**Evaluation of High-Level Waste RECEIVED
Vitrification Feed Preparation APR 01 1996
Chemistry for an NCAW Simulant, OSTI
FY 1994: Alternate Flowsheets
(DRAFT)**

H. D. Smith
M. D. Merz
K. D. Wiemers
G. L. Smith

February 1996

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

Pacific Northwest National Laboratory
Richland, Washington 99352

MASTER

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EXECUTIVE SUMMARY

High-level radioactive waste stored in tanks at the U.S. Department of Energy's (DOE's) Hanford Site will be pretreated to concentrate radioactive constituents and fed to the vitrification plant. A flowsheet for feed preparation within the vitrification plant (based on the Hanford Waste Vitrification Plant (HWVP) design) called for HCOOH addition during the feed preparation step to adjust rheology and glass redox conditions. However, the potential for generating H_2 and NH_3 during treatment of high-level waste (HLW) with HCOOH was identified at Pacific Northwest Laboratory (PNL)¹ by Wiemers (1988).² Studies at the University of Georgia, under contract with Savannah River Technology Center (SRTC) (King et al. 1994) and PNL, have verified the catalytic role of noble metals (Pd, Rh, Ru), present in the waste, in the generation of H_2 and NH_3 . Both laboratory-scale and pilot-scale studies at SRTC have documented the H_2 and NH_3 generation phenomena.³ Because H_2 and NH_3 may create hazardous conditions in the vessel vapor space and offgas system of a vitrification plant, reducing the H_2 generation rate and the NH_3 generation to the lowest possible levels consistent with desired melter feed characteristics is important.

The Fiscal Year 1993 and 1994 studies were conducted with simulated (non-radioactive), pretreated neutralized current acid waste (NCAW). Neutralized current acid waste is a high-level waste originating from the plutonium/uranium extraction (PUREX) plant that has been partially denitrated with sugar, neutralized with NaOH, and is presently stored in double-shell tanks (Peterson et al. 1989). The non-radioactive simulant used for the present study includes all of the trace components found in the waste, or substitutes a chemically similar element for radioactive or very toxic species. The composition and simulant preparation steps were chosen to best simulate the chemical processing characteristics of the actual waste.

This report provides an evaluation of 11 tests conducted in FY 1993 and FY 1994 for the purpose of assessing the effects of modifying flowsheet use of reductants other than formic acid on offgas composition and generation rate, and slurry chemistry. The selection of alternate reductants was based on consideration of practicality for plant operation and potential for process improvement. The evaluation of the effects of alternate reductants was based on the comparison of offgas profiles with a standard profile. The standard profile is viewed as occurring in three stages: carbonate decomposition, nitrite destruction, and H_2 plus NH_3 formation.

One source of stock NCAW simulants was used for the FY 1993 and FY 1994 tests. The

¹ Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

² Wiemers, K.D. 1990. The Effect of HWVP Feed Nitrate and Carbonate on Glass Redox Adjustment. Technical Report HWVP-900-1.2.2.03.03A, Pacific Northwest Laboratory, Richland, Washington.

³ Hutson, N. 1984. Integrated DWPF Melter System (IDMS) Campaign Report: Hanford Waste Vitrification Plant (HWVP) Process Demonstration, 1994 draft report to Westinghouse Hanford Company, Revision 1. WSRC-TR-92-403, Westinghouse Savannah River Company, Aiken, South Carolina.

simulant, slurry integrated performance test (SIPT), was prepared on a laboratory scale using a large-scale preparation procedure.

Test methods and equipment used during FY 1993-94 were essentially identical to those used during FY 1991 (Wiemers et al. 1993) and FY 1992 (Smith et al. 1995), with the exception that offgas monitoring was done with a different offgas system for the FY 1993-94 tests. The test apparatus consisted of a 2-L Pyrex®⁴ kettle placed in a temperature-controlled heating mantle. The Pyrex® kettle lid was modified to accept a thermocouple, acid addition tube, pH electrode, pH automatic temperature compensator, agitator shaft, condenser, sweep gas inlet, slurry sampling/recycle waste stream simulant addition port, and baffle to enhance vertical mixing. A second condenser was added in series to the first condenser connected to the vessel lid. Acid was introduced below the surface of the simulant through a Teflon tube; a peristaltic pump controlled the addition rate. The argon (Ar) sweep gas carried offgases from the reaction vessel plenum through condensers at a rate of ~1.95 slpm. . Slurry pH was collected at ~5 min intervals on the data acquisition system and recorded manually when other observations were recorded. Slurry and gas temperatures were recorded manually.

The extensive offgas evaluation of the alternate flowsheets showed that all of the candidates produced little or no NH_3 and H_2 . This was predicted by previous University of Georgia studies and the reason the four were selected for this evaluation from a larger group. (Thirteen alternate reductant candidates were screened in a series of laboratory tests by Dr. R. B. King and his associates at the University of Georgia to evaluate the potential for H_2 and NH_3 generation during treatment of a simplified NCAW simulant.⁵) However, this left too many candidates to be evaluated and a down selection to oxalic acid, nitric acid, and glycolic acid was made on the basis of redox considerations. The HTM will produce a more reduced melt because of the higher temperatures involved and make it uncertain what level of reduction will be most beneficial in the melter cold cap during melter operation. Therefore, three alternate flowsheets (oxidizing to reducing) were taken to the melter feed make up step to see if they would produce a melter feed slurry with both an acceptable rheology for pipe transfers from mixing tanks to the melter and have an acceptable total oxide loading

The rheological evaluation showed that the glycolic acid treated feed had acceptable rheological properties at a total oxide loading of 400 while the nitric acid feed could not be more concentrated than 380 and display acceptable rheology and oxalic acid treated feed could only be concentrated to 280. Hence, oxalic acid was eliminated from further testing and a nitric acid processed and a glycolic acid processed feed were recommended for the SSHTM melter tests.

⁴ Pyrex is registered trademark of Corning Glass Works, Corning, New York.

⁵R.B. King, N.K. Bhattacharyya, and V. Kumar. December 1993, Monthly Technical Report, "Hanford Waste Vitrification Plant Hydrogen Study: Preliminary Evaluation of Alternatives to Formic Acid." Prepared for Pacific Northwest Laboratory under contract number 125770-A-A2.

1.0 INTRODUCTION

1.1 Programmatic Overview

High-level radioactive waste stored in tanks at the U.S. Department of Energy's (DOE's) Hanford Site will be pretreated to concentrate radioactive constituents and fed to the vitrification plant. A flowsheet for feed preparation within the vitrification plant (based on the Hanford Waste Vitrification Plant (HWVP) design) called for HCOOH addition during the feed preparation step to adjust rheology and glass redox conditions. However, the potential for generating H_2 and NH_3 during treatment of high-level waste (HLW) with HCOOH was identified at Pacific Northwest Laboratory (PNL)¹ by Wiemers (1988).² Studies at the University of Georgia, under contract with Savannah River Technology Center (SRTC) (King et al. 1994) and PNL, have verified the catalytic role of noble metals (Pd, Rh, Ru), present in the waste, in the generation of H_2 and NH_3 . Both laboratory-scale and pilot-scale studies at SRTC have documented the H_2 and NH_3 generation phenomena.³ Because H_2 and NH_3 may create hazardous conditions in the vessel vapor space and offgas system of a vitrification plant, reducing the H_2 generation rate and the NH_3 generation to the lowest possible levels consistent with desired melter feed characteristics is important.

High level waste feed preparation flowsheet development was initiated in FY 1994 to select a melter feed preparation process flowsheet for high temperature melter (HTM) testing based on the feed preparation flowsheet that was developed for HWVP. The split acid addition flowsheet (Smith et al., 1994) was one approach that was applied to HWVP feed. This approach allowed the HLW program to build upon the extensive feed preparation flowsheet database developed under the HWVP project. Primary adjustments to the HWVP flowsheet were to the acid adjustment and glass component additions. However, though this approach did reduce the H_2 and NH_3 production, it increased the complexity and preparation time. Therefore, three other potential feed preparation flowsheets were considered as candidates for HTM testing which may be described as follows:

1. No acid adjustment flowsheet
2. No reductant flowsheet
3. Alternate reductant flowsheet

The Fiscal Year 1993 and 1994 studies were conducted with simulated (non-radioactive), pre-treated neutralized current acid waste (NCAW). Neutralized current acid waste is a high-level waste originating from the plutonium/uranium extraction (PUREX) plant that has been partially denitrated with sugar, neutralized with NaOH, and is presently stored in double-shell tanks (Peterson et al. 1989). The non-radioactive simulant used for the present study includes all of the trace components found in the waste, or substitutes a chemically similar element for radioactive or very toxic species. The composition and simulant preparation steps were chosen to best simulate the chemical

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² Wiemers, K.D. 1990. The Effect of HWVP Feed Nitrate and Carbonate on Glass Redox Adjustment. Technical Report HWVP-900-1.2.2.03.03A, Pacific Northwest Laboratory, Richland, Washington.

³ Hutson, N. 1984. Integrated DWPF Melter System (IDMS) Campaign Report: Hanford Waste Vitrification Plant (HWVP) Process Demonstration, 1994 draft report to Westinghouse Hanford Company, Revision 1. WSRC-TR-92-403, Westinghouse Savannah River Company, Aiken, South Carolina.

processing characteristics of the actual waste.

The alternate/no reductant flowsheets were evaluated on the following basis:

- offgas generation amounts and peak rates (see also, SSHTM Data Package, C95-02.02Y)
- aqueous phase chemistry related to offgas generation and glass redox components (see also, PVTD-T3C-95-129)
- exothermic reaction potential
- rheology
- cold cap reactions and glass redox.

The latter three topics are addressed in separate reports, milestone numbers PVTD-C95-02.02L⁴ (Sills 1995), PVTD-C94-03.02W⁵, and PVTD-T3C-95-129⁶, respectively. The amount of offgas generated, peak gas generation rates and aqueous phase chemistry are addressed in this report.

This report provides an evaluation of 11 tests conducted in FY 1993 and FY 1994 for the purpose of assessing the effects of modifying flowsheet use of reductants other than formic acid on offgas composition and generation rate, and slurry chemistry. The selection of alternate reductants was based on consideration of practicality for plant operation and potential for process improvement. The evaluation of the effects of alternate reductants was based on the comparison of offgas profiles with a standard profile. The standard profile is viewed as occurring in three stages: carbonate decomposition, nitrite destruction, and H₂ plus NH₃ formation.

In addition, this report includes an appendix that summarizes all the pertinent alternate reductant processing runs made during FY 1993 and FY 1994. Other tests made during FY 1993 were included in an earlier report (Patello et al. 1994). The appendix includes the offgas and analytical chemistry data and a complete description and time line of the tests.

This report summarizes work conducted according to the FY 1993 test plan, *Evaluation of Pretreated Neutralized Current Acid Waste (NCAW): Reductant Requirements, Offgas Productivity, and Feed Preparation Reactions*⁷ and was developed on the basis of the FY 1992 PNL HWVP Technology Development Project Work Plan.⁸

⁴ Sills, J.A. 1995. "Evaluation of Hanford High Level Waste Vittrification Chemistry for an NCAW Simulant - Fiscal Year 1994: Potential Exothermic Reactions in the Presence of Formic Acid, Glycolic Acid, and Oxalic Acid." PVTD-C95-02.02L. Pacific Northwest Laboratory, Richland, Washington.

⁵ Tracey, E.M, P.A. Smith, and K.D. Wiemers. 1994. "Draft Copy: Slurry Characterization Data Package." Pacific Northwest Laboratory, Richland, Washington.

⁶ Smith, G.L., D.K. Peeler, H.D. Smith, P.A. Smith, E.M. Tracey, and K.D. Wiemers. 1995. "SSHTM Draft Letter Report: Effect of Feed Chemistry on Waste Melter Vittrification Kinetics," Draft Report PVTD-T3C-95-129, Pacific Northwest Laboratory, Richland, Washington.

⁷ Langowski, M. H., and K. D. Wiemers. 1992. *Evaluation of Pretreated Neutralized Current Acid Waste (NCAW): Reductant Requirements, Offgas Productivity and Feed Preparation Reactions*. Test Plan PHTD-C92-03.02B, Pacific Northwest Laboratory.

⁸ FY 1992 Pacific Northwest Laboratory, Hanford Waste Vittrification Plant Technology Development (PHTD) Project Work Plan. PHTD-92-002-Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

1.2 Alternate Flowsheet Selection Criteria

The selection of the melter feed process flowsheets for the SSHTM-1 run are based on: 1) mitigation of H₂ and NH₃ generation during feed preparation, 2) acceptable feed rheological properties, 3) maximum total oxide loading, 4) simplicity, and 5) adaptability to feed compositional variability.

The first downselection criteria for chemical additives employed to adjust glass redox and melter feed rheology was mitigation (ideally elimination) of H₂ and NH₃ generation. The peak H₂ generation rate and total amount of NH₃ produced were compared with results observed during HCOOH reference flowsheet tests.

