS17A

All other test NO3- values are derived from ARF FP19

**NO2- and CO3 values are based on the amount of NaNO2 and Na2CO3 physically added to simulant.

***The density of the simulant prior to concentration (125 to 140gWO/L) was 1.1gml.

TABLE 1.3.1. Test Variables for Redox/Rheology Control Evaluation (cont)

Test No.	Amount HCOOH added (excluding recycle)			HCOOH addition rate	HCOOH one batch or two	Recycle Addition (refer also to Table 1.1.5)			Boil off during digestion	Sweep Gas Composition
	(mol)	(mol/L)	(ml 86.7wt%/L)	(ml/min)		Amount of Recycle (ml)	HCOOH in recycle (mol)	NO3 in recycle amount (mol)		
1.1	2.59	1.67	74.06	0.6	1	297.3	0.06	0.19	yes	95.6%Ar/4.4%O2
1.2	0.91	0.61	27.05	0.6	1	292	0.06	0.19	yes	95.6%Ar/4.4%O2
1.3	1.60	1.10	48.78	0.57	1	277.7	0.05	0.18	yes	95.6%Ar/4.4%O2
2.1	1.52	1.11	49.22	2, 1, 0.52	1	251.8	0.04	0.16	yes	95.6%Ar/4.4%O2
2.2	1.51	1.07	47.45	0.99	1	280.3	0.05	0.18	yes	95.6%Ar/4.4%O2
3.1	1.56	1.10	48.78	0.64	1	251.8	0.05	0.16	yes	95.6%Ar/4.4%O2
3.2	1.51	1.04	46.12	0.57	1	237.3	0.05	0.16	yes	95.6%Ar/4.4%O2
4.1	1.53	1.01	44.79	0.56	1	270.9	0.05	0.18	reflux	95.6%Ar/4.4%O2
5.1	1.52	1.43	63.41	0.46	2	333.2	0.07	0.22	yes	Air
5.2	2.20	1.54	68.29	0.51	1	not added	not added	not added	yes	Air
6.1	2.03	1.46	64.75	0.49	1	not added	not added	not added	N/A	95.6%Ar/4.4%O2
6.2	2.05	1.51	66.96	0.49	1	not added	not added	not added	N/A	95.6%Ar/4.4%O2
7.1	1.68	1.24	54.99	0.48	1	258.6	0.05	0.17	yes	95.6%Ar/4.4%O2

Test No.	Comments
1.1	High HCOOH amount.
1.2	Low HCOOH amount. Addition of HCOOH was interrupted for 10 minutes.
1.3	Medium (estimated nominal) HCOOH amount.
2.1	High HCOOH addition rate. Rate was decreased twice due to excess foaming.
2.2	Medium HCOOH addition rate.
3.1	Low nitrite.
3.2	Medium nitrite.
4.1	Reflux during digestion.
5.1	Recycle was added at 95C. H2O/HCOOH mixture and frit added at 99C. HCOOH added in two batches with 2 increments per batch. 5 minute intervals existed between increments. This feed contained no noble metals.
5.2	HCOOH added in one batch to w/o noble metals feed.
6.1	Terminated HCOOH addition when 2nd H2 peak initiated. Monitored offgases at temperature of 95C-100C.
6.2	Terminated HCOOH addition and shut off temperature controller when 2nd H2 peak initiated. Monitored offgases through cool down (63C), reheat to 100C, and cool down (73C).
7.1	High nitrate and low nitrite.

TABLE 1.4.1. Key Test Events List

<u>Test</u>	<u>Time</u>	<u>Event</u>
1.1	0	-HCOOH addition begins
	127±3	-Hydrogen spike begins
	185	-HCOOH addition ends
	395	-vessel heater turned off. Data taken for 30 minutes while slurry cooled.
	428	-shut down for the day
	500	-begin next day of test
	526	-begin recycle addition
	534-540	-sweep gases off -- gas data not valid
	545	-end of recycle addition
	642	-end of test
1.2	0	-HCOOH addition begins
	41	-end of first HCOOH addition
	54	-begin second HCOOH addition
	76	-end of second HCOOH addition
	297	-shut down for the day
	350	-begin next day of test
	357	-begin recycle addition
	381	-end of recycle addition
1.3	0	-begin HCOOH addition
	10	-HCOOH addition line pulled up so that HCOOH dripping down onto slurry surface
	11.5	-HCOOH addition line re-submerged
	122	-end of HCOOH addition
	348	-shut down for the day
	400	-begin next day of test, begin recycle add
	432	-end recycle addition
	550	-end of test
2.1	0	-begin HCOOH addition at about 2 ml/min
	3	-HCOOH line submerged -- was initially above slurry surface
	7	-excessive foaming, HCOOH shut off
	16	-HCOOH addition resumes
	17	-severe foaming, HCOOH shut off
	21	-HCOOH addition resumed at 1 ml/min
	22	-HCOOH shut off
	29	-HCOOH addition resumes

TABLE 1.4.1. Key Test Events List (cont)

	32	-HCOOH shut off
	41	-HCOOH addition resumed at 0.5 ml/min
	46	-HCOOH shut off -- shaft seal leaking gas
	152	-HCOOH addition resumed at 0.6 ml/min
	200	-GC computer failed -- no hydrogen data for the remainder of the test
	239	-end of HCOOH addition
	272	-shut down for the day
	350	-resumed slurry digestion next day
	435	-leak in vessel seal found -- remainder of gas data for this test not valid
2.2	0	-HCOOH addition begins at 0.99 ml/min
	1	-HCOOH delivery line submerged in slurry
	68	-end of HCOOH addition
	72	-begin heating up for digestion
	335	-shut down for the day
	400	-begin next day of test
	408	-recycle addition begins
	423	-end of recycle addition
	499	-end of test
3.1	0	-begin HCOOH addition
	75±3	-beginning of hydrogen spike
	110	-end of HCOOH addition
	127	-beginning of digestion
	308	-shut down for the day
	400	-begin next day of test, begin recycle add
	418	-end of recycle addition
	501	-end of test
3.2	0	-begin HCOOH addition at about 0.53 ml/min
	103±3	-beginning of hydrogen spike
	124	-end of HCOOH addition, begin digestion
	364	-end of digestion, shut down for the day
	400	-begin next day of test
	415	-begin recycle addition
	428	-end of recycle addition
	496	-end of test
4.1	0	-begin HCOOH addition
	122	-end of HCOOH addition
	135	-begin digestion
	308	-shut down for the day

TABLE 1.4.1. Key Test Events List (cont)

	350	-begin next day, continue digestion
	677	-shut down for the day
	700	-begin next day of test
	720	-begin recycle addition
	737	-end recycle addition
	807	-end of test
5.1	Data taken on 7/1/91	-no gas generation was observed, pH was stable at 9.00
	0 (7/9/91)	-HCOOH addition begins
	35	-approx. end of first HCOOH batch
	40	-approx. beginning of second HCOOH batch
	78	-end of second HCOOH addition
	89	-begin digestion
	331	-shut down for the day
	400	-begin next day of test
	421	-begin recycle addition
	438	-end of recycle addition
	515	-begin HCOOH addition
	549	-end of 1st HCOOH addition
	554	-begin 2nd HCOOH addition
	587	-end of 2nd HCOOH addition
	599	-begin digestion
	724	-shut down for the day
	Data taken on 7/12/91 (frit addition)	-The only gas observed was hydrogen which was constant at about 20 ppm (about 10^{-6} moles/min). -pH initially at 4.3 falls to 4.2 during the addition of a small amount of HCOOH. Then pH rose to 5.6 during frit addition. Slowly climbed to 6.04 over the next 45 minutes.
5.2	0	-begin HCOOH addition
	194	-end of HCOOH addition
	204	-begin digestion
	330	-shut down for the day
	400	-begin next day of test -- continue digestion
	530	-end of test
6.1	0	-begin HCOOH addition
	178 $\pm$ 3	-beginning of hydrogen spike