The values of 15 Pa and 25 Pa·s for the Bingham yield stress and viscosity, respectively, were chosen as the laboratory rheological screening data⁹ based upon communication with PVTD cost account 1.2.2.04.14 (Beckett and Jagoda 1994) and the Hanford Waste Vitrification Technical Data Package¹⁰.

Discussions with PVTD cost account 1.2.2.04.14 personnel regarding the SIPT 2/LFCM 8 campaign revealed that a solids loading of approximately 485 g TO/L for the FY 91 NCAW reference melter feed met the above conditions and was satisfactorily pumped into the melter. This value was also used to screen the laboratory, alternate flowsheet melter feeds for the small-scale feed preparation system which will be used for SSHTM-1.

Simplicity and adaptability to compositional variability are considered long-term assessment goals. For this study, the simplicity of the tested process flowsheets will be compared with previous reference HCOOH flowsheet test experience, primarily in a qualitative manner. The description may include such issues as number of process steps and a subjective evaluation of ease of operation. Additional testing will be required to evaluate sensitivity to operation control parameters and feed composition, and process predictability and reliability.

The selection of the specific alternate reductants (citric, glycolic, lactic, oxalic) to be tested was generally based on acidic nature, nontoxicity, cost, and availability. They were selected from a much larger draft list of potential compounds put together by Lambert and Seymour of WHC (1994 communication).

1.3 Background Chemistry

The basic aqueous phase chemistry for treatment of an NCAW simulant with formic acid has been addressed in detail by Wiemers et al. 1993, Smith et al. 1995, and King et al. 1994. The reactions identified to date consist primarily of nitrite and carbonate destruction, noble metal catalyzed decomposition of formic acid and reduction of nitrate to ammonia. The reactions are generally observed in three stages as described by Smith et al. 1995.

Stage I

⁹The rheological screening data is taken from a PNL Don't Say It--Write It (DSI) memo: Laboratory Rheological Screening Data to distribution from P. A. Smith dated May 23, 1994.

¹⁰Hanford Waste Vitrification Technical Data Package, WHC-SD-HWV-DP-001.

$$\log\{[H_2CO_3]/[HCO_3^-]\} = 6.45 - pH$$

Stage II

Stage III

where Me = Pd, Rh, Ru, Cu, Ag, Te, Se and Pb, for example

The reduction of manganese dioxide (MnO_2) during stage I has also been suggested:

An equivalent set of reactions might be proposed for the alternate reductants selected for this investigation (refer to equations 2a-d, 3a-d and 4a-d and reaction equation 2 which is driven by pH reduction).

Stage II (lactic acid)

Stage II (citric acid)

Stage II (glycolic acid)

Stage II (oxalic acid)

The stoichiometry of carbonic acid decomposition (Stage I) is expected to remain unchanged. However, the stoichiometry of stage II reactions suggests that differences in CO_2 production might be observed for the various reductants, and as for HCOOH , would depend on the favored reaction pathway.

As for stage III, decomposition reactions might occur via catalysis or due to thermal sensitivities such as the catalysed decomposition of HCOOH shown in equation (5). The NH_3

producing reaction (6) is also a catalysed reaction which might have a counterpart among the

alternate reductant candidates. By using each alternate reductant under similar waste slurry processing conditions which result in the generation of H_2 and NH_3 when HCOOH is used, any tendency for comparable reaction pathways to occur should be observed as H_2 and/or NH_3 in the offgas or condensate

2.0 CONCLUSIONS AND RECOMMENDATIONS

Very low to nondetectable generation rates of NH_3 and H_2 have been observed when processing simulated (non-radioactive), pre-treated neutralized current acid waste (NCAW) with the organic acids, citric, glycolic, lactic, oxalic and with nitric acid. Further evaluation demonstrated that Glycolic and nitric acids could be used to make melter feeds with both acceptable rheological properties and total oxide loading while melter feed made using oxalic acid treated waste slurry does not meet both criteria. Two HTM melter feeds, one made with waste slurry simulant treated with glycolic acid and the other made with nitric acid treated slurry are recommended for evaluation as melter feeds in the SSHTM.

3.0 OBJECTIVES

The overall objective of the laboratory-scale feed preparation chemistry tests is to provide data needed for plant design, safety, permitting, and operations. The primary objectives of the laboratory testing were to study the effects of modifying the baseline flowsheet on the offgas composition, generation rate and total volume, to use the flowsheet selection criteria to narrow the number of alternative flowsheets, and further recommend these down selected flowsheets for testing through the melter feed processing stage to determine if the melter feed composition, physical

properties, and melter processing steps met all of the flowsheet selection criteria. The melter feed would be processed to meet the N508 glass composition specifications. This information would ultimately be used to select two alternate melter feed preparation process flowsheets for HTM testing. A fundamental understanding of the chemical reactions is necessary to adapt the feed preparation process to a variety of feed compositions and to predict outcomes under both routine and upset processing conditions.

The specific objectives of the FY 1993 and FY 1994 Tests were to down select the number of potential candidate flowsheets from six to two which would be further evaluated by using for pilot scale runs (SSHTM). The down selection process is diagrammed in Figure 3.1. Baseline data is first established for the standard HCOOH processing. The candidates were first compared to the base line data for H_2 and NH_3 production and then on rheological properties and total redox capacity. A brief description and specific objective is given in Table 3.2 for each of the 11 tests conducted.

Table 3.1 - Alternate Flowsheet Selection Procedure

Establish Baseline	- Three Formic Acid baseline flowsheets were used to establish benchmark levels of hydrogen and ammonia production	
Select Candidates	<u>Nonreducing Flowsheet</u>	<u>Reducing Flowsheets</u>
	<ul style="list-style-type: none"> - Nitric Acid - Untreated Waste Slurry 	<ul style="list-style-type: none"> - Citric Acid - Glycolic Acid - Lactic Acid - Oxalic Acid
Evaluate Candidates - Gas Production	- Evaluate each Waste Slurry Processing flowsheet on the basis of hydrogen and ammonia production compared to the Formic Acid baseline .	
Evaluate Candidates - Rheology	- Evaluate selected melter feed slurry processing flowsheets on the basis of mainly rheological properties and waste loading criteria.	
Choose Two Finalists	- Choose the candidate capable of providing the best waste loading and rheological properties.	- Demonstrates acceptable reductions of H ₂ and NH ₃ compared to baseline and high waste loading. Choose the successful candidate with the lowest reducing potential.

Table 3.2 Test Descriptions and Objectives.

<u>Test Identification</u>	<u>Description</u>	<u>Objectives</u>
T94-HCOOH-BASE-1 T94-HCOOH-BASE-2 T94-HCOOH-BASE-3	Process w/formic acid	Base case for reference processing conditions; establish reproducibility of laboratory tests.
T94-LACTIC-1	Process w/lactic acid	Examine H ₂ and NH ₃ generation.
T94-CITRIC-1	Process w/citric acid	Examine H ₂ and NH ₃ generation.
T94-GLYCOLIC-1	Process w/glycolic acid	Examine H ₂ and NH ₃ generation.
T94-FPGLYC-1	Process w/glycolic acid	Produce simulated melter feed using minimum amount of organic acid for suitable feed rheology. Examine H ₂ and NH ₃ generation.
T94-HNO3-1	Process w/nitric acid	Rheology characteristics; examine H ₂ and NH ₃ generation.
T94-FPHNO3-1	Process w/nitric acid	Produce simulated melter feed using minimum amount of acid for suitable feed rheology. Rheology characteristics; examine H ₂ and NH ₃ generation.
T94-OXALIC-1	Process w/oxalic acid	Examine H ₂ and NH ₃ generation.
T94-FPOXAL-1	Process w/oxalic acid	Produce simulated melter feed using minimum amount of organic acid for suitable feed rheology. Examine H ₂ and NH ₃ generation.

4.0 APPROACH

The approach taken to perform the testing is described below. The HWVP feed simulants and formulations are described along with test methods and equipment. Comparisons of test conditions for FY 1994 tests and tests completed in FY 1991-93 are indicated where significant differences exist to provide a basis for comparisons of data.

4.1 Description of Simulants

One source of stock NCAW simulants was used for the FY 1993 and FY 1994 tests. The simulant, slurry integrated performance test (SIPT), was prepared on a laboratory scale using a large-scale preparation procedure. The FY 1991 reference NCAW and simulant target compositions are given in Table 4.1. The flow diagram of the formulation procedures for the various simulants were given in an earlier report (Smith et al. 1995, see Appendix B of that report for general information and reference). Note that "noble metals" refers to Pd, Rh, and Ru in the amounts indicated in Table 4.1.

Table 4.1. Reference and Simulant NCAW Feed Compositions

FY 1991 Pretreated NCAW Feed Composition(a)				NCAW Simulant Composition(b)	
Oxide (O)	Feed Oxides wt%	Moles Element/L Feed (125 gWO/L)	Substitute/ Delete*	Feed Oxides wt%	Moles Element/L Feed (125 gWO/L)
Ag ₂ O	1.20E-01	1.29E-03	--*	1.22E-01	1.32E-03
Al ₂ O ₃	9.04E+00	2.22E-01	--	9.25E+00	2.27E-01
Am ₂ O ₃	7.22E-02	5.38E-07	Del(d)	--	--
As ₂ O ₃	4.25E-05	3.41E-04	Del(e)	--	--
B ₂ O ₃	5.75E-03	2.06E-04	--	5.86E-03	2.10E-04
BaO	1.76E-01	1.43E-03	--	1.79E-01	1.46E-03
BeO	1.01E-01	5.04E-03	Sub Mg(e)	--	--
Br	--	--	N/A(f)	--	--
CaO	7.91E-01	1.76E-02	--	8.06E-01	1.80E-02
CdO	3.02E+00	2.94E-02	--	3.08E+00	3.00E-02
CeO ₂	6.05E-01	4.39E-03	--	6.56E-01	4.77E-03
Co ₂ O ₃	--	--	to be determined(f)	--	--
Cr ₂ O ₃	2.62E-01	4.30E-03	--	2.67E-01	4.39E-03
Cs ₂ O	6.05E-01	5.32E-03	--	6.12E-01	5.43E-03
CuO	2.45E-01	3.85E-03	--	2.50E-01	3.93E-03
Dy ₂ O ₃	1.04E-04	6.98E-07	Sub Nd(g)*	--	--
Er ₂ O ₃	3.08E-06	2.02E-08	Sub Nd(g)*	--	--
Eu ₂ O ₃	2.02E-02	1.42E-04	Sub Nd(g)	--	--
F	9.70E-02	6.38E-03	--	9.90E-02	6.52E-03
Fe ₂ O ₃	2.82E+01	4.42E-01	--	2.88E+01	4.51E-01
Gd ₂ O ₃	3.70E-03	2.57E-05	Sub Nd(g)*	--	--
GeO ₂	1.57E-04	1.82E-06	Add*	1.56E-04	1.86E-06
HgO	--	--	N/A(f)	--	--
Ho ₂ O ₃	5.32E-06	3.52E-08	Sub Nd(g)*	--	--
I	4.50E-06	4.36E-08	--(h)	4.60E-06	4.53E-08
In ₂ O ₃	--	--	N/A	--	--
K ₂ O	1.96E-01	5.21E-03	--	2.00E-01	5.32E-03
La ₂ O ₃	6.53E-01	5.01E-03	--*	6.67E-01	5.12E-03
Li ₂ O	1.84E-04	5.92E-06	--	7.23E-05	6.05E-06
MgO	2.02E-01	6.25E-03	--	3.72E-01	1.15E-02
MnO ₂	2.14E+00	3.08E-02	--	2.19E+00	3.15E-02
MoO ₃	5.59E-01	4.85E-03	--	5.70E-01	4.95E-03
Na ₂ O	2.14E+01	8.64E-01	--	2.19E+01	8.82E-01
Nb ₂ O ₃	1.01E-02	1.08E-04	--	1.03E-02	1.10E-04
Nd ₂ O ₃	5.78E-01	4.29E-03	--	3.56E+00	2.64E-02
NiO	2.30E+00	3.85E-02	--	2.35E+00	3.93E-02
NpO ₂	--	--	N/A(f)	--	--
P ₂ O ₅	8.72E-01	1.53E-02	--	8.87E-01	1.56E-02
PbO ₂	7.00E-01	3.66E-03	--	7.15E-01	3.74E-03
PdO	1.20E-01	1.23E-03	--*	1.23E-01	1.26E-03
Pm ₂ O ₃	4.60E-02	3.32E-04	Sub Nd	--	--
Pr ₂ O ₃	1.53E-01	1.16E-03	--	1.56E-01	1.18E-03
PuO ₂	6.00E-02	2.77E-04	Sub Ce	--	--
Rb ₂ O ₃	5.75E-02	6.56E-04	--	5.87E-02	6.70E-04