TABLE 1.4.1. Key Test Events List (cont)

	184	-end of HCOOH addition
	310	-increased slurry temp to 100°C
	365	-shut off vessel heater
	374	-end of test
6.2	-57	-begin heating slurry
	0	-begin HCOOH addition
	186±4	-beginning of hydrogen spike
	190	-end of HCOOH addition
	190	-shut off vessel heater
	275	-reactivated vessel heater
	308	-slurry reaches 100°C
	340	-shut off vessel heater
	394	-end of test
7.1	0	-begin HCOOH addition
	94±3	-beginning of hydrogen spike
	160	-end of HCOOH addition
	412	-end of digestion, shut down for the day
	500	-begin increasing slurry temp. from 31°C
	563 ⁷	-begin recycle addition
	580	-end recycle addition
	653	-end of test

TABLE 1.4.2. Peak Gas Generation Rates, mmole/min

<u>Test</u>	<u>H₂</u>	<u>CO₂</u>	<u>NO_x</u>	<u>N₂O</u>
1.1	0.56	7.48	0.40	2.83
1.2	<0.05	8.60	0.37	2.11
1.3	<0.05	7.92	0.49	2.70
2.1	<0.05	7.25	2.18	1.79
2.2	<0.05	13.95	1.09	3.35
3.1	0.42	8.01	0.27	2.04
3.2	0.31	8.17	0.41	2.42
4.1	<0.05	8.41	0.48	2.23
5.1	<0.05	6.97	1.55	0.15
5.2	<0.05	6.65	3.89	0.28
6.1	1.12	7.33	0.65	2.40
6.2	0.73	6.23	0.51	2.59
7.1	0.31	6.28	0.093	1.34

*Approximate slurry volume was 1.5L (125 gWO/L) for all except 5.1 which was 1.5L (140 gWO/L).

11/11/91

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time

The following tables list the hydrogen generation rates (mmoles/min) as a function of time (minutes).

Test # 1.1		Test # 3.1		Test # 3.2	
Time	mmol/min	Time	mmol/min	Time	mmol/min
-12.3667	0	-14.1333	0	-14.1167	0
-9.83333	0	-11.6667	0	-11.6333	0
-7.28333	0	-9.21667	0	-9.16667	0
-4.75	0	-6.75	0	-6.71667	0
-2.21667	0	-4.28333	0	-4.26667	0
0.316667	0	-1.81667	0	-1.8	0
2.85	0	0.65	0	0.65	0
5.383333	0	3.116667	0	3.1	0
7.916667	0	5.583333	0	5.55	0
10.45	0	8.033333	0	8.033333	0
13	0	10.48333	0	10.5	0
15.53333	0	12.95	0	12.96667	0
18.06667	0	15.41667	0	15.43333	0
20.6	0.000174	17.88333	0	17.88333	0
23.13333	0.000729	20.35	6.01E-05	20.33333	0
25.66667	0.001458	22.8	0.000318	22.8	0.000259
28.2	0.002246	25.26667	0.000789	25.26667	0.000653
30.75	0.003831	27.73333	0.001122	27.73333	0.0011
33.28333	0.006016	30.2	0.001506	30.2	0.001551
35.81667	0.009463	32.66667	0.002296	32.66667	0.00229
38.35	0.01373	35.15	0.003789	35.11667	0.00321
40.88333	0.020406	37.61667	0.005483	37.58333	0.004724
43.41667	0.02793	40.08333	0.00737	40.03333	0.007392
45.95	0.036108	42.55	0.009305	42.5	0.0097
48.48333	0.036617	45.01667	0.011867	44.96667	0.013004
51.01667	0.036943	47.46667	0.014715	47.41667	0.015002
53.56667	0.048579	49.95	0.015668	49.88333	0.027037
56.1	0.045906	52.4	0.012886	52.35	0.023067
58.63333	0.044882	54.86667	0.014917	54.81667	0.027461
61.16667	0.052016	57.33333	0.013206	57.28333	0.037103
63.7	0.055374	59.8	0.014134	59.75	0.045634
66.23333	0.049039	62.26667	0.012505	62.2	0.036637
68.76667	0.046612	64.71667	0.013078	64.65	0.039995
71.31667	0.054109	67.18333	0.00827	67.11667	0.028637
73.85	0.054882	69.65	0.006105	69.6	0.037786
76.38333	0.047248	72.11667	0.003448	72.05	0.032149
78.91667	0.03839	74.6	0.005182	74.51667	0.025826
81.45	0.039827	77.06667	0.010201	76.98333	0.030371
83.98333	0.039964	79.53333	0.025744	79.45	0.019002
86.51667	0.041514	82	0.095092	81.91667	0.023385
89.05	0.035139	84.46667	0.227388	84.38333	0.019911
91.6	0.035596	86.93333	0.277975	86.85	0.019717
94.13333	0.031153	89.4	0.32107	89.33333	0.015258
96.66667	0.034185	91.86667	0.3852	91.8	0.012949
99.2	0.032293	94.35	0.415562	94.26667	0.010911
101.7333	0.028668	96.81667	0.41698	96.71667	0.009836
104.2667	0.026628	99.28333	0.406151	99.18333	0.008156
106.8	0.027348	101.75	0.412563	101.65	0.00563