FY 1991 Pretreated NCAW Feed Composition ^(a)				NCAW Simulant Composition ^(b)	
Oxide (O)	Feed Oxides wt%	Moles Element/L Feed (125 gWO/L)	Substitute/ Delete*	Feed Oxides wt%	Moles Element/L Feed (125 gWO/L)
Rh ₂ O ₃	1.04E-01	1.02E-03	--	1.06E-01	1.04E-03
Ru ₂ O ₃	3.80E-01	3.77E-03	--	3.87E-01	3.85E-03
SO ₃	6.55E-01	1.02E-02	--	6.69E-01	1.04E-02
Sb ₂ O ₃	5.88E-03	5.00E-05	--	5.95E-03	5.11E-05
SeO ₂	1.59E-02	1.78E-04	--	1.61E-02	1.82E-04
SiO ₂	4.03E+00	8.38E-02	--	4.11E+00	8.56E-02
Sm ₂ O ₃	7.50E-02	5.42E-04	-(d)	7.72E-02	5.54E-04
SnO	1.08E-02	9.78E-05	--	1.08E-02	9.99E-05
SrO	1.19E-01	1.43E-03	--	1.21E-01	1.46E-03
Ta ₂ O ₅	3.33E-03	1.88E-05	--	3.39E-03	1.92E-05
Tb ₂ O ₃	2.26E-04	1.54E-06	Sub Nd	--	--
Tc ₂ O ₇	1.52E-01	1.23E-03	--	--	--
TeO ₂	1.07E-01	7.77E-04	--	1.01E-01	7.94E-04
ThO ₂	--	--	Sub Zr	--	--
TiO ₂	6.52E-01	1.02E-02	--	6.66E-01	1.04E-02
Tm ₂ O ₃	1.68E-10	1.09E-12	Sub Nd ^(e)	--	--
U ₃ O ₈	4.74E+00	2.11E-02	Sub Nd ^{(d)*}	--	--
Y ₂ O ₃	7.99E-02	8.85E-04	--	8.17E-02	9.04E-04
ZnO	3.34E-01	5.13E-03	-(d)	3.41E-01	5.24E-03
ZrO ₂	1.51E+01	1.53E-01	-(e)	1.54E+01	1.56E-01
Sum	1.00E+02	2.02E+00	-(d)	1.00E+02	2.06E+00

FY 1991 Pretreated NCAW Feed Composition			NCAW Simulant
An- ions	g/100g Total Oxides	gmol element/L	moles anion/L
NO ₃ ⁻	5.76E+00	1.16E-01	1.16E-01
NO ₂ ⁻	1.60E+01	4.35E-01	4.35E-01
Cl ⁻	3.00E-01	1.06E-02	1.06E-02
OH ⁻	--	--	--
SO ₄ ⁻²	7.86E-01	1.02E-02	1.03E-02
PO ₄ ⁻³	7.84E-02	1.03E-03	--
CO ₃ ⁻²	6.00E+00	1.25E-01	1.25E-01
F ⁻	9.70E-02	6.38E-03	6.42E-03
TOC ⁻	1.34E-01	1.39E-02	1.39E-02
I ⁻	4.50E-06	4.36E-08	4.46E-08

FY 1991 Pretreated NCAW Feed Composition ^(a)				NCAW Simulant Composition ^(b)		
Oxide (O)	Feed Oxides wt%	Moles		Feed Oxides wt%	Moles	
		Element/L Feed (125 gWO/L)	Substitute/ Delete*		Element/L Feed (125 gWO/L)	

- (a) NCAW target composition supplied by WHC for FY 91 testing per: Smith, R. A. 1991. Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing-Errata Correction. Letter to J. M. Creer. #915051.
- (b) Adjusted target composition based on (a).
- (c) Target composition for FY 1992 Base Case #1. Equal to (b) except for increased Pd, Rh, and Ru concentrations to match actual FY 1991 base case simulant composition.
- (d) Radioactive.
- (e) Toxic.
- (f) None in reference feed composition.
- (g) Expensive.
- (h) Addition of 0.25 g/L of feed is necessary to meet the gas chromatograph's detection limit for the analysis of volatilized iodine.

* New addition to simulant.

Note: All substitutions are based on the addition of the equivalent amount of mole element/L.

The SIPT stock simulant was prepared in the laboratory according to the pilot-scale procedure¹¹ using the same batch materials that were used to eventually produce the pilot scale batch. Test simulants used for the 11 tests are provided in Table 4.2. The procedures and source materials used to make all of the simulants were the same. Earlier work indicated that SIPT slurry simulant and the NCAW Base Case #1 (RSM) used in earlier tests behaved in a similar manner.

The SIPT feed was prepared as summarized below. A mixed hydroxide slurry containing the major waste oxide elements (Fe, Ni, Zr, Al, and Mn) was prepared. A second slurry, prepared by precipitating cation species from soluble nitrates (possibly including those of the noble metals) with insoluble components (oxides, fluorides), was added to the mixed hydroxide slurry. Excess nitrate and sodium were removed by washing. A third slurry of solubles/slightly soluble salts (halides, hydroxides, nitrates, nitrites, sulfates, borates, phosphates, oxides, and oxalate) was added to the resulting mixture. For the batching of the SIPT slurry simulant, the batch components were added to the main batch in smaller groups, but the product was expected to be similar. For large-scale preparation, toxic minor components such as SeO_2 were added last. The mixture was analyzed for Na^+ and NO_3^- , which were added in various amounts with other elements, and appropriate additions of NaNO_3 were made to bring these components to target levels.

A separate noble-metals slurry was prepared to adjust the noble-metals concentration. That slurry was prepared with a nitric acid solution of the three noble metals (Pd, Rh, Ru) nitrates at known concentrations and in the desired proportions. The nitrate solution was titrated with 10 N NaOH to pH 7.5. During the NaOH addition, a brown precipitate began to form before pH 6 was attained. Once the NaOH addition was completed, the solution was boiled for 10 to 15 minutes to complete the precipitation of Ru. The slurry was then washed with deionized water to remove nitrate and sodium. The wash water was allowed to separate as a supernate over a period of 12 to 24 h and was then decanted. Several wash/decant cycles were completed. Analyses of the decanted supernates gave noble metals concentrations around 20 to 30 ppm, indicating that the hydroxide slurry retained 99.7% of the noble metals (i.e., assume 30 ppm Rh in 500 mL of washes [15 mg] out of 5,560 mg in the slurry, or 0.27%).

Though the process of producing a noble metal hydroxide slurry was similar to precipitating the noble metals directly into the slurry feed, the relationship of the noble metals to the other metal hydroxide precipitates may not be the same. When the noble metals are coprecipitated with the other hydroxides during slurry production, mixing of the hydroxides will be more complete, which may alter catalytic activity. Any differences that exist between the two noble metal processes for addition to the slurry feed simulants will most likely affect reactions catalyzed by noble metals such as the production of H_2 . This may be important when considering the results between tests performed using different stock simulants. Note, however, that all the test simulants are targeted to the composition given in Table 4.1 for the nominal NCAW composition. Analytical uncertainties associated with elemental analysis of waste simulants were reported by Wiemers et al. 1993.

Nitrite (NO_2^-) and nitrate (NO_3^-) are the principle nitrogen-containing species in the waste slurry. Nitrite is decomposed by adding reductants (in these tests, acids) to form NO_x , N_2O , and some NO_3^- in the offgas. Nitrate is reduced to NH_3 when the noble metals are catalytically active (i.e., when the NO_2^- concentration is very low or zero). For the reference NCAW composition, the target level for NO_2^- is 0.435 moles/L of slurry simulant at 125 gWO/L. The target level for NO_3^- is

¹¹ "Procedure for the Preparation of Simulated HWVP NCAW Feed," TP92-SIPT-100, October 30, 1992.

¹² "Test Instructions for Slurry-Integrated Performance Testing-Weight Out of Chemicals and Preparation of NCAW Simulant," TI92-SIPT-100, Rev. 0, October 15, 1992.

0.116 moles/L of slurry simulant at 125 gWO/L. For the alternate reductant tests, the NO_2^- level was targeted at 1/3 of the NCAW value, and the NO_3^- level at 300% of the NCAW value. This was done to accentuate conditions that could possibly increase H_2 and NH_3 generation based on indications from FY 1992 tests. Thus the experimental conditions were designed to somewhat accentuate generation of H_2 and NH_3 as a conservative approach to evaluating alternate reductants. The analytical values suggest that NO_2^- was on target and that NO_3^- ran a little high (not serious for the objectives of these tests).

Table 4.2 Test Simulants Used for Testing in Fiscal Years 1993 and 1994.

<u>Test Designation</u>	<u>Simulants</u>
T94-HCOOH-BASE-1	FY 94 SIPT/NCAW slurry simulant with 30% NO ₂ ⁻ & 300% NO ₃ ⁻
T94-HCOOH-BASE-2	FY 94 SIPT/NCAW slurry simulant with 30% NO ₂ ⁻ & 300% NO ₃ ⁻
T94-HCOOH-BASE-3	FY 94 SIPT/NCAW slurry simulant with 30% NO ₂ ⁻ & 300% NO ₃ ⁻
T94-LACTIC-1	FY 94 SIPT/NCAW slurry simulant with 30% NO ₂ ⁻ & 300% NO ₃ ⁻
T94-CITRIC-1	FY 94 SIPT/NCAW slurry simulant with 30% NO ₂ ⁻ & 300% NO ₃ ⁻
T94-GLYCOLIC-1	FY 94 SIPT/NCAW slurry simulant with 30% NO ₂ ⁻ & 300% NO ₃ ⁻
T94-FPGLYC-1	FY 94 SIPT/NCAW slurry simulant
T94-HNO3-1	FY 94 SIPT/NCAW slurry simulant
T94-FPHNO3-1	FY 94 SIPT/NCAW slurry simulant
T94-OXALIC-1	FY 94 SIPT/NCAW slurry simulant
T94-FPOXAL-1	FY 94 SIPT/NCAW slurry simulant

(a) The difference in the two simulants is based on observations that decreased nitrite and increased nitrate may increase H₂ and NH₃ generation respectively. The procedures and source materials used to make all of the simulants were the same.

4.2 Test Methods and Equipment

Test methods and equipment used during FY 1993-94 were essentially identical to those used during FY 1991 and FY 1992 (Wiemers et al. 1993; Smith et al. 1995), with the exception that offgas monitoring was done with a different offgas system for the FY 1993-94 tests. Figure 4.2.1 is a schematic of the instrumented reaction vessel. An overall schematic of the laboratory-scale feed preparation process system detailing the offgas system is given in Figure 4.2.2.

The test apparatus shown in Figure 4.2.1 consisted of a 2-L Pyrex[®] kettle placed in a temperature-controlled heating mantle. The Pyrex[®] kettle lid was modified to accept a

¹³ Pyrex is registered trademark of Corning Glass Works, Corning, New York.

Figure 4.2.1 - Schematic of the Laboratory-Scale Reaction Vessel Used for Waste Slurry Simulant Processing Tests and Melter Feed Preparation.

Figure 4.2.2 - Schematic of the Laboratory-Scale Offgas Equipment Configuration for Waste Slurry Simulant Processing Tests and Melter Feed Preparation.

thermocouple, acid addition tube, pH electrode, pH automatic temperature compensator, agitator shaft, condenser, sweep gas inlet, slurry sampling/recycle waste stream simulant addition port, and baffle to enhance vertical mixing. A second condenser was added in series to the first condenser connected to the vessel lid. Acid was introduced below the surface of the simulant through a Teflon tube; a peristaltic pump controlled the addition rate. The argon (Ar) sweep gas carried offgases from the reaction vessel plenum through condensers at a rate of ~1.95 slpm. . Slurry pH was collected at ~5 min intervals on the data acquisition system and recorded manually when other observations were recorded. Slurry and gas temperatures were recorded manually.

Figure 4.2.2 is a schematic of the offgas equipment configuration. Real-time monitoring capabilities were used to characterize the changing generation rates of the major gaseous reaction products. The offgas was monitored using an MTI¹⁴ M200 gas chromatograph for helium flow rate, H₂, CO, N₂, O₂, CO₂, and N₂O, a Nicolet¹⁵ 550 FTIR gas analyzer for NH₃, CO₂, N₂O, NO, NO₂, and identification of unknown species, and chemiluminescent analyzers for NO and NO_x. Total exit gas flow rate was monitored by reference to calibrated inlet flow of helium with the argon purge gas. The nominal argon flow rate was 0.117 m³/h at standard temperature and pressure (STP). The slurry pH was continuously monitored during processing. The vessel was opened briefly to remove a sample for rheology testing but only during a period of low gas generation to minimize effects on offgas measurement.

The gas chromatograph produced data at a nominal gas sampling rate of ~1 sample/ 2 min, and the NO/NO_x analyzers at a rate of 1 sample/1 min. The FTIR analyzer was set up to sample and produce data at 1 sample/5 min.