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

109.3333	0.025272	104.2167	0.405948	104.1167	0.010017
111.8833	0.023037	106.6833	0.419542	106.5833	0.027095
114.4167	0.020224	109.15	0.387704	109.05	0.11722
116.95	0.018868	111.6167	0.381214	111.5167	0.233181
119.4833	0.018193	114.0833	0.275623	113.9833	0.301263
122.0167	0.012892	116.5667	0.229009	116.45	0.259438
124.55	0.008921	119.0333	0.175727	118.9167	0.218759
127.0833	0.008146	121.5	0.16401	121.3833	0.160446
129.6167	0.021121	123.9667	0.142453	123.85	0.140937
132.1667	0.13937	126.4333	0.135993	126.3	0.123206
134.7	0.329146	128.9	0.125488	128.7833	0.102272
137.2333	0.406897	131.3667	0.149549	131.25	0.093989
139.7667	0.491824	133.8333	0.174389	133.7	0.082107
142.3	0.547608	136.3167	0.145742	136.1667	0.094249
144.8333	0.544809	138.7833	0.10276	138.6167	0.135887
147.3667	0.522751	141.25	0.105036	141.0833	0.09798
149.9167	0.540439	143.7167	0.139526	143.55	0.073583
152.45	0.555495	146.1833	0.146414	146.0333	0.107752
154.9833	0.542433	148.65	0.135209	148.5	0.113381
157.5167	0.495115	151.1167	0.112694	150.9667	0.085246
160.05	0.490383	153.5833	0.10925	153.4333	0.073212
162.5833	0.491993	156.0667	0.11227	155.9	0.088653
165.1167	0.468485	158.5333	0.10777	158.3667	0.092594
167.65	0.421652	161	0.11203	160.8333	0.086027
170.1833	0.413586	163.4667	0.107785	163.3	0.08582
172.7333	0.422226	165.9333	0.102965	165.7667	0.081269
175.2667	0.418213	168.4	0.102903	168.25	0.080873
177.8	0.387617	170.8667	0.09819	170.7167	0.08137
180.3333	0.381005	173.3333	0.09942	173.1833	0.079327
182.8667	0.401364	175.8167	0.09706	175.65	0.07638
185.4	0.330006	178.2833	0.092469	178.1167	0.074708
187.9333	0.254038	180.75	0.086956	180.5667	0.07708
190.4833	0.220528	183.2167	0.090122	183.0333	0.076285
193.0167	0.21081	185.6833	0.089623	185.5	0.073897
195.55	0.203637	188.15	0.084895	187.9667	0.071718
198.0833	0.19269	190.6167	0.083476	190.45	0.06942
200.6167	0.236906	193.0833	0.0843	192.9167	0.067817
203.15	0.214134	195.5667	0.08394	195.3833	0.066321
205.6833	0.17182	198.0333	0.081156	197.85	0.067434
208.2167	0.144645	200.5	0.073803	200.3167	0.067494
210.7667	0.153269	202.9667	0.081018	202.7833	0.066064
213.3	0.18664	205.4333	0.080568	205.25	0.080893
215.8333	0.176722	207.9	0.079765	207.7167	0.101441
218.3667	0.137926	210.3667	0.079559	210.2	0.054909
220.9	0.131856	212.8333	0.075724	212.6667	0.060189
223.4333	0.191913	215.3167	0.077364	215.1333	0.072828
225.9667	0.180208	217.7833	0.077157	217.6	0.069813
228.5167	0.148041	220.25	0.075388	220.0667	0.060123
231.05	0.130552	222.7167	0.075676	222.5167	0.063946
233.5833	0.14766	225.1833	0.075411	224.9833	0.060984
236.1167	0.170579	227.65	0.07371	227.4333	0.064884
238.65	0.143563	230.1167	0.074147	229.9	0.065622
241.1833	0.147601	232.5833	0.073466	232.3667	0.060297
243.7167	0.142068	235.0667	0.07347	234.8333	0.061274

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

246.25	0.14157	237.5333	0.074078	237.3	0.061228
248.7833	0.146402	240	0.072056	239.7667	0.058371
251.3333	0.149872	242.4667	0.077223	242.2167	0.058512
253.8667	0.145517	244.9333	0.0834	244.6667	0.058816
260.7167	0.145517	247.4	0.071443	247.1167	0.057615
263.3333	0.136519	249.8667	0.071913	249.5667	0.059423
265.8667	0.13815	252.3333	0.072179	252.0167	0.055752
268.5833	0.13515	254.8167	0.077903	254.4833	0.056194
271.15	0.133023	257.2833	0.073686	256.9333	0.055101
273.6833	0.12456	259.75	0.066607	259.4	0.05411
276.2167	0.117255	262.2167	0.066463	261.85	0.001634
278.7333	0.122381	264.6833	0.075228	264.3	0.001631
281.25	0.126894	267.15	0.076225	266.75	0.031284
283.7667	0.123076	269.6167	0.070079	269.2	0.052526
286.3	0.121965	272.0833	0.066229	271.6667	0.051481
288.8167	0.117983	274.5667	0.068242	274.1167	0.050845
291.3333	0.119949	277.0333	0.067451	276.5833	0.05138
293.85	0.118883	279.5	0.067489	279.0333	0.051499
296.3667	0.117679	281.9667	0.070531	281.5	0.046333
298.8833	0.117519	284.4333	0.066209	283.95	0.048989
301.4167	0.117737	286.9	0.068184	286.4167	0.04911
303.95	0.106638	289.3667	0.064489	288.8833	0.047729
306.4833	0.113815	291.85	0.065579	291.35	0.046875
309.0167	0.113811	294.3167	0.062366	293.8	0.047078
311.5333	0.112517	296.7833	0.059195	296.25	0.045928
314.05	0.108721	299.25	0.063859	298.7167	0.045704
316.5833	0.110027	301.7167	0.063438	301.1667	0.045275
319.1	0.109213	304.1833	0.06179	303.6167	0.044054
321.6333	0.105447	306.65	0.062839	306.0667	0.043932
324.1667	0.106717	309.1167	0.064943	308.5167	0.044218
326.6833	0.109408	311.5833	0.058454	310.9667	0.043807
329.2	0.10899	314.0667	0.001835	313.45	0.042834
331.7167	0.108679	401.9167	0.039355	315.9167	0.042162
334.2333	0.105555	404.3833	0.043938	318.3667	0.041811
336.75	0.16164	406.8333	0.050464	320.8333	0.041793
339.2667	0.102214	409.2833	0.055997	323.3	0.04086
341.8	0.106793	411.7333	0.08669	325.7667	0.039957
344.3333	0.10557	414.2	0.05589	328.2333	0.04004
346.8667	0.100858	416.65	0.05955	330.7	0.040064
349.4	0.095692	419.1167	0.091612	333.1833	0.038077
351.9167	0.091689	421.5833	0.0966	335.6333	0.039561
354.4333	0.098264	424.0333	0.078665	338.0833	0.039059
356.95	0.100832	426.5	0.049051	340.55	0.038071
359.4833	0.095728	428.95	0.056436	343.0167	0.035828
362	0.094827	431.4	0.104561	345.4667	0.03718
364.5333	0.089244	433.85	0.051052	347.9333	0.037048
367.0667	0.095548	436.3	0.050933	350.3833	0.035371
369.5833	0.097856	438.75	0.067765	352.85	0.036455
372.1167	0.097085	441.2	0.088617	355.3167	0.03564
374.6333	0.094528	443.6667	0.050141	357.7833	0.035179
377.15	0.092989	446.1167	0.052633	360.25	0.034907
379.6667	0.093123	448.5667	0.105828	362.7	0.033239
382.2167	0.093212	451.0167	0.051049	401.55	0.017332
384.75	0.094988	453.4667	0.049906	404.0167	0.017666