There was a difference in the time response of the gas chromatograph data and the NO_x analyzer data because of differences in the amount of time to completely purge the systems of gas entering the analyzer lines. The net result was that gas chromatograph data (He, CO₂, N₂O and H₂) were delayed about 15 minutes compared to the NO_x analyzer data. A simple way to correct this effect would be to shift the GC data 15 minutes toward earlier time to correlate He, CO₂, N₂O and H₂ data with NO_x data. In general, this was not done because the exact shift was not determined until many of the test data sets had been analyzed. Since the offgas flow rate of NO_x is calculated by a method that utilizes ppm He measurements, a small systematic error was introduced by not time shifting the GC data before calculations were performed. Because total gas flow rate generally changed slowly with time and the total range was only about 10% of the nominal flow rate (generally maintained by Ar purge gas), the error was not very large, probably less than 5%. One test, Test T94-HCOOH-BASE-3, was corrected for the time shift to evaluate the effect, and the NO_x profiles with and without the time-shift correction were indistinguishable when superimposed except for the time shift. Therefore, no further correction of other data was deemed necessary. It should be kept in mind that the major NO_x peak would coincide closely with a secondary CO₂ peak in many of the offgas profiles if this time-shift correction were made. Moreover, the apparent time delay between initiation of acid addition and the start of CO₂ offgas generation is an artifact of the time delay of the gas chromatograph.

Ammonia was monitored by analyses of slurry and condensate samples, and NH₃ and CO₂ were monitored with the FTIR analyzer. Ammonia was expected to be trapped in the condensate until the condensate reached a fairly alkaline pH. Soluble NH₄⁺ was measured in the slurry and condensate

¹⁴ MTI Corporation, Fremont, California.

¹⁵ Nicolet Corporation, Madison, Wisconsin

samples by selective ion electrode (SIE). The FTIR was also used to monitor CO_2 for a portion of Test T94-FPOxalic-1, and CO_2 and N_2O for Test T94-Oxalic-1.

Slurry and condensate samples were collected at the beginning and ending of specific stages or substages of the slurry processing. Typically, samples were taken at the initiation of processing and after acid addition and digestion. Condensate samples, by the way they are formed and collected, represent an average composition of the condensate for the previous processing period. Primary condensate was collected at the base of the first condenser at a rate of about 0.3 mL/min during acid addition at 95°C and about 2 mL/min during digestion at 101° to 102°C. Secondary condensate was collected at the base of the second condenser at a much slower rate, so that much smaller quantities were available for analysis.

Slurry and condensate samples were analyzed for NO_2^- , NO_3^- , and acid salt anions by ion chromatography (IC) and for NH_4^+ by selective ion electrode. Total slurry analysis was not carried out because all the test materials except for the SIPT simulant had been analyzed previously (Wiemers et al. 1993). The SIPT simulant prepared for the laboratory tests was fabricated using the same procedure and chemicals used to make up the pilot-scale batch. (Sodium was the only other component checked in this batch.) Nitrite, acid salt anions (species depending on which acid was added), and CO_3^{2-} were the chief reactants consumed during slurry processing. An accurate measurement method for carbon was unavailable at the time of testing; therefore, carbonate analyses were not done.

The procedures common to the tests are outlined in the following sections. In some tests, deviations from these procedures may have been necessary to accomplish the purpose of the test, and these deviations are included in the information summarized in Appendix A.

4.2.1 Preparations for Acid Addition

1. Place a given weight of slurry simulant with known gram oxide waste loading and specific gravity into the precleaned reaction vessel.
2. Add preweighed shim chemicals (NaNO_2 , NaNO_3 , and Na_2CO_3), if required.
3. Clamp the reaction vessel lid, modified for the instrumentation, agitation, sampling, and offgas collection, in place.
4. Heat the slurry to boiling, with vigorous agitation, for a period of 10 minutes to an hour and cool to the temperature at which acid is added. Air is used as the sweep gas during this stage.

4.2.2 Acid Addition

1. Establish the sweep gas (99.99% Ar) flow rate.
2. Add acid at predetermined rate until addition complete.
3. Maintain temperature within $\pm 1^\circ\text{C}$ (except under upset conditions).
4. Measure temperature, pH, and offgas generation rate as a function of process time.
5. Collect condensate or reflux depending on gWO/L objective.

4.2.3 Hold Period at the Acid Addition Temperature (if required)

1. Maintain the slurry temperature.
2. Continue all measurements.
3. Collect condensate or reflux depending on gWO/L objective.

4.2.4 Digestion Period (4 h)

1. Raise the slurry temperature to boiling.
2. Continue all measurements.
3. Collect condensate or reflux depending on gWO/L objective.

During the tests, both condensate and slurry samples were taken. Primary condensate was collected from the first condenser while secondary condensate was collected from the second condenser. There was always 100 to 1000 times more primary condensate volume than secondary. A particular condensate sample was collected over a period of time and thus was a summation of condensed volatiles for a test period of significant duration. Slurry samples, on the other hand, were collected at specific times, generally before and after acid addition and after digestion. Other slurry samples were taken at different points in processing, depending on the test objectives. Slurry samples destined for chemical analysis were refrigerated.

A technical data log was maintained during the test. The primary function of the log was to record observations of slurry color and slurry behavior. The log was also used to record slurry temperature and pH as a backup record to the data acquisition system and to record the beginning and ending of the various test stages. Slurry observations included the degree of foaming, the actions taken to control foaming, the appearance of secondary phases in the form of films or scums on the slurry surface, and slurry color, which, for slurries in previous work (Smith et al. 1995), changed from an initial chocolate red-brown to a brown or dark gray-brown when the slurry was extensively formed.

Following the test, the remaining treated simulant was placed in a tightly capped, labeled container. This material was held in reserve for future melting, rheology, or chemical studies.

The FY 1993-94 tests continued to use the modified feed preparation process procedures as initiated and practiced in FY 1992, with regard to the composition and flow rate of the sweep gas, boiling conditions, and refluxing during acid addition. Ar-4.4% O₂ sweep gas was used during FY 1991, and Argon sweep gas plus 4.4% CH₄ was used during FY 1992 and 1993. The change to pure Ar plus a helium tracer (FY 1994) was made so that offgas reactions involving O₂, such as the oxidation of NO to NO₂, would not occur and the true slurry reaction products could be measured without interference. In FY 1991, condensate was refluxed during HCOOH addition, but in FY 1992 and later, the condensate was collected and analyzed. In FY 1992 and later, the slurry was boiled before adding HCOOH (and other acids for FY 1994) to purge the slurry of dissolved gases and during digestion to accelerate reactions and to more completely remove reaction gases. Rapid boiling was believed to be more prototypic of plant operating conditions. These differences should be kept in mind when comparing FY 1991, FY 1992, FY 1993 and FY 1994 results.

4.2.5 Melter Feed Preparation

The following outline covers the major stages of waste slurry simulant processing to make melter feed. The details resulting from implementing these steps are recorded in the "Laboratory Melter Feed Preparation Activity Log" included in this section. An accounting sheet for the gram waste oxide is also provided.

Laboratory Flowsheet

Step 1: Obtain pre-concentrated slurry simulant from the small-scale slurry processing tank prior to processing (~179 gWO/L). Place 1.5 L of that slurry in reaction vessel. Set stirrer at 6 or higher and establish argon sweep gas flow.

- Take slurry and condensate samples.

Step 2: Heat slurry to 93°C. Titrate with nitric acid to a pH of 4.8 ± 0.1 . Add 70 wt % acid solution: Period #1 - 1.04 g/min. for 14 minutes; Period #2 - 1.53 g/min. for 10 minutes; Period #3 - 1.94 g/min. for the remainder of the test. (Incremental rates duplicate the small-scale processing run more precisely.)

- Take slurry and condensate samples.

Step 3: Concentrate slurry to 240 gWO/L by boiling during digestion period of 8 hours. (The longer digestion/concentration period more accurately duplicates the small-scale processing run.)

- Take slurry and condensate samples.

Step 4: Add NaNO_3 and SiO_2 to complete melter feed preparation. (12 g Na_2O per 100 gWO as 32.0 g NaNO_3 per 100 gWO, 88 g SiO_2 as sand (F-110) per 100 gWO). Final target HTM feed concentration is 433 gTO/L.

- Take melter feed samples.

Step 5: Melter feed rheology evaluated.

5.0 RESULTS AND DISCUSSION

Three HCOOH reductant tests were completed to establish the reproducibility of laboratory-scale tests and to provide a baseline for evaluation of the alternate reductant tests. Alternate reductants, (lactic, citric, glycolic and oxalic acids) were compared to the reference HCOOH reductant in eight tests. Tests using HNO₃ in place of HCOOH are also reported. The complete offgas data and analytical data for these tests are tabulated and plotted in the appendix, with selected data presented in the following sections to support discussion and major conclusions.

5.1 Baseline Formic Acid Flowsheet

Three tests were completed to provide a baseline and examine reproducibility of test data for the reference flowsheet with formic acid addition, Tests HCOOH-BASE-1, HCOOH-BASE-2 and HCOOH-BASE-3. In addition to baseline slurry preparation, additional processing was explored after digestion to determine effects of NaNO₂ addition (Test HCOOH-BASE-2) and HNO₃ addition (Test HCOOH-BASE-3). These effects will also be discussed separately in this section.

The individual offgas profiles are shown in Figures 5.1.1 through 5.1.3 and to provide a visual comparison of the time dependency and evolution rates from the three formic acid flowsheet replicate runs an overlay of the three offgas profiles is provided in Figure 5.1.4. The average amounts of each gas measured are given in Table 5.1.1. For an equivalent elapsed time period of 300 minutes (representing the approximate end of Stage III), the total offgas for CO₂, H₂, N₂O and NO_x varied at most 1.4%, 20%, 30%, and 6.6% from the average, respectively (refer to ranges shown in Table 5.1). The relative standard deviation (RSD) varied from 0.7% to 15%.

The average peak gas generation rates, ranges, and relative standard deviations for the three replicate formic acid flowsheet tests are given in Table 5.1.2. Reproducibility was best for Stages I and II. The calculated values for RSD were 4.8% for CO₂ (Stage I), 5.9% for NO_x, and 11% for N₂O (worse case given for each gas). The greatest variations were observed for CO₂ and H₂ during Stage III, 16% and 23% RSD, respectively.

Only two of the three tests were used to estimate experimental error in the H₂ measurement due to an equipment malfunction during Test HCOOH-BASE-1. Known differences in the operation and process conditions between Tests HCOOH-BASE-2 and HCOOH-BASE-3 were an increase in the final pH of test HCOOH-BASE-3 (pH 4.2) compared with Test HCOOH-BASE-2 (pH 3.3); a 5% increase in the amount of condensate collected and oxide loading for test HCOOH-BASE-2 compared with test HCOOH-BASE-3; and a more rapid heating to the boil after acid addition for test HCOOH-BASE-2 compared with test HCOOH-BASE-3.

Heating rate after acid addition is believed to be the primary contributor to differences observed in the amount and peak generation rates for H₂ and CO₂ during stage III. The temperature was increased from 95 to 101 °C in 10 minutes for test HCOOH-BASE-2 compared to 51 minutes elapsed time for heat up in test HCOOH-BASE-3. Wiemers et al. 1993, Smith et al. 1995, and Ritter et al. 1992 have shown the dependency of gas generation rate on temperature, especially above 75 °C. The potential for using a lower processing temperature to reduce the H₂ generation rate was also discussed by Smith et al. (1995).

The total NH₃ measured in the slurry and condensate for each of the three tests was 0.019, 0.0032, and 0.0041 moles/130gWO for Tests HCOOH-BASE-1, HCOOH-BASE-2 and HCOOH-BASE-3, respectively. Note that additional steps taken with tests HCOOH-BASE-2 and HCOOH-BASE-3, are likely the reason for the higher NH₃ levels which are composite values

Offgas Generation HCOOH-Base 1

Figure 5.1.1 - Baseline Test T94-HCOOHBase-1 Offgas Profiles Covering a Period of 400 Minutes after the Initiation of HCOOH Addition. Temperature, pH, CO₂, H₂, NO_x, and N₂O profiles are shown.

Offgas Generation HCOOH Base 2

Figure 5.1.2 - Baseline Test T94-HCOOHBase-2 Offgas Profiles Covering a Period of 400 Minutes after the Initiation of HCOOH Addition. Temperature, pH, CO₂, H₂, NO_x, and N₂O profiles are shown.

Offgas Generation HCOOH-Base 3

Figure 5.1.3 - Baseline Tests T94-HCOOHBase-3 Offgas Profiles Covering a Period of 450 Minutes after the Initiation of HCOOH Addition. Temperature, pH, CO₂, H₂, NO_x, and N₂O profiles are shown.

Offgas Generation HCOOH Base 1,2 and 3

Figure 5.1.4 - Composit of the Three Baseline Test Offgas Profiles Illustrating the Observed Reproducibility over the First 300 Minutes after the Initiation of HCOOH Addition. Temperature, pH, CO₂, H₂, NO_x, and N₂O profiles are shown.