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

387.2833	0.092493	455.9167	0.057733	406.4833	0.018049
389.8167	0.092947	458.3833	0.082719	408.95	0.017862
392.35	0.089734	460.85	0.046693	411.4167	0.018838
394.8667	0.08963	463.3167	0.053614	413.8833	0.018315
397.3833	0.085031	465.7667	0.079951	416.35	0.016644
399.9	0.063427	468.2167	0.05357	418.8167	0.019581
402.4333	0.059505	470.6667	0.047657	421.3	0.023637
404.9667	0.056396	473.1333	0.056031	423.7667	0.026386
407.4833	0.04694	475.5833	0.061595	426.2333	0.025864
410	0.045841	478.05	0.0523	428.7	0.027221
412.5333	0.041943	480.5	0.054129	431.1667	0.036851
415.05	0.039126	482.9667	0.056059	433.6333	0.022207
417.5833	0.037287	485.4333	0.050001	436.1	0.023024
420.1	0.03483	487.8833	0.051625	438.5667	0.027974
422.65	0.032694	490.3333	0.053472	441.05	0.024521
425.1833	0.031101	492.7833	0.050024	443.5167	0.022604
427.7	0.029442	495.25	0.049382	445.9833	0.021553
501.9333	0.067836			448.45	0.023135
504.4833	0.065313			450.9167	0.021947
507.0167	0.063742			453.3833	0.021554
509.55	0.065374			455.85	0.021481
512.0833	0.067467			458.3167	0.021248
514.6167	0.064335			460.8	0.021718
517.15	0.065503			463.2667	0.020355
519.6833	0.063261			465.7333	0.021272
522.2167	0.064543			468.2	0.021397
524.75	0.065623			470.6667	0.020826
527.2667	0.052579			473.1333	0.020864
529.8	0.067976			475.6	0.020999
532.3167	0.073845			478.0667	0.020588
534.85	0.107237			480.5333	0.019646
537.3833	0.010867			483.0167	0.019086
539.9	0			485.4833	0.018812
542.45	0.068293			487.95	0.018571
544.9833	0.115295			490.4167	0.018677
547.5167	0.1569			492.8833	0.018237
550.05	0.103382			495.35	0.016823
552.5833	0.183519				
555.1167	0.120122				
557.65	0.080875				
560.1833	0.082544				
562.7333	0.119353				
565.2667	0.111725				
567.8	0.075832				
570.3333	0.08441				
572.8667	0.096462				
575.4	0.099036				
577.9167	0.080446				
580.45	0.080081				
582.9833	0.083127				
585.5	0.08537				
588.05	0.082382				
590.5833	0.077023				
593.1167	0.078718				

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

595.65	0.078494
598.1833	0.078519
600.7167	0.079264
603.25	0.07786
607.3333	0.078132
609.8667	0.072694
612.4	0.076189
614.9333	0.076273
617.4667	0.080026
620	0.075006
622.5333	0.073572
625.0667	0.074404
627.6167	0.073101
630.15	0.073048
632.6833	0.07344
635.2167	0.073372
637.75	0.069215
640.2833	0.069788
642.8167	0.069788

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

Test # 6.1		Test # 6.2		Test # 7.1	
Time	mmol/min	Time	mmol/min	Time	mmol/min
-15.65	0	-56.5333	0	-15.9667	3.66E-05
-13.6333	0	-54.7667	0	-13.4167	3.87E-05
-11.6167	0	-53.0167	0	-10.8667	5.51E-05
-9.6	0	-51.25	0	-8.31667	5.74E-05
-7.58333	0	-49.5	0	-5.76667	6.62E-05
-5.56667	0	-47.75	0	-3.21667	6.18E-05
-3.55	0	-46	0	-0.66667	4.82E-05
-1.53333	0	-44.25	0	1.883333	6.14E-05
0.483333	0	-42.5	0	4.45	4.46E-05
2.5	0	-40.75	0	7	4.09E-05
4.533333	0	-39	0	9.55	5.24E-05
6.55	0	-37.25	0	12.1	5.54E-05
8.566667	0	-35.5	0	14.65	4.31E-05
10.58333	0	-33.75	0	17.2	3.76E-05
12.6	0	-31.9833	0	19.75	5.68E-05
14.61667	0	-30.2333	0	22.3	5.83E-05
16.63333	0	-28.4833	0	24.85	8.73E-05
18.65	0	-26.7333	0	27.41667	0.000165
20.66667	0	-24.9833	0	29.95	0.00024
22.68333	0	-23.2333	0	32.51667	0.000347
24.7	0	-21.4833	0	35.06667	0.000466
26.71667	0.000219	-19.7333	0	37.61667	0.000569
28.75	0.000254	-17.9833	0	40.16667	0.000717
30.76667	0.000162	-16.2333	0	42.73333	0.001048
32.78333	0.000144	-14.4833	0	45.28333	0.001319
34.8	0.000147	-12.7333	0	47.83333	0.00158
36.81667	0.000157	-10.9833	0	50.38333	0.001962
38.83333	0.00018	-9.23333	0	52.93333	0.00266
40.85	0.000307	-7.48333	0	55.5	0.003323
42.86667	0.000285	-5.71667	0	58.05	0.003396
44.88333	0.000346	-3.96667	0	60.6	0.003274
46.9	0.000447	-2.21667	0	63.15	0.003551
48.91667	0.000539	-0.46667	0	65.71667	0.004066
50.93333	0.000714	1.283333	0	68.26667	0.004039
52.95	0.000884	3.033333	0	70.81667	0.003625
54.98333	0.001136	4.783333	0	73.36667	0.003159
57	0.001284	6.533333	0	75.95	0.003415
59.01667	0.001483	8.283333	0	78.51667	0.003036
61.03333	0.001782	10.03333	0	81.06667	0.002414
63.05	0.002025	11.78333	0	83.61667	0.002061
65.06667	0.002123	13.53333	0	86.16667	0.001471
67.08333	0.002317	15.3	0	88.71667	0.000983
69.1	0.002416	17.05	0	91.26667	0.00145
71.11667	0.00249	18.8	0	93.83333	0.002754
73.13333	0.002445	20.55	0	96.38333	0.004242
75.15	0.002585	22.3	0	98.95	0.005647
77.18333	0.002522	24.05	0	101.5333	0.009354
79.2	0.002561	25.8	0	104.1	0.01905
81.21667	0.00258	27.55	7.67E-05	106.65	0.034668

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

83.23333	0.002631	29.3	0.000221	109.2	0.056825
85.25	0.002847	31.06667	0.000179	111.75	0.086962
87.26667	0.002775	32.83333	0.00014	114.3167	0.130224
89.28333	0.002561	34.6	0.000137	116.8833	0.181406
91.3	0.002567	36.36667	0.00012	119.45	0.207247
93.31667	0.002643	38.13333	0.000127	122.0333	0.228521
95.33333	0.002841	39.9	0.000137	124.6	0.261859
97.35	0.002936	41.66667	0.000149	127.1667	0.265306
99.36667	0.00291	43.43333	0.00017	129.7333	0.270468
101.4	0.002889	45.2	0.00022	132.3	0.281402
103.4167	0.003029	46.96667	0.000194	134.8667	0.296845
105.4333	0.003027	48.73333	0.000303	137.4333	0.313083
107.45	0.003274	50.51667	0.000389	140	0.305623
109.4667	0.003612	52.28333	0.00047	142.5667	0.294909
111.4833	0.003349	54.05	0.000503	145.1333	0.305791
113.5	0.003254	55.81667	0.000592	147.7	0.305127
115.5167	0.0034	57.58333	0.000703	150.2833	0.302907
117.5333	0.003463	59.35	0.000821	152.85	0.281594
119.55	0.003884	61.11667	0.000937	155.4167	0.286405
121.5667	0.004002	62.88333	0.00104	157.9833	0.302106
123.6	0.003863	64.65	0.001159	160.55	0.27784
125.6167	0.003703	66.41667	0.001256	163.1167	0.203886
127.6333	0.003969	68.18333	0.001316	165.6833	0.184232
129.65	0.004351	69.95	0.001339	168.25	0.194126
131.6667	0.004886	71.71667	0.001435	170.8167	0.160364
133.6833	0.004719	73.48333	0.001511	173.4	0.121027
135.7	0.004544	75.25	0.001581	175.9667	0.081845
137.7167	0.004647	77.01667	0.001693	178.5333	0.170957
139.7333	0.004939	78.8	0.001778	181.1	0.187398
141.75	0.005382	80.55	0.001837	183.6667	0.169105
143.7833	0.005601	82.31667	0.001898	186.2333	0.137703
145.8	0.005734	84.08333	0.001952	188.8	0.150955
147.8167	0.005874	85.85	0.002134	191.3667	0.163458
149.85	0.006154	87.61667	0.002269	193.95	0.151173
151.8667	0.00675	89.38333	0.002525	196.5167	0.122279
153.8833	0.007163	91.15	0.002518	199.0833	0.128755
155.9	0.007639	92.91667	0.002479	201.6667	0.156582
157.9167	0.007813	94.68333	0.002492	204.25	0.143722
159.9333	0.008514	96.45	0.002573	206.8333	0.105589
161.95	0.008982	98.21667	0.002799	209.4167	0.115014
163.9667	0.009736	99.98333	0.002967	212	0.149193
165.9833	0.010436	101.75	0.002927	214.5833	0.12964
168	0.01058	103.5333	0.002832	217.1667	0.099608
170.0167	0.006258	105.3	0.002962	219.75	0.103607
172.0333	0.004551	107.0667	0.003078	222.3167	0.153247
174.0667	0.010131	108.8333	0.003259	224.8833	0.129777
176.0833	0.011059	110.6	0.003279	227.45	0.101037
178.1	0.014853	112.3667	0.003086	230.0167	0.097458
180.1167	0.035551	114.1333	0.003152	232.5833	0.150591
182.1333	0.384623	115.9	0.003403	235.15	0.12601
184.15	1.124179	117.6667	0.003635	237.7167	0.101312
186.1667	1.009776	119.4333	0.003576	240.2833	0.08894
188.1833	0.797056	121.2167	0.003599	242.85	0.157726
190.2	0.677867	122.9667	0.00354	245.4333	0.120708

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

192.2167	0.569793	124.75	0.003663	248	0.102795
194.25	0.487069	126.5167	0.003778	250.5667	0.089576
196.2833	0.439227	128.2833	0.003901	253.1333	0.14219
198.3167	0.385611	130.05	0.00407	255.7	0.120183
200.35	0.346641	131.8167	0.003898	258.2667	0.116544
202.3667	0.286948	133.5833	0.003985	260.8333	0.0854
204.3833	0.284269	135.35	0.004102	263.4	0.138243
206.4	0.254765	137.1333	0.004299	265.9667	0.113873
208.4167	0.253853	138.9	0.004449	268.5333	0.108906
210.4333	0.238913	140.6667	0.004434	271.1167	0.074628
212.45	0.210964	142.4333	0.004471	273.6833	0.124639
214.4667	0.221597	144.2	0.00455	276.25	0.117846
216.4833	0.20691	145.9667	0.004682	278.8167	0.100945
218.5	0.200441	147.7333	0.00496	281.3833	0.077624
220.5333	0.1912	149.5	0.005154	283.95	0.121068
222.55	0.183471	151.2833	0.005316	286.5167	0.118356
224.5667	0.183952	153.0333	0.005202	289.0833	0.100834
226.5833	0.178071	154.8167	0.005388	291.65	0.067308
228.6	0.179158	156.5833	0.005726	294.2167	0.10931
230.6167	0.166919	158.35	0.006241	296.8	0.12535
232.6333	0.166812	160.1167	0.00677	299.3667	0.097674
234.65	0.158207	161.8833	0.007061	301.9333	0.068361
236.6667	0.154908	163.65	0.007213	304.5	0.098078
238.6833	0.156423	165.4167	0.007682	307.0667	0.134901
240.7	0.157901	167.1833	0.008207	309.6333	0.096343
242.7167	0.154703	168.95	0.009144	312.2	0.072537
244.7333	0.150857	170.7167	0.009761	314.7667	0.079317
246.7667	0.150983	172.4667	0.010652	317.3333	0.150448
248.7833	0.143388	174.2333	0.011228	319.9	0.094917
250.8	0.144365	176	0.011858	322.4833	0.071578
252.8167	0.15172	177.7667	0.010489	325.05	0.071366
254.8333	0.142177	179.5167	0.006012	327.6167	0.132342
256.85	0.142422	181.2667	0.005657	330.1833	0.096287
258.8667	0.144958	183.0167	0.008316	332.75	0.085858
260.8833	0.140645	184.7667	0.010269	335.3167	0.064751
262.9	0.147112	186.5167	0.012226	337.8833	0.107331
264.9167	0.132945	188.2833	0.015419	340.45	0.102766
266.9333	0.14322	190.0167	0.017241	343.0167	0.078444
268.9667	0.072344	191.7833	0.080065	345.6	0.06119
270.9833	0.142787	193.5333	0.501698	348.1667	0.079447
273	0.137973	195.2833	0.726745	350.7333	0.130968
275.0167	0.141192	197.0333	0.682896	353.3	0.083676
277.0333	0.12919	198.8	0.575635	355.8667	0.081076
279.05	0.135554	200.55	0.480992	358.4333	0.053644
281.0667	0.137815	202.3	0.394085	361	0.06456
283.0833	0.137562	204.05	0.335005	363.5667	0.095711
285.1	0.138535	205.8	0.276763	366.1333	0.084339
287.1333	0.123879	207.55	0.24399	368.7167	0.074572
289.15	0.124389	209.3	0.212248	371.2833	0.054626
291.1667	0.128963	211.05	0.188599	373.85	0.061286
293.2	0.134711	212.8	0.163982	376.4167	0.114675
295.2167	0.133563	214.5667	0.14918	378.9833	0.075762
297.2333	0.129838	216.3167	0.126378	381.55	0.065447
299.25	0.131435	218.0667	0.116731	384.1167	0.058257