Table 5.1.1 - Offgas Generated per 130gWO/L for the Baseline Tests

Test	Total Test Time (min)	Stage III Ending Time (min)	Total H ₂ Generated (mM/130gWO)				Initial vol	Init gWO/l
			Stage I	Stage II	Stage III	Total		
T94-HCOOH-Base1	448.00	300.00	0.00	0.64	58.22	49.35	1.56	128.00
T94-HCOOH-Base2	465.00	300.00	0.00	0.81	54.50	73.65	1.55	128.00
T94-HCOOH-Base3	347.00	300.00	0.02	0.93	47.31	48.26	1.57	128.00
			Total NO _x Generated (mM/130gWO)					
			Stage I	Stage II	Stage III	Total		
T94-HCOOH-Base1	448.00	300.00	16.21	62.24	0.78	79.95		
T94-HCOOH-Base2	465.00	300.00	10.75	64.15	0.66	79.09		
T94-HCOOH-Base3	347.00	300.00	22.64	50.98	0.58	74.39		
			Total CO ₂ Generated (mM/130gWO)					
			Stage I	Stage II	Stage III	Total		
T94-HCOOH-Base1	448.00	300.00	164.58	90.43	151.50	460.94		
T94-HCOOH-Base2	465.00	300.00	154.77	108.11	139.70	475.05		
T94-HCOOH-Base3	347.00	300.00	172.92	95.93	132.16	422.16		
			Total N ₂ O Generated (mM/130gWO)					
			Stage I	Stage II	Stage III	Total		
T94-HCOOH-Base1	448.00	300.00	2.66	10.49	1.43	15.23		
T94-HCOOH-Base2	465.00	300.00	2.15	14.69	1.31	26.47		
T94-HCOOH-Base3	347.00	300.00	4.97	13.66	1.29	20.51		

Table 5.1.2 - Peak Offgas Generation Rates per 130gWO/L for the Baseline Tests

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representing the entire test. Hence for purposes of comparison Test HCOOH-BASE-1 provides the best direct comparison while the other two results indicate the affects of two relatively small variations in the basic flowsheet with formic acid.

The results of the three formic acid tests, in general, appeared suitable for making an evaluation of alternate reductant tests, particularly since the reproducibility was good for most of the species and the range of values observed could be used as an upper and lower limit for comparing with measurements of offgas for a single test of each of the alternate reductants.

5.2 Alternate Flowsheet Waste Slurry Results

The four alternate reductants selected for evaluation were lactic, citric, glycolic and oxalic acids. The basis for selection of these reductants is given in Section 4. In addition, a "no reductant addition" flowsheet was also tested. For the "no reductant addition" flowsheet, nitric acid was used to adjust the melter feed rheology.

In this subsection of the report, gas generation for four alternate reductants, lactic, citric, glycolic, and oxalic acids and the no-reductant/nitric acid flowsheets are presented and compared with the baseline flowsheet, formic acid.

The offgas generation profiles for these tests are shown in Figures 5.2.1 to 5.2.5. The amounts of offgas generated and peak gas generation rates for the alternate reductant and nitric acid flowsheets are given in Tables 5.2.1 and 5.2.2, respectively. These data were derived from the data description provided in Appendix A. The values were normalized to 130 gWO for comparison purposes. The four gases observed were H_2 , CO_2 , NO_x , and N_2O . Total measured NH_3 , based on slurry and condensate analyses is also presented below.

The total elapsed time for each test, the duration of the period for which the total gas release was calculated (Stage III Ending Time), the amount of gas released for each stage, and the total amount of each gas measured for each test are listed in Table 5.2.1. The average gas releases for the three replicate formic acid tests are given in Table 5.1.1 as a basis for comparison.

5.2.1 H_2 Generation

Hydrogen was observed only when processing with formic acid and a small amount during a process test with glycolic acid (~1/100th the total amount compared with the formic acid flowsheet) see Figure 5.3.1. Hydrogen was not observed during processing with lactic, citric, oxalic and nitric acids and was so low in the glycolic acid test that it does not show in Figure 5.2.4.

The H_2 generation rate for the reference formic acid flowsheet, ~1.0 mM/min, was several orders of magnitude greater than the peak rate detected for the glycolic acid process test in which H_2 was observed. Hydrogen was not observed in the other alternate reductant process flowsheets tested.

5.2.2 Total Measured NH_3

The amounts of measured NH_3 for the alternate reductant tests were very small and likely represent tramp amounts. From the measured amounts and comparable results obtained from the formic acid tests the conclusion was that, within experimental error, very little NH_3 was produced using any of the alternate reductants under the conditions tested.

Offgas Generation CITRIC - 1

Figure 5.2.1 - Offgas Profiles from Test T94-CITRIC-1 Covering the First 450 Minutes after the Initiation of Citric Acid Addition. Temperature, pH, CO₂, NO_x, and N₂O profiles are shown. No H₂ was detected.

Figure 5.2.2 - Offgas Profiles from Test T94-GLYCOLIC-1 Covering the First 450 Minutes after the Initiation of Glycolic Acid Addition. Temperature, pH, CO₂, NO_x, and N₂O profiles are shown. H₂ was detected but was not plotted.

Figure 5.2.3 - Offgas Profiles from Test T94-LACTIC-1 Covering the First 450 Minutes after the Initiation of Lactic Acid Addition. Temperature, pH, CO₂, NO_x, and N₂O profiles are shown. No H₂ was detected.

Offgas Generation T94 Oxalic - 1

Figure 5.2.4 - Offgas Profiles from Test T94-OXALIC-1 Covering the First 350 Minutes after the Initiation of Oxalic Acid Addition. Temperature, pH, CO₂, NO_x, and N₂O profiles are shown. No H₂ was detected.

Figure 5.2.5 - Offgas Profiles from Test T94-HNO₃-1 Covering the First 300 Minutes after the Initiation of Nitric Acid Addition. Temperature, pH, CO₂, NO_x, and N₂O profiles are shown. No H₂ was detected.

Table 5.2.1 - Offgas Generated per 130gWO/L for the Alternate Flowsheet Tests

	Total Test	Stage II	Total H2 Generated				Total CO2 Generated					
Test	Time	Ending Time										
	(min)	(min)	Stage I	Stage II	Stage III	Total	Stage I	Stage II	Stage III	Total	initial vol	init gWO/L
T84-Lactic-1	485.00	300.00	0.00	0.00	0.00	0.00	152.15	47.09	2.85	204.94	1.57	128.00
T84-Citric-1	469.00	300.00	0.00	0.00	0.00	0.00	128.18	247.90	1.24	380.05	1.48	135.00
T84-Glycolic-1	449.00	300.00	0.00	0.00	0.00	0.00	151.04	50.33	2.93	206.97	1.56	128.00
T84-FPGlycolic-1	330.00	290.00	0.05	0.48	(a)	0.58	138.22	21.33	(a)	159.56	1.75	140.00
T84-FPGlycolic-1a	243.00	243.00	0.04	0.01	0.58	0.63	163.16	67.64	21.88	252.68	0.75	225.00
T84-HNO3-1	277.00	277.00	0.00	0.00	0.00	0.00	(a)	(a)	(a)	187.15	1.54	141.00
T84-Oxalic-1	337.00	300.00	0.00	0.00	0.00	0.00	(a)	(a)	201.27	204.26	1.49	146.00
T84-FPOxalic-1	248.00	248.00	0.00	0.00	0.00	0.00	(a)	(a)	358.22	358.22	1.74	151.00
a. no identifiable stage												
Average B1,B2,B3			0.01	0.79	53.34	57.09	164.09	98.16	141.12	452.72		
RSD (%)			173.21	18.60	10.40	25.15	5.54	9.22	6.91	6.05		
Ave. for Stage I +II				0.80				262.25				
RSD (%)				19.62				2.65				
Ave. total @300 min					54.14					403.37		
RSD (%)					9.96					0.70		
Range (%)					19.57					1.36		
	Total Test	Stage II	Total NOx Generated				Total N2O Generated					
Test	Time	Ending Time										
	(min)	(min)	Stage I	Stage II	Stage III	Total	Stage I	Stage II	Stage III	Total		
T84-Lactic-1	485.00	300.00	3.78	68.66	0.97	73.88	0.50	15.02	0.52	16.11		
T84-Citric-1	469.00	300.00	1.64	79.04	0.13	81.20	0.01	5.28	0.31	6.18		
T84-Glycolic-1	449.00	300.00	2.86	89.92	0.39	93.49	0.05	3.65	0.01	3.71		
T84-FPGlycolic-1	330.00	290.00	8.01	20.32	(a)	40.64	0.12	1.42	(a)	2.18		
T84-FPGlycolic-1a	243.00	243.00	14.71	83.20	37.44	135.35	0.56	4.90	5.09	10.55		
T84-HNO3-1	277.00	277.00	(a)	(a)	(a)	256.84	(a)	(a)	(a)	0.18		
T84-Oxalic-1	337.00	300.00	(a)	(a)	184.24	185.03	(a)	(a)	2.64	2.64		
T84-FPOxalic-1	248.00	248.00	(a)	(a)	28.55	28.55	(a)	(a)	1.29	1.29		
a. no identifiable stage												
Average B1,B2,B3			16.53	59.12	0.67	77.81	3.26	12.95	1.35	20.74		
RSD (%)			36.01	12.04	14.96	3.84	46.21	16.88	5.62	27.11		
Ave. for Stage I +II				75.65				16.21				
RSD (%)				3.31				17.24				
Ave. total @300 min					76.33					17.55		
RSD (%)					3.41					15.50		
Range (%)					6.59					30.43		

Table 5.2.2 - Peak Offgas Generation Rates per 130gWO/L for the Alternate Flowsheet Tests

			H2	CO2 Stage I			CO2 Stage II	
Test	Description	Time (min)	H2 Peak(c) (mM/min)	Time (min)	Peak CO2 (mM/min)	Time (min)	Peak CO2 (mM/min)	
T84-Lactio-1	lactic reductant	(b)	0	49	7.6	110	1.14	
T84-Citric-1	citric reductant	(b)	0	59	8.4	105	6.76	
T84-Glycolic-1	glycolic reductant	(b)	0	48	8.4	240	0.46	
T84-FPGlycolic-1	glycolic reductant	234	0.0078	59	8.7	(b)	(b)	
	final titration	310	0.004	(b)	(b)	320	0.94	
T84-FPGlycolic-1a	re-titrate 3rd day	150	0.021	28	12.7	(b)	(b)	
T84-HNO3-1	nitric reductant	(b)	0	56	7.9	Stage I & II merged and no Stage III		
T84-Oxalic-1	oxalic reductant	(b)	0	70	6.4	Stage I & II merged and no Stage III		
T84-FPOxalic-1	oxalic reductant	(b)	0	124	6.6	Stage I & II merged and no Stage III		
			CO2 Stage III	N2O		NOx		
Test	Description	Time (min)	Peak CO2 (mM/min)	Time (min)	Peak N2O (mM/min)	Time (min)	Peak NOx (mM/min)	
T84-Lactio-1	lactic reductant	220	0.07 (a)	125	0.352	115	2.07	
T84-Citric-1	citric reductant	250	0.04 (a)	113	0.68	102	3.09	
T84-Glycolic-1	glycolic reductant	(a)	(a)	142	0.06	114	1.63	
T84-FPGlycolic-1	glycolic reductant			280	0.017	66	0.408	
	final titration	no stage III		323	0.12	305	1.59	
T84-FPGlycolic-1a	re-titrate 3rd day	150	~ 0.5	61	0.16	50	3.16	
T84-HNO3-1	nitric reductant			128	0.0058	119	6.34	
T84-Oxalic-1	oxalic reductant			141	0.071	155	6.41	
T84-FPOxalic-1	oxalic reductant			212	0.024	95	2.67	

a. no peak, if value given it is highest value observed for gradual changes
b. not applicable
c. Values not normalized to 130 gWO/L. The gWO/L values for each slurry are given in Table 5.2.1

5.2.3 CO₂ Generation

The highest peak CO₂ generation occurred during stage I. The stage I peak CO₂ generation rate varied from 6.4 to 8.4 mM/min for the alternate reductants, nitric acid and formic acid reference flowsheets; the highest rates being observed with glycolic and citric acids.

The amount of CO₂ evolved is compared for each stage, except for the nitric acid and oxalic acid flowsheets where transition from Stage I to II was not well defined. Within experimental error, the amount of CO₂ released during Stage I was consistent with decomposition of carbonic acid, based on the target amount of carbonate added (130 mmole of carbonate per 130 gWO). The average Stage I CO₂ evolution for the three formic acid tests was 164 mmole/130 gWO, or about 25% higher than the amount of carbonate. The extra CO₂ can be attributed to the reduction of MnO₂ (Equation 8) which would produce an additional 32 mmole/130gWO. The amounts of CO₂ during Stage I for the various reductants were about the same as for the formic acid tests, see Table 5.2.1.