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

301.2667	0.125683	219.8167	0.110775	386.6833	0.053804
303.2833	0.139525	221.5667	0.101874	389.25	0.06275
305.3	0.133069	223.3167	0.093413	391.8167	0.094409
307.3167	0.161899	225.0667	0.085347	394.3833	0.065171
309.3333	0.197837	226.8167	0.078956	396.9667	0.04737
311.35	0.200415	228.5667	0.072316	399.5333	0.048909
313.3667	0.176039	230.3333	0.070792	402.1	0.070346
315.3833	0.179823	232.0833	0.066253	404.6667	0.052157
317.4167	0.21133	233.8333	0.074441	407.2333	0.111409
319.4333	0.224184	235.5833	0.064593	409.8	0.063171
321.4667	0.207846	237.3333	0.056347	412.3667	0.046276
323.5	0.182328	239.1	0.052593	499.6833	0.000551
325.5167	0.176028	240.85	0.050347	502.3	0.000544
327.5333	0.198539	242.6	0.047983	504.85	0.000564
329.55	0.19798	244.35	0.046449	507.4	0.000839
331.5667	0.189938	246.1	0.044659	509.95	0.001391
333.5833	0.192496	247.85	0.042896	512.5167	0.002392
335.6	0.196505	249.6	0.040108	515.0667	0.004204
337.6167	0.190782	251.35	0.038177	517.6167	0.007476
339.6333	0.191948	253.1	0.036612	520.1667	0.010707
341.6667	0.184982	254.85	0.03569	522.7333	0.020989
343.6833	0.174646	256.6	0.034957	525.3	0.043775
345.7167	0.183338	258.35	0.033825	527.85	0.037774
347.7333	0.176517	260.1167	0.032637	530.4	0.055768
349.75	0.184523	261.8833	0.030425	532.95	0.018194
351.7667	0.177702	263.6333	0.029664	535.5167	0.025445
353.7833	0.172428	265.4	0.029612	538.0667	0.012503
355.8	0.170966	267.15	0.027933	540.6167	0.018747
357.8333	0.178845	268.9	0.026682	543.1667	0.08067
359.85	0.171726	270.65	0.025401	545.7333	0.061159
361.8667	0.174278	272.4	0.025593	548.3	0.041995
363.8833	0.177275	274.15	0.024994	550.85	0.028183
365.9167	0.166241	275.9	0.024045	553.4	0.029438
367.95	0.142263	277.65	0.024157	555.9667	0.057688
369.9667	0.112338	279.4	0.02421	558.5333	0.04418
371.9833	0.089633	281.1667	0.025126	561.1	0.032752
		282.9167	0.027025	563.65	0.067326
		284.6667	0.031137	566.2	0.04767
		286.4167	0.035575	568.7667	0.020797
		288.1667	0.042722	571.3333	0.024266
		289.9333	0.051573	573.9	0.036658
		291.6833	0.060512	576.45	0.073625
		293.45	0.066642	579	0.044758
		295.2167	0.071434	581.55	0.050617
		296.9667	0.074593	584.1167	0.08974
		298.7167	0.085108	586.6833	0.036985
		300.4833	0.106082	589.25	0.020131
		302.2333	0.143089	591.8167	0.021043
		303.9833	0.203035	594.3833	0.063486
		305.7333	0.2646	596.95	0.02832
		307.4833	0.320298	599.5	0.019319
		309.25	0.297386	602.0667	0.01763
		311	0.295158	604.6167	0.025895
		312.7667	0.27519	607.1667	0.032715

TABLE 1.4.3. Tabulated H₂ Generation Rates as a Function of Time (continued)

314.5167	0.251985	609.75	0.020691
316.2667	0.246772	612.3167	0.020278
318.0167	0.246092	614.8667	0.024729
319.7667	0.260705	617.4333	0.034059
321.5167	0.254815	619.9833	0.020449
323.2667	0.255865	622.55	0.019314
325.0333	0.258612	625.1	0.026389
326.7833	0.246958	627.65	0.025835
328.5333	0.232862	630.2	0.019604
330.2833	0.239221	632.75	0.018795
332.05	0.238235	635.3167	0.025822
333.8	0.179039	637.8833	0.034991
335.5667	0.091075	640.4333	0.020172
337.3333	0.095379	642.9833	0.016599
339.0833	0.085771	645.5333	0.02254
340.85	0.08447	648.0833	0.027018
342.6	0.175997	650.65	0.016788
344.35	0.164998	653.2	0.017218
346.1	0.140545		
347.8667	0.128913		
349.6333	0.110492		
351.3833	0.106872		
353.1333	0.093681		
354.9	0.089593		
356.65	0.08299		
358.4	0.078621		
360.1667	0.070607		
361.9333	0.064563		
363.6833	0.059869		
365.45	0.055065		
367.2167	0.050471		
368.9667	0.049965		
370.7333	0.044231		
372.4833	0.041406		
374.2333	0.040242		
376	0.037612		
377.75	0.035162		
379.5	0.032915		
381.2667	0.03147		
383.0167	0.029928		
384.7833	0.02949		
386.55	0.027804		
388.3167	0.026318		
390.0833	0.025127		
391.8667	0.023894		
393.65	0.023015		

TABLE 1.4.4. Molar Gas Releases during Lab-Scale Formating

<u>Test</u>	<u>Species</u>	<u>moles Formating</u>	<u>moles Digestion</u>	<u>moles Recycle</u>	<u>moles Total</u>
1.1	CO ₂	0.876	0.1385	0.055	1.066
	N ₂ O	0.236	0.00015	0.00015	0.236
	NO _x	0.030	0.00024	5.3E-5	0.0303
	H ₂	0.0271	0.0298	0.0111	0.068
1.2	CO ₂	0.276	0.0177	0.0082	0.303
	N ₂ O	0.087	0.0575	0.007	0.153
	NO _x	0.012	0.0019	9.2E-5	0.014
	H ₂	0.00079	0.00024	0.00011	0.0011
1.3	CO ₂	0.585	0.0343	0.023	0.642
	N ₂ O	0.210	0.0324	0.0005	0.243
	NO _x	0.034	0.0013	0.000	0.0353
	H ₂	0.0028	0.0040	0.0049	0.0116
2.1	CO ₂	0.452	0.047	NA	0.499
	N ₂ O	0.143	0.019	NA	0.162
	NO _x	0.108	0.010	NA	0.118
	H ₂	0.0006 -- H ₂ dataset incomplete for this test			
2.2	CO ₂	0.490	0.066	0.0106	0.567
	N ₂ O	0.145	0.072	0.0025	0.219
	NO _x	0.026	0.0055	4.2E-5	0.032
	H ₂	1.6E-4	6.9E-5	2.7E-5	2.5E-4
3.1	CO ₂	0.457	0.102	0.043	0.602
	N ₂ O	0.077	8.3E-4	6.2E-4	0.077
	NO _x	0.0067	5.25E-5	3.8E-5	0.0067
	H ₂	0.0107	0.0197	0.006	0.036
3.2	CO ₂	0.535	0.081	0.035	0.652
	N ₂ O	0.146	0.0011	0.0005	0.148
	NO _x	0.019	0.0002	1.7E-5	0.0192
	H ₂	0.005	0.0145	0.002	0.0215
4.1	CO ₂	0.550	0.043	0.021	0.614
	N ₂ O	0.190	0.0524	0.0004	0.243
	NO _x	0.029	0.0034	5.4E-5	0.0323
	H ₂	8.3E-4	1.9E-4	0.0009	0.0019

7.1	CO ₂	0.524	0.180	0.057	0.761
	N ₂ O	0.080	0.00012	0.00	0.080
	NO _x	0.0041	0.00011	0.00014	0.00434
	H ₂	0.0127	0.0277	0.0045	0.0449

Gradient	CO ₂	0.380	0.120	NA	0.501
Furnace	N ₂ O	0.092	0.041	NA	0.133
	NO _x	0.096	0.038	NA	0.134
	H ₂	2.4E-4	6.4E-4	NA	9.0E-4

Test	Species	1st HCOOH	Digest	Recycle	2nd HCOOH	Digest	Total
5.1	CO ₂	0.169	0.034	0.0072	0.093	0.0383	0.3403
	N ₂ O	2.5E-4	2.1E-4	2.1E-4	0.0062	0.0014	0.0083
	NO _x	0.0046	0.016	0.0047	0.0659	0.0391	0.1300
	H ₂	2.4E-6	3.3E-5	9.7E-6	3.6E-5	1.5E-4	2.3E-4

		HCOOH Addition	Digestion	Total
5.2	CO ₂	0.412	0.0036	0.416
	N ₂ O	0.020	0.0008	0.021
	NO _x	0.254	0.0117	0.265
	H ₂	0.0001	0.0005	0.0006
6.1	CO ₂	0.743	0.0993	0.842
	N ₂ O	0.239	0.0020	0.241
	NO _x	0.051	0.0006	0.052
	H ₂	0.0026	0.0395	0.042

		<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
6.2	CO ₂	0.0	0.720	0.049	0.010	0.026	0.006	0.812
	N ₂ O	0.0	0.222	0.0007	0.0	0.0	0.0	0.223
	NO _x	0.0	0.046	0.0	0.0	0.0	0.0	0.046
	H ₂	0.0	0.0006	0.012	0.0027	0.0073	0.0036	0.026

Key: 1 = Heat up (-57, 0 min) 5 = Temp. = 100°C (308, 340 min)
 2 = HCOOH Addition (0, 190 min) 6 = Cool Down (340, 394 min)
 3 = Cool Down (190, 275 min) 7 = Total moles evolved
 4 = Heat Up (275, 308 min)

TABLE 1.5.1. Nitrate Salt and Organic Reactions - Summary of Data

Sample	Sample weight for STG		Sample weight for DSC		Measured Nitrate and Organic (formate), g/g dried slurry		
	estimated		estimated		Organic Carbon	Nitrate	Nitrite
	dry wt, mg	slurry wt, mg	dry wt, mg	slurry wt, mg			
1.1-47.1	9.34	47.63	7.43	37.89	5.44E-02	6.99E-02	not detectable
1.3-7.1	5.515	39.39	7.50	53.57	0.00E+00	5.28E-02	1.32E-01
1.3-32.1	9.334	14.38	8.10	44.85	4.54E-02	4.24E-02	not detectable
1.3-47.1	8.28	42.23	7.51	35.76	3.52E-02	7.58E-02	not detectable

Sample	Region I Endotherm (50-130 C)				Region II Exotherm (125-250 C)				Region III Endotherm (230-310 C)		
	DSC Data			STG Data	DSC Data			STG Data	DSC Data		
	Temp, C	Onset, C	J/gm		Temp, C	Onset, C	J/gm		Temp, C	Onset, C	J/gm
1.1-47.1				43-139 78.3	156-274	177 -354		183-295 2.8	274-314	274	30.5
1.3-7.1	46-137	46	97	43-115 78.5					137-305	184	265
1.3-32.1				43-138 77.7	132-225	141 -223		149-239 1.8	225-302	254	69
1.3-47.1	45-124	46	78	43-124 76.6	124-236	156 -283		151-304 2.7	237-297	247	48

DETAILED DESIGN DATA PACKAGE

PHTD Redox/Rheology Evaluation Control

Milestone 1.2.2.03.02B

December 6, 1991

FIGURES

FIGURE 1.4.1. Test 1.1

F1.4.1.-1

910/91

FIGURE 1.4.2. Test 1.2

F1.4.1.-2

FIGURE 1.4.3. Test 1,3

F1.4.1.-3

FIGURE 1.4.4. Test 2.1

F1.4.1.-4

FIGURE 1.4.5. Test 2.2

F1.4.1.-5

FIGURE 1.4.6. Test 3.1

F1.4.1.-6

4/10/71

FIGURE 1.4.7. Test 3.2

F1.4.1.-7

FIGURE 1.4.8. Test 4.1

F1.4.1.-8

FIGURE 1.4.9. Test 5.1

F1.4.1.-9

q, w, a

FIGURE 1.4.10. Test 5.2

F1.4.1.-10

FIGURE 1.4.11. Test 6.1

F1.4.1.-11

FIGURE 1.4.12. Test 6.2

F1.4.1.-12

FIGURE 1.4.13. Test 7.1

F1.4.1.-13

FIGURE 1.4.2.1a. Amount of Formic Acid, H₂ profile

FIGURE 1.4.2.1b. Amount of Formic Acid, N₂O profile

FIGURE 1.4.2.1c. Amount of Formic Acid, NO_x profile

FIGURE 1.4.2.1d. Amount of Formic Acid, CO₂ profile

F1.4.2.-1d

FIGURE 1.4.2.2a. Formic Acid Addition Rate, H₂ profile

F1.4.2.-2a

9/9/91

FIGURE 1.4.2.2b. Formic Acid Addition Rate, N₂O profile

F1.4.2.-2b

FIGURE 1.4.2.2c. Formic Acid Addition Rate, NO_x profile

F1.4.2.-2c

FIGURE 1.4.2.2d. Formic Acid Addition Rate, CO₂ profile

F1.4.2.-2d

FIGURE 1.4.2.3a. Nitrite Concentration, H_2 profile

F1.4.2.-3a

FIGURE 1.4.2.3b. Nitrite Concentration, N_2O profile

F1.4.2.-3b

FIGURE 1.4.2.3c. Nitrite Concentration, NO_x profile

F1.4.2.-3c

FIGURE 1.4.2.3d. Nitrite Concentration, CO₂ profile

F1.4.2.-3d

FIGURE 1.4.2.4a. Reflux versus Boil-off During Digestion, H₂ profile

F1.4.2.-4a

FIGURE 1.4.2.4b. Reflux versus Boil-off During Digestion, N₂O profile

F1.4.2.-4b

FIGURE 1.4.2.4c. Reflux versus Boil-off During Digestion, NO_x profile

F1.4.2.-4c

9/6/71

FIGURE 1.4.2.4d. Reflux versus Boil-off During Digestion, CO₂ profile

F1.4.2.-4d

FIGURE 1.4.2.5a. Effect of Noble Metals, H₂ profile

F1.4.2.-5a

FIGURE 1.4.2.5b. Effect of Noble Metals, N₂O profile

F1.4.2.-5b

9/6/91

FIGURE 1.4.2.5c. Effect of Noble Metals, NO_x profile

F1.4.2.-5c

FIGURE 1.4.2.5d. Effect of Noble Metals, CO₂ profile

F1.4.2.-5d

1/6/94

FIGURE 1.4.2.6a. Low Nitrite, High Nitrate, H₂ profile

F1.4.2.-6a

FIGURE 1.4.2.6b. Low Nitrite, High Nitrate, N₂O profile

F1.4.2.-6b

9/10/91

FIGURE 1.4.2.6c. Low Nitrite, High Nitrate, NO_x profile

F1.4.2.-6c

9/6/91

FIGURE 1.4.2.6d. Low Nitrite, High Nitrate, CO₂ profile

F1.4.2.-6d

9/6/41

FIGURE 1.4.3.1. Test 1.1, Cool Down Profile for H_2

F1.4.3.-1

FIGURE 1.4.3.2. Test 6.1, Cool Down Profile for H_2

F1.4.3.-2

FIGURE 1.4.3.3. Test 6.2, Cool Down Profile for H_2 during peak generation

F1.4.3.-3

FIGURE 1.4.3.4. Test 6.2, Heat Up Profile for H₂

F1.4.3.-4

FIGURE 1.4.3.5. Test 6.2, Cool Down Profile for H₂

F1.4.3.-5

FIGURE 1.4.3.6. Test 1.1, Hydrogen Generation Rate Variation with Temperature

F1.4.3-6

FIGURE 1.4.3.7. Test 6.2, Hydrogen Generation Rate Variation with Temperature

FIGURE 1.4.4.1a Test Set 6, Quenching Tests, H₂ Profile

F1.4.4.-1a

FIGURE 1.4.4.1b Test Set 6, Quenching Tests, N₂O Profile

F1.4.4.-1b

FIGURE 1.4.4.1c Test Set 6, Quenching Tests, NO_x Profile

F1.4.4.-1c

FIGURE 1.4.4.1d Test Set 6, Quenching Tests, CO₂ Profile

F1.4.4.-1d

ENDS

Date: Jun 24, 1991 2: 40pm
Scanning Rate: 10.0 C/min
Sample Wt: 7.500 mg

FIGURE 1.5.1. Test 1.3, Feed Simulant, DSC

Date: Jun 18, 1991 07:12am
 Scanning Rate: 10.0 C/min
 Sample Wt: 5.515 mg
 File: TGA.1048