The total amount of CO₂ produced during processing was dependent on the type of reductant added and the presence of stage III reactions, i.e., production of H₂ and NH₃. The total amount of CO₂ produced during processing with the lactic, glycolic, oxalic and nitric acids (187 to 201 mM/130gWO) was less than that observed for stages I and II of the formic acid flowsheet, ~262 mM/130 gWO. Note that the equivalents of oxalic acid added was higher than for the formic acid tests (1.8 vs 1.6 acid equiv/130 gWO), which probably increased the amount of CO₂ somewhat. Stages I and II only are used for comparison in this case, as little to no H₂, NH₃ and associated CO₂ generation were observed during processing with these additives.

The total amount of CO₂ produced during processing with citric acid was greater than that observed for the baseline formic acid tests stages I and II (376 compared with 262 mM/130 gWO); but somewhat less than the total (403 mM/130 gWO) for the baseline formic acid flowsheet (including stage III to 300 minutes).

The peak generation rates of CO₂ for the alternate reductants (stage I) were about the same as for the formic acid baseline tests. All were somewhat higher with the greatest deviation being 22% higher for glycolic acid, see Table 5.2.2.

5.2.4 NO_x Generation

The total NO_x generated for lactic, citric and glycolic acid reductants was about the same as for the baseline formic acid tests, with the greatest difference being glycolic acid, 94 mM/130gWO compared to an average of 78 mM/130 gWO for the three formic acid baseline tests. The peak NO_x generation rates were less than that observed for the reference formic acid flowsheet (4.0 mM/min), with the exception of the nitric acid flowsheet. During processing with nitric acid, the NO_x peak generation rate was 6.3 mM/min, or a factor of 1.6 greater than that measured for the reference formic acid flowsheet. The peak NO_x generation rates for the tests with lactic, citric and glycolic acids were in general lower than for the baseline formic acid tests (in the range of 40% to 80% of the baseline values, see Table 5.2.2).

A comparison of the amount generated for Test T94-OXALIC-1 and Test T94-HNO3-1 compared to the baseline tests was not appropriate because the NO₂⁻ and NO₃⁻ concentrations and amounts of acid added were different. Instead, a comparison was made with a comparable formic acid test (Test 1.01) performed in FY 1992 (Smith et al. 1995) for comparison with the oxalic acid test. The relative amounts were 184 mM/gWO for the oxalic test compared to about 270 mM/130gWO

for the most directly comparable formic acid test (Test 1.02). The nitric acid test produced 257 mM/130 gWO, which was higher than the comparable formic acid test, 207 mM/130 gWO (Test SIPTnm, Smith et al. 1995). The peak NO_x generation rate for oxalic was 6.4 mM/min, or about 90% of the peak for the comparable formic acid test (Test 1.02 Smith et al. 1995), and was 6.3 mM/min for the nitric acid test, or about 183% of the peak rate for the comparable formic acid test (Test 1.16b, Smith et al. 1995).

5.2.5 N_2O Generation

The total N_2O generated for lactic, citric and glycolic tests depended on the type of reductant and was less than the baseline formic acid tests. For oxalic acid, the total N_2O was 2.6 mM/130 gWO compared to 20 mM/130 gWO for formic acid. For nitric acid, essentially no N_2O was generated compared to 34 mM/130 gWO for a formic acid flowsheet (Test 1.16b, Smith et al. 1994) under comparable conditions.

The peak N_2O generation rates depended on the type of reductant and were equal to or less than that observed for the baseline formic acid flowsheet (0.63 mM/min). The lowest N_2O generation rates were observed during processing with nitric acid (< 0.01 mM/min). The peak N_2O generation rate for lactic acid was lower (~56%), for citric acid it was about the same (8% higher), and for glycolic acid it was lower (~10%). A comparison of the peak N_2O generation rates for oxalic acid and nitric acid with earlier tests (Smith et al. 1994) indicated much smaller amounts for these two acids,

5.3 Alternate Flowsheet Melter Feed Slurry Results

The extensive offgas evaluation of the alternate flowsheets showed that all of the candidates produced little or no NH_3 and H_2 . This was predicted by previous University of Georgia studies and the reason the four were selected for this evaluation from a larger group. (Thirteen alternate reductant candidates were screened in a series of laboratory tests by Dr. R. B. King and his associates at the University of Georgia to evaluate the potential for H_2 and NH_3 generation during treatment of a simplified NCAW simulant.¹⁶) However, this left too many candidates to be evaluated and a down selection to oxalic acid, nitric acid, and glycolic acid was made on the basis of redox considerations. The HTM will produce a more reduced melt because of the higher temperatures involved and make it uncertain what level of reduction will be most beneficial in the melter cold cap during melter operation. Therefore, the three alternate flowsheets (oxidizing to reducing) were taken to the melter feed make up step to see if they would produce a melter feed slurry with both an acceptable rheology for pipe transfers from mixing tanks to the melter and have an acceptable total oxide loading

Previously processed waste slurries were processed with excess acid to accentuate any tendency for NH_3 or H_2 formation and were therefore not suitable for melter feed fabrication. Hence, the three candidate acids were used to make melter feeds with an acceptable level of acidity. (There is no need for excess acid since it does not improve the rheology to lower the pH below about 6 and adds additional offgas volume.) These tests were conducted using the same flowsheet procedures but only enough acid was added to lower the pH to less than 5 allowing for some pH rebound. The offgas profiles shown in Figures 5.3.1 to 5.3.3 show that the offgas profiles for feed preparation were essentially the same as for the original screening for NH_3 and H_2 production. The offgas data is summarized in Tables 5.3.1 and 5.3.2. These slurries were made into melter feeds by concentrating them to about 225 gWO/L and then added the glass components silica and sodium oxide (as sodium

¹⁶R.B. King, N.K. Bhattacharyya, and V. Kumar. December 1993, Monthly Technical Report, "Hanford Waste Vitrification Plant Hydrogen Study: Preliminary Evaluation of Alternatives to Formic Acid." Prepared for Pacific Northwest Laboratory under contract number 125770-A-A2.

Offgas Generation T94 FP Glyc-1

Figure 5.3.1 - Offgas Profiles from Feed Preparation Test T94-FPGLYC-1 Covering the First 250 Minutes after the Initiation of Glycolic Acid Addition. Temperature, pH, CO₂, NO_x, and N₂O profiles are shown. H₂ was detected as indicated on the plot.

Figure 5.3.2 - Offgas Profiles from Feed Preparation Test T94-FPHNO3-1 Covering the First 300 Minutes after the Initiation of Nitric Acid Addition. Temperature, pH, CO₂, NO_x, and N₂O profiles are shown. No H₂ was detected.

Offgas Generation T94.FPOXAL- 1

Figure 5.3.3 - Offgas Profiles from Feed Preparation Test T94-FPOXAL-1 Covering the First 250 Minutes after the Initiation of Oxalic Acid Addition. Temperature, pH, CO₂, Nox, and N₂O profiles are shown. No H₂ was detected.

Table 5.3.2 - Peak Offgas Generation Rates per 130gWO/L for the Alternate Flowsheet Melter Feed Preparation Tests

			H2			CO2 Stage I	CO2 Stage I
Test	Description	Time (min)	H2 Peak(c) (mM/min)	Time (min)		Peak CO2 (mM/min)	
T94-FPGlycolic-1	glycolic reductant	234	0.0078	59		8.7	
	final titration	310	0.004	(b)		(b)	
T94-FPGlycolic-1a	re-titrate 3rd day	150	0.021	28		12.7	
T94-FPOxalic-1	oxalic reductant	(b)	0	124		6.6	
T95-FPHNO3-3	nitric acid	0	0	43		7	
			CO2 Stage II			CO2 Stage III	CO2 Stage III
Test	Description	Time (min)	Peak CO2 (mM/min)	Time (min)		Peak CO2 (mM/min)	
T94-FPGlycolic-1	glycolic reductant	(b)	(b)	no stage III			
	final titration	320	0.94				
T94-FPGlycolic-1a	re-titrate 3rd day	(b)	(b)	150		- 0.5	
T94-FPOxalic-1	oxalic reductant	Stage I & II merged and no Stage III					
T95-FPHNO3-3	nitric acid	Stage I & II merged			129	1	
			NOx			N2O	N2O
Test	Description	Time (min)	Peak NOx (mM/min)	Time (min)		Peak N2O (mM/min)	
T94-FPGlycolic-1	glycolic reductant	66	0.408	280		0.017	
	final titration	305	1.59	323		0.12	
T94-FPGlycolic-1a	re-titrate 3rd day	50	3.16	61		0.16	
T94-FPOxalic-1	oxalic reductant	95	2.67	212		0.024	
T95-FPHNO3-3	nitric acid	47	2.51	na		na	

nitrate). The resulting feeds were evaluated for rheological properties using a Haaka (model xxxxx) Rheometer. (An acceptable feed will display a viscosity which is less than 25 pa · s and a shear strength which is less than 15 pa while having a total oxide loading of greater than 400 g/L.)

The rheological evaluation showed that the glycolic acid treated feed had acceptable rheological properties at a total oxide loading of 400 while the nitric acid feed could not be more concentrated than 380 and display acceptable rheology and oxalic acid treated feed could only be concentrated to 280. Hence, oxalic acid was eliminated from further testing and a nitric acid processed and a glycolic acid processed feed were recommended for the SSHTM melter tests.

6.0 References

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

Appendix

This appendix contains summary documents which bring together the data that pertains to the tests discussed in the text but was not presented specifically there. They include:

- ° The objective and outline for each test
- ° A set of summary time lines for each test including key events and observations.
- ° A transcribed activity log for each tests giving more detail.
- ° A set of tables giving a summary of the analytical result for samples taken from each test.

Test Objectives and Outline for Test-T94-HCOOHBase-1

Objectives

The objective of this test is to establish a baseline set of values for off-gas and slurry chemistry in terms of rates and amounts. Utilizing SIPT 94 version of NCAW nominal slurry simulant. Nitrite and nitrate were shimmed to 30% and 300% of the nominal values to develop worst case conditions in the simulant for H_2 and NH_3 generation.

Test Outline

- I. Weigh out required amount of slurry (1540g NCAW slurry) and Noble metals slurry (57.8g) add required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating of slurry. Start offgas system.
- III. Boil for approximately 15 minutes. Replace condensate with deionized water. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to 95°C. Prepare to add HCOOH acid at 0.67g/min. (90.6wt. %), measure pH.
- V. Add 122.0g HCOOH acid solution during test.
- VI. Collect condensate during HCOOH acid addition. Take HCOOH acid addition slurry sample at completion of HCOOH addition.
- VII. Digest slurry at boiling for 4 hours. Remove condensate and replace with deionized water.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

Test Objectives and Outline for Test-T94-HCOOHBase-2

Objectives

The objective of this test is to rerun T94-HCOOHBase-1 for reproducibility. Once the test has run a sufficient time to establish reproducibility the effect of NaNO_2 addition on H_2 generation will be observed.

Test Outline

- I. Weigh out required amount of slurry (1540g NCAW slurry) and Noble metals slurry (57.8g) add required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating of slurry. Start offgas system.
- III. Boil for approximately 15 minutes. Replace condensate with deionized water. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to 95°C. Prepare to add HCOOH acid at 0.67g/min. (90.6wt. %), measure pH.
- V. Add 122.0g HCOOH acid solution during test.
- VI. Collect condensate during HCOOH acid addition. Take HCOOH acid addition slurry sample at completion of HCOOH addition.
- VII. Digest slurry at boiling. Remove condensate and replace with deionized water to maintain <140gWO/L. Hold at boiling for 1.5 hours. Add 5.0g NaNO_2 in 10.0g deionized water. Hold at boiling conditions for 2.5 hours. Collect condensate.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

Test Objectives and Outline for Test-T94-CITRIC-1

Objectives

The objective of this test is to compare the titration of NCAW waste simulant with Citric acid and a similar titration with HCOOH. Citric acid will be added and conditions generated under which H_2 and NH_3 would be generated if HCOOH were used.

Test Outline

- I. Weigh out required amount of slurry (1540g NCAW slurry) and Noble metals slurry (57.8g) add required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating of slurry. Start offgas system.
- III. Boil until 80.0g condensate removed. Replace condensate with deionized water. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to 95°C. Prepare to add Citric acid at 2.33g/min. (55.6wt. %), measure pH. Start addition at half rate until acid is entering vessel.
- V. Add 414.0g Citric acid solution during test.
- VI. Collect condensate during Citric acid addition. Take Citric acid addition slurry sample at completion of Citric addition.
- VII. Digest slurry at boiling for four hours. Remove condensate and replace with deionized water to maintain <140gWO/L.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

Test Objectives and Outline for Test-T94-GLYCOLIC-1

Objectives

The objective of this test is to compare the titration of NCAW waste simulant with Glycolic acid and a similar titration with HCOOH. Glycolic acid will be added and conditions generated under which H_2 and NH_3 would be generated if HCOOH were used.

Test Outline

- I. Weigh out required amount of slurry (1540g NCAW slurry) and Noble metals slurry (57.8g) add required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating of slurry. Start offgas system.
- III. Boil until 131.6g condensate removed. Replace condensate with deionized water. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to 95°C. Prepare to add Glycolic acid at 1.46g/min. (70.6wt. %), measure pH. Start addition at half rate until acid is entering vessel.
- V. Add 259g Glycolic acid solution during test.
- VI. Collect condensate during Glycolic acid addition. Take Glycolic acid addition slurry sample at completion of Glycolic addition.
- VII. Digest slurry at boiling for four hours. Remove condensate and replace with deionized water to maintain <140gWO/L.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

Test Objectives and Outline for Test-T94-FPGLYC-1

Objectives

The objective of this test is to produce simulated melter feed for both the HTM and SM using a minimum amount of organic acid to produce good feed rheology.

Test Outline

- I. Weigh out required amount of slurry (1870g NCAW slurry) and Noble metals slurry (38.5g) add required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating of slurry. Start offgas system.
- III. Boil for 15 minutes. Reflux condensate and collect slurry sample for chemical analysis.
- IV. Cool slurry to 95°C. Prepare to add Glycolic acid at 1.7g/min. (70.6wt. %), measure pH. Start addition at half rate until acid is entering vessel.
- V. Add 99.7g Glycolic acid solution during test.
- VI. Collect 354g condensate during Glycolic acid addition or the equivalent to 180g WO/L. Take Glycolic acid addition slurry sample at completion of Glycolic addition.
- VII. Cool slurry to 95°C. Prepare to add 29g Glycolic acid at 1.7g/min. (70.6wt. %), until pH reaches ~5.5. Start addition at half rate until acid is entering vessel.

Test Objectives and Outline for Test-T94-LACTIC-1

Objectives

The objective of this test is to add Lactic acid under the same conditions as HCOOH in Test T94-HCOOHBase-1 and compare the offgas composition. Lactic and HCOOH have the same acid equivalent per mole. The Lactic acid will be added at the same rate of HCOOH and conditions generated under which H₂ and NH₃ would be generated if HCOOH were used.

If the gas evolution becomes too intense the addition rate will be reduced.

Test Outline

- I. Weigh out required amount of slurry (1540g NCAW slurry) and Noble metals slurry (57.8g) add required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating of slurry. Start offgas system.
- III. Boil for approximately 15 minutes. Replace condensate with deionized water. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to 95°C. Prepare to add Lactic acid at 1.4g/min. (85.0wt. %), measure pH.
- V. Add 257.6g Lactic acid solution during test.
- VI. Collect condensate during Lactic acid addition. Take lactic acid addition slurry sample at completion of lactic addition.
- VII. Digest slurry at boiling for four hours. Remove condensate and replace with deionized water to maintain <140gWO/L.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

Test Objectives and Outline for Test-T94-HNO₃-1

Objectives

The objective of this test is to utilize an NCAW simulant processed with HNO₃ in the same manner as HCOOH. First, to determine gases generated upon HNO₃ addition. Second, to establish H₂ and NH₃ are/are not generated when NH₄OH is used for processing slurry.

Test Outline

- I. Weigh out required amount of slurry (1665g) add Noble metals slurry (29.7g) and required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating. Start off-gas system.
- III. Boil approximately 15 minutes. Replace condensate with deionized water. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to 95°C. Prepare to add HNO₃ at 1.22g/min. (70.0wt. %), measure pH.
- V. Add 130.4g HNO₃ solution during test.
- VI. Collect condensate during HNO₃ addition. Take HNO₃ addition slurry sample at completion of HNO₃ addition.
- VII. Digest slurry at boiling conditions for four hours. Collect condensate.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

Test Objectives and Outline for Test-T94-OXAL

Objectives

The objective of this test is to utilize an NCAW simulant processed with Oxalic acid to determine what compounds are formed. The formation of dissolved compounds in slurry and off-gas will be observed. Oxalic acid will be added until all nitrite is destroyed and conditions are generated under which H_2 and NH_3 would be generated if $HCOOH$ were used.

Test Outline

- I. Weigh out required amount of slurry (1920g dilute SIPT slurry) and add required amount of shim chemicals.
- II. Place slurry in reaction vessel. Begin agitation and heating. Start offgas system.
- III. Boil until 199.4g of condensate has been removed. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to $95^{\circ}C$. Prepare to add Oxalic acid at 2.2g/min. (28.6wt. %), measure pH.
- V. Add 460.0g Oxalic solution during test.
- VI. Collect condensate during Oxalic acid addition. Take Oxalic acid addition slurry sample at completion of Oxalic addition.
- VII. Digest slurry at boiling until nitrogen oxides generation ceases then continue for an hour. Collect condensate.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

Test Objectives and Outline for Test-T94-FPOXAL

Objectives

The objective of this test is to produce an HTM melter feed from an NCAW slurry simulant processed with Oxalic acid. An evaluation of chemistry changes via offgas measurements and chemical analysis of slurry and melter feed samples will be made.

Test Outline

- I. Weigh out required amount of slurry (1980g concentrated SIPT slurry) and Noble metals slurry (39.6g) add required amount of shim chemicals. Add 83.1g of NaHCO_3 .
- II. Place slurry in reaction vessel. Begin agitation and heating of slurry. Start offgas system.
- III. Boil until 189.0g condensate removed. Collect condensate and slurry sample for chemical analysis.
- IV. Cool slurry to 95°C . Prepare to add Oxalic acid at 2.2g/min. (28.5wt. %), measure pH.
- V. Add 423.4g Oxalic acid solution during test.
- VI. Collect condensate during Oxalic acid addition. Take Oxalic acid addition slurry sample at completion of Oxalic addition.
- VII. Digest slurry at boiling until 107.8g condensate removed.
- VIII. Take post digestion slurry sample for physical property and chemical analysis.

TEST RUN SUMMARIES

T94-HCOOHBase-1

10:25	0	acid start
10:48	21	foaming
10:59	34	surface foam
11:40	75	fine gray foam
12:38	134	black residue & bubble raft
12:50	148	sample 1-2-2
13:15	170	end acid add.
13:17	172	sample 1-2-2a
13:20	175	sample 1-1-2
13:55	210	boiling
14:30	245	black residue near shaft
14:57	272	black residue over surface
15:35	310	black residue over surface
15:55	330	black residue & foaming
16:30	385	black residue subsiding
17:20	415	sample 1-1-3
17:28	423	black residue gone except edge
17:30	425	sample 1-2-3
17:34	429	sample 1-2-3a

T94-HCOOHBase-2

10:06	0	acid start
10:37	31	surface foam
10:42	38	moderate foam
10:58	52	slight foam
11:08	60	black coloring
11:38	90	foam stopped
11:45	99	black coloring
11:51	105	sample 2-2-2
13:13	187	end acid add.
13:14	188	sample 2-2-2a
13:22	196	sample 2-1-2
13:28	202	black scum
13:43	217	boiling, black scum & surface foam
14:08	240	black residue
15:01	295	samples 2-1-3, 2-2-3, & 3a
15:15	309	added 5 g NaNO2
17:47	481	samples 2-2-4 & 4a
17:50	484	sample 2-1-4

T94-HCOOHBase-3

9:34	0	acid start
10:04	30	foaming lightly
10:26	52	foaming lightly
10:41	67	foaming stopped
10:50	76	black residue
11:47	133	slight foaming
12:38	182	end acid add.
12:48	192	samples 3-2-2 & 2a
12:51	197	sample 3-1-2
12:52	198	sample 3-1-2
13:10	216	black residue near shaft
13:16	222	black residue & slight foaming
13:23	229	residue & foam dissipating
13:50	256	boiling
14:10	276	black residue near shaft
14:25	291	samples 3-2-3 & 3a
14:30	296	sample 3-1-3
14:35	301	sample 3-2-2a & 3a
14:37	303	add NaOH
14:57	323	slight foam
15:29	355	stop NaOH
15:47	373	slurry thick, foam layer
15:50	376	add HNO3
15:54	380	foaming
16:02	388	stop HNO3
16:17	403	black residue near shaft
16:24	410	slurry darker
17:05	451	slight foaming
17:30	476	slight foaming
17:47	493	sample 3-2-4 & 4a
17:54	500	sample 3-1-4

TEST RUN SUMMARIES

T94-Lactie-1

9:36	0	acid start
9:57	21	sample 1-2-2
10:12	36	surface foam
11:02	86	foaming lightly
11:25	109	foam setting, cinnamon residue
11:42	126	foaming lightly
11:53	137	moderate foaming
12:36	180	end acid add.
13:00	204	sample 1-2-2a
13:04	208	sample 1-1-2
13:37	241	boiling
13:09	213	no foam
17:00	444	slight foaming
17:18	482	no foam
17:22	468	sample 1-2-3
17:26	470	sample 1-2-3a
17:50	484	sample 1-1-3

T94-Citric-1

9:50	0	acid start
10:30	40	white-gray foam
11:09	79	black residue near shaft
11:50	120	islands of black bubbles
12:00	130	some foaming
12:20	150	no foaming
13:05	195	no residue or foam
13:10	200	end acid add.
13:16	208	samples 1-2-2 & 2a
13:20	210	sample 1-1-2
13:47	237	boiling
14:10	260	no foam
17:35	465	condensate light yellow
17:38	468	samples 1-2-3 & 3a
17:46	476	sample 1-1-3

T94-Glycolic-1

9:00	0	acid start
9:45	45	some foaming
9:48	48	add anti-foam
9:51	51	gray residue
11:05	125	sample 1-2-2
12:03	183	end acid add.
12:05	185	sample 1-1-2
12:10	190	sample 1-2-2a
12:16	196	gray white residue
12:22	202	boiling
12:32	212	gray residue
15:54	414	sample 1-2-3
16:24	444	sample 1-2-3a
16:27	447	sample 1-1-3

T94-FPGLYC-1

9:11	0	acid start
10:02	51	slight foaming
10:15	64	end acid add.
10:18	67	samples 1-2-1 & 1a
10:30	79	sample 1-1-2
10:45	94	slurry sample has black granules
11:28	137	slight foaming
11:55	164	slight foaming
12:16	185	samples 1-2-2 & 2a
12:48	215	slight foaming
8:00	1389	removed 575 g rheology sample
8:45	1414	add 30.9 g Na2CO3
8:55	1424	end addition
9:00	1429	no foaming
9:35	1464	samples 1-2-3 & 3a
9:40	1469	concentration complete
11:30	1579	70 ml rheology sample added
7:54	2803	sample 1-1-3
9:35	2904	acid start
9:47	2916	surface foam
10:00	2929	black residue near shaft
10:01	2930	sample 1-1-4
10:24	2953	end acid add.
10:26	2955	black residue turning gray
10:36	2965	residue & foam disappearing
10:53	2982	boiling
11:00	2989	slight foaming
11:24	3013	sample 1-2-4
11:36	3025	no foaming
12:45	3094	removed 75 ml rheology sample
		slurry thin

TEST RUN SUMMARIES

T84-HNC3-1

9:43	0	acid start
9:56	13	slight foaming
10:15	32	increased foaming
10:20	37	foaming to top of mantle
10:35	52	foaming to 1/4" below mantle
10:42	58	foam on surface
10:47	64	1/2" foam
11:02	79	island of foam at shaft
11:08	83	acid add. stopped
11:18	93	restart acid add.
11:23	100	acid add. stopped
11:30	107	restart acid add.
11:37	114	slight foam
11:45	122	end acid add., sample 1-2-1a
11:50	127	sample 1-2-2
12:05	142	sample 1-1-2
12:15	152	grayish surface foam
13:10	207	no foam, white streaks
13:35	232	sample 1-2-2a
13:48	243	slight foam
14:10	287	samples 1-1-3 & 1-2-3

T84-Oxalic-1

9:36	0	acid add. start
10:23	47	foaming
10:37	61	no foam
10:57	81	some foaming
11:08	92	foaming stopped
11:59	143	slight foaming
12:09	153	scum on surface
12:34	178	grayish slick near shaft
12:58	202	gray residue on surface
13:18	222	sample 1-2-2
13:20	224	sample 1-1-2
13:21	225	sample 1-2-2s
13:32	236	reddish brown slurry
13:43	247	boiling, gray white scum
15:10	334	samples 1-2-3 & 3s
15:20	344	sample 1-1-3

T84-FPOxal-1

13:12	0	acid add. start
13:15	3	sample 1-2-1s
14:40	88	very slight foaming
14:50	98	surface foaming
15:22	130	still surface foaming
15:27	135	gray white scum
15:35	143	still surface foaming
15:59	167	very slight foaming
16:23	191	last acid add.
16:30	198	sample 1-2-1
16:31	199	slurry appears thin
16:35	203	sample 1-1-2
16:50	218	increased surface foam
17:08	237	slurry appears thin
17:23	251	sample 1-2-2
8:49	1177	sample 1-1-3
10:58	1304	white scum, boiling
11:08	1314	surface foaming
11:52	1360	still foaming
12:28	1396	still foaming
12:40	1408	very slight foaming
12:55	1423	removed 56 g rheology sample
15:30	1578	removed 56 g rheology sample
16:00	1608	added rheology sample back
16:11	1619	removed 54 g rheology sample
16:35	1643	added rheology sample back
16:42	1650	removed 52 g rheology sample
17:05	1673	added rheology sample back
9:10	5518	removed 136 g redox sample
9:25	5533	removed 645 sample
9:25	5533	removed 638 g sample
12:47	5735	sample 1a
15:12	5880	sample 1-conc
15:28	5896	sample 1-2-3

Laboratory Melter Feed Preparation Activity Log

The "Laboratory Melter Feed Preparation Activity Log" is a transcription of the actual log kept during the test run. Though it does not contain all of the entries (redundant entries were eliminated) it contains all of the information of the original log. Its main purpose is to provide a record of observations made during the test that were not being recorded by other means and that would correlate with other data such as the off-gas data. The basis for correlation with other data is "24 hour" military time. The observations recorded relate principally to the slurry condition: color, foaming, other phases present but also includes a record of condenser temperatures (laboratory tests) and other activities carried out during the test run along with comments about the operation of the apparatus itself.