FIGURE 1.5.2. Test 1.3, Feed Simulant, TGA 1

Date: Jun 18, 1991 07:12am
Scanning Rate: 10.0 C/min
Sample Wt: 5.515 mg

FIGURE 1.5.3. Test 1.3, Feed Simulant, TGA 2

F1.5.-3

Date: Jun 25, 1991 09:56am
Scanning Rate: 10.0 C/min
Sample Wt: 8.100 mg

FIGURE 1.5.4. Test 1.3, Formated Feed Simulant, DSC

F1.5.-4

Date: Jun 18, 1991 09: 14am
Scanning Rate: 10.0 C/min
Sample Wt: 9.334 mg Path:

FIGURE 1.5.5. Test 1.3, Formated Feed Simulant, TGA 1

Date: Jun 18, 1991 09: 14am
 Scanning Rate: 10.0 C/min
 Sample Wt: 9.334 mg

FIGURE 1.5.6. Test 1.3, Formated Feed Simulant, TGA 2

F1.5.-6

Date: Jun 25, 1991 07:17am

Scanning Rate: 10.0 C/min

Sample Wt: 7.510 mg

FIGURE 1.5.7.

Test 1.3, Formated Feed Simulant plus Recycle, DSC

F1.5.-7

Date: Jun 18, 1991 10:52am

Scanning Rate: 10.0 C/min

Sample Wt: 8.280 mg

FIGURE 1.5.8. Test 1.3, Formated Feed Simulant plus Recycle, TGA 1

F1.5.-8

Date: Jun 25, 1991 08:27am
Scanning Rate: 10.0 C/min
Sample Wt: 7.430 mg

FIGURE 1.5.10. Test 1.1, Formated Feed Simulant plus Recycle, DSC

F1.5.-10

Date: Jun 18, 1991 12:29am
 Scanning Rate: 10.0 C/min
 Sample Wt: 9.340 mg

FIGURE 1.5.11. Test 1.1, Formated Feed Simulant plus Recycle, TGA 1 F1.5.11

Date: Jun 18, 1991 12: 29am
 Scanning Rate: 10.0 C/min
 Sample Wt: 9.340 mg

FIGURE 1.5.12. Test 1.1, Formated Feed Simulant plus Recycle, TGA 2 F1.5.12

FIGURE 2.1 Threshold for Initiation of Second Hydrogen Release

FIGURE 2.2 Process Profile: Hydrogen Peak Induction Time Dependence on Initial Nitrite Concentration

FIGURE 2.3 Hydrogen Peak Induction Time Dependence on Initial Nitrite Concentration

FIGURE 2.4 Ammonia Generation Dependence on Hydrogen Generation and Nitrate Concentration

DETAILED DESIGN DATA PACKAGE
PHTD Redox/Rheology Evaluation Control
Milestone 1.2.2.03.02B
December 6, 1991

**APPENDIX A.1. SUMMARY OF BENCH-SCALE PROCEDURE FOR
FORMATING**

Appendix A: Summary of Bench Scale Procedure for Formating

1. A tared 2L reaction vessel was filled with approximately 1.5L of stock NCAW simulant. The weight of the simulant was determined. The initial volume was calculated using the density of the simulant (1.08g/ml of stock NCAW simulant). The initial volumes for each test are listed in Table 4.

2. The vessel was placed in the forming set-up and heated to 95C. Calculation of the amounts of NaNO_2 , NaNO_3 , and Na_2CO_3 per test conditions were performed. Anion concentration targets were used to determine the amounts. For a nominal composition test (ie. 1.1, 1.2, 1.3 etc.) the calculations are as follows:

NaNO_3 -None was added to nominal nitrate tests. Stock simulant contained nominal NO_3 .

NaNO_2 -target is $4.35\text{e-}1$ mole NO_2 /L

---> $(4.35\text{e-}1\text{mole NO}_2\text{/L})(1\text{ mole NaNO}_2\text{/mole NO}_2\text{-})(69\text{g NaNO}_2\text{/mole})$

---> $(30\text{g NaNO}_2\text{/L})(1.5\text{L})$

---> 45g of NaNO_2

Na_2CO_3 -target is $1.25\text{e-}1$ mole CO_3 /L

---> $(1.25\text{e-}1\text{mole CO}_3\text{/L})(1\text{mole Na}_2\text{CO}_3\text{/mole of CO}_3\text{})(106\text{g Na}_2\text{CO}_3\text{/mole})$

---> $(13.25\text{g of Na}_2\text{CO}_3\text{/L})(1.5\text{L})$

---> 19.9g of Na_2CO_3

Sodium nitrite, nitrate and carbonate compounds were added to the simulant during initial heat up via a port in the reaction vessel lid.

3. The rate of formic acid used for each test is given in table 4. Slurry samples were collected during formic acid addition. Both condensate and slurry samples were collected during digestion. The temperature was increased to 100C for digestion. About 80ml/hr of condensate was removed during digestion from the first condenser (coolant temp=10C). The second condenser (coolant temp= 25C-29C) generally produced less than 10ml during the entire average two days of testing. The simulant was allowed to cool to room temperature overnight after digestion. Samples were removed for redox, physical characterization and chemical analyses. The vessel plus simulant were weighed before heat up for recycle addition.

The slurry volume change reported in the process profiles (Figures 1-13) was calculated by subtracting the weight of the condensate and slurry samples from the initial weight of the slurry. The volume was calculated using the new simulant weight and the density of 1.08 g/ml. This calculation was done on the assumption that the density of the slurry was a constant 1.08 g/ml. In actuality the density varied plus or minus 6%.

4. The simulant was heated to 100C prior to recycle addition. The recycle simulant was added at a rate of approximately 10ml/min. The recycle simulant was at room

APPENDIX A.1 SUMMARY OF BENCH-SCALE PROCEDURE FOR FORMATING (cont)

temperature. Settling within the line occurred during the addition of the recycle simulant. The tubing was turned constantly by hand to prevent any build up of solids. The condensate was allowed to reflux back into the vessel during heat up and recycle addition. Approximately 0.15g of HCOOH/g of recycle oxide was added to recycle slurry before its addition to the formatted simulant. See table 4 for the amount of formic acid added to each test recycle simulant. This was based on specifications from WHC. Table 2.1 shows the composition of the recycle slurry in grams of oxide/L and grams of sources/L. Table 2.2 shows the composition in oxides of each recycle slurry aliquot which was added to each test. Table 4 contains the ml of recycle slurry added per test.

5. After recycle addition condensate was collected for ~1 hour. Slurry samples were removed for redox and chemical analyses. The final weight of the vessel and slurry was determined for the ammonia balance.