The Date/Time column gives the day the run activity was occurring and the "24 hour" time that the data was recorded or an activity commenced. Zero time is defined as the start of acid addition and the final log entry is entered at the time off-gas data collection stopped. The pH was a manually recorded value from the pH probe (temperature compensated for laboratory tests but not for the small-scale system). The Activity/Observations column attempts to succinctly express relevant activities or actions at the time indicated in the first column. Activities may include:

- Heating or cooling the slurry.
- Observations about the slurry such as slurry color or degree of foaming.
- Condensate or slurry sample collection.
- Unusual off-gas activity.
- Start of acid addition and the rate of addition.

Laboratory-scale tests Activity Logs T94-HCOOHBase-1, T94-HCOOHBase-2, T94-HCOOHBase-3, T94-Citric-1, T94-Glycolic-1, T94-Lactic-1, T94-HNO₃-1, T94-Oxalic-1 and laboratory Melter Feed Preparation Activity Logs T94-FPGLYC-1, T94-FPOXAL-1, and T95-FPHNO₃-3, follow respectively.

Activity Log - Test T94-HCOOH-Base1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/15/93</u>						
6:35	11.478	23	23	24	23	Start heating and agitation. Argon on.
8:10	-	97	-	-	22	Increased heat.
8:33	10.442	102	74	24	23	Boiling and foaming.
8:48	-	100	-	-	24	Reduced heat.
9:20	-	-	-	-	-	Removed 22g slurry T94-HCOOHBase-1-1-1.
9:35	-	-	-	-	-	Removed 75.3g condensate T94-HCOOHBase-1-2-1.
9:40	-	-	-	-	-	Removed 2g secondary condensate T94-HCOOHBase-1-2-1a.
9:47	10.240	92	-	-	-	Add 10g DIW with 0.17g of antifoam.
10:15	9.795	94	-	-	-	Add 71.1g DIW.
10:24	9.562	94	-	-	-	HCOOH begins to enter vessel. Target add rate 0.67 g/min.
10:46	7.213	95	-	-	-	Foaming.
10:59	6.443	94	-	-	-	Some surface foam.
11:40	4.707	95	-	-	-	Fine gray foam on surface.
11:56	4.488	94	71	33	25	Add 39.4g DIW
12:10	-	-	-	-	-	Add 32.8g DIW. Gray foam or residue on surface.
12:39	4.12	-	-	-	-	Black residue on surface.
12:50	-	-	-	-	-	Removed 257.6g condensate T94-HCOOHBase-1-2-2.
12:54	-	-	-	-	-	Add 73.7g DIW.

Activity Log - Test T94-HCOOH-Base1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/15/93</u>						
13:15	3.814	95	-	-	-	HCOOH addition complete. Removed addition line. Start heating for digestion.
13:17	-	-	-	-	-	Removed 15.5g secondary condensate T94-HCOOHBase-1-2-2a.
13:20	-	-	-	-	-	Removed 22.5g slurry T94-HCOOHBase-1-1-2.
13:40	3.925	99	-	-	-	Increased heat. Black residue around center shaft.
13:45	3.963	101	-	-	-	Boiling.
13:55	-	-	-	-	-	Add 90.0g DIW.
14:10	4.185	102	-	-	-	Slurry more fluid than usual. Add 86.2g DIW. Black residue still around center shaft.
14:57	4.091	102	-	-	-	Add 80.8g DIW. Black residue covering ~ 90% of surface foam. Appears to be foaming on residue area only.
15:35	4.200	103	-	-	-	Black residue covering ~95% of surface foam.
15:40	-	-	-	-	-	Add 75.8g DIW.
15:55	4.419	102	-	-	-	Black residue covering ~95% of surface. Foaming.
16:08	-	-	-	-	-	Add 81.7g DIW.
16:30	4.755	103	-	-	-	Residue breaking up in center of vessel. Add 78.6g DIW.
17:02	-	-	-	-	-	Add 82.3g DIW.

Activity Log - Test T94-HCOOH-Base1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/15/93</u>						
17:28	4.899	103	-	-	-	Residue has dissipated except for 10cm band rotating around inside vessel wall.
17:30	-	-	-	-	-	Removed 766.2g condensate T94-HCOOHBase-1-2-3. Heat off. Add 86.7g DIW.
17:34	-	-	-	-	-	Removed 19.0g secondary condensate T94-HCOOHBase-1-2-3a.
17:40	-	-	-	-	-	Removed 21.5g slurry T94-HCOOHBase-1-1-3.
17:49	4.942	87	-	-	-	Stopped agitation. Argon off.

Activity Log - Test T94-HCOOH-Base2

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/30/93</u>						
6:45	-	23	25	25	25	Start heating and agitation. Argon on.
7:44	9.469	100	-	-	-	Removed 40.5g condensate T94-HCOOHBase-2-2-1.
8:00	9.748	101	82	27	25	Boiling. Removed pH probe.
8:18	-	101	-	-	-	Decreased heat. Removed 38.9g of condensate T94-HCOOHBase-2-2-1.
8:33	-	93	-	-	-	Removed 22.5g of condensate T94-HCOOHBase-2-2-1.
8:33	-	-	-	-	-	Removed 31.2g slurry T94-HCOOHBase-2-1-1 Add 101.9g DIW. Add 10ml DIW with 0.17g antifoam.
9:22	-	93	-	-	-	Start HCOOH addition. Target add rate 0.67 g/min
9:38	8.424	94	-	-	-	Pump re-calibrated due to discrepancy. HCOOH addition stopped..
10:06	-	-	-	-	-	Start HCOOH addition.
10:10	-	-	-	-	-	Add rate 0.9g/min.
10:20	-	-	-	-	-	Add rate 0.74g/min.
10:27	7.912	94	-	-	-	Add rate 0.68g/min.
10:37	-	-	-	-	-	Surface foam.
10:42	6.275	94	-	-	-	HCOOH addition rate 0.66 g/min. Moderate foaming.
11:06	4.708	95	72	31	25	Moderate surface foaming. Some black discoloring.

Activity Log - Test T94-HCOOH-Base2

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/30/93</u>						
11:45	3.461	95	74	31	24	Surface foam stopped. Some black discoloring around center stir shaft.
12:38	2.942	95	75	32	25	
13:13	-	-	-	-	-	Stopped HCOOH addition.
13:22	2.684	95	-	-	-	Removed 16.1g slurry T94-HCOOHBase-2-1-2. Start heating.
13:28	2.756	95	-	-	-	Some black surface foam around center stir shaft.
13:32	2.835	101	-	-	-	Small amount of black foam on surface foam.
13:43	2.998	101	-	-	-	Boiling.
13:49	3.074	101	-	-	-	Add 116.3g DIW.
14:06	3.221	101	-	-	-	Some black residue mixed with surface foam.
14:25	-	-	-	-	-	Add 78.2g DIW.
15:01	-	-	-	-	-	Removed 13.6g slurry T94-HCOOHBase-2-1-3. Add 76.7g DIW.

Activity Log - Test T94-HCOOH-Base3

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>12/6/93</u>						
6:30	10.72	23	23	23	-	Start heating and agitation. Argon on.
7:28	-	101	-	-	-	Boiling.
7:30	-	-	-	-	-	Took first initial condensate T94-HCOOHBase-3-2-1.
7:45	10.39	101	-	-	-	Reduced heating power.
7:49	-	-	-	-	-	Add 67.2g DIW.
8:05	-	93	71	26	25	-
8:20	-	-	-	-	-	Removed 14.0g slurry T94-HCOOHBase-3-1-1.
8:23	-	-	-	-	-	Add 10ml DIW with 0.17g of antifoam.
9:23	-	-	-	-	-	HCOOH addition begins. Target addition rate 0.67g/min.
10:04	-	-	-	-	-	Slight foaming. Add rate 0.67g/min.
10:15	6.58	94	-	-	-	Still slight foaming.
10:26	5.84	95	-	-	-	Still slight foaming.
10:41	5.26	95	-	-	-	Foaming stopped.
10:50	4.61	95	-	-	-	Small amount of black residue on surface.
11:07	4.23	95	-	-	-	Add rate 0.60g/min.
11:28	4.16	95	75	32	25	Slight foaming and surface mist.
11:52	3.82	95	74	33	25	-

Activity Log - Test T94-HCOOH-Base3

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>12/6/93</u>						
12:36	-	-	-	-	-	HCOOH addition complete.
12:51	-	-	-	-	-	Removed 21.9g HCOOH addition slurry T94-HCOOHBase-3-1-2.
12:57	-	-	-	-	-	Add 100g DIW.
12:58	-	-	-	-	-	Add 100g DIW.
12:59	-	-	-	-	-	Start heating for digestion.
13:08	3.61	98	-	-	-	Black residue around center shaft.
13:16	3.68	100	-	-	-	Slight foam and black residue on surface.
13:23	3.75	100	-	-	-	Light foam and black residue dissapating.
13:50	3.93	101	-	-	-	Boiling.
14:00	3.97	101	82	32	25	-
14:10	4.07	101	-	-	-	Black residue around center shaft.
14:16	-	-	-	-	-	Add 85.3g DIW.
14:25	4.14	100	-	-	-	Add 32.4g DIW. Condensate T94-HCOOHBase-3-2-3, 3-2-2, 3-2-3a and 3-2-2a have a slight yellow tint.
14:30	-	-	-	-	-	Removed 17.4g slurry T94-HCOOHBase-3-1-3.

Notes* Initial slurry T94-HCOOHBase-3-1-1 appears to be smooth.
Slurry T94-HCOOHBase-3-1-2, 3-1-3 have a noticeable gritty texture.

Activity Log - Test T94-CITRIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/22/93</u>						
6:00	-	-	-	-	-	Start heating and agitation. Argon on.
7:19	-	75	-	-	-	Increased heating.
7:30	-	93	25	25	24	Slurry is a light brown color.
7:50	-	100	-	-	-	Removed condensate T94-CITRIC-1-2-1. Calibrated pH probe 3A with buffer solutions 7 and 10.
7:55	-	100	-	-	-	Boiling.
8:10	-	101	-	-	-	Decreased heating.
8:38	-	93	-	-	-	Removed 18.3g slurry T94-CITRIC-1-1-1.
9:20	-	94	-	-	-	Setting up off gas equipment.
9:30	-	-	-	-	-	Calibrate pH probe 3A with buffer solution 4 and 7.
9:45	9.358	93	-	-	-	Start Citric acid addition. Target addition rate 2.33g/min.
9:52	-	-	-	-	-	Add rate 1.1g/min. Increase rate.
9:54	8.864	94	-	-	-	pH on off gas equipment is reading 0.5 low.
10:02	-	-	-	-	-	Add rate 1.09g/min. Increase rate.
10:09	8.683	94	-	-	-	Rebooting NO,NOx computer.
10:11	-	-	-	-	-	Add rate 1.65g/min. Increase flow.
10:15	8.418	94	-	-	-	Removed condensate T94-CITRIC-1-2-2.

Activity Log - Test T94-CITRIC-1

Date/ Time	pH	Slurry	Temperatures (C)			Activity/Observations
			Con.#1	Con.#2	Con.#3	
<u>11/22/93</u>						
10:19	8.093	94	-	-	-	Add rate 1.57g/min. Increase flow.
10:30	-	-	-	-	-	Grayish white foam on surface.
10:32	7.277	94	-	-	-	Increase pump setting.
10:39	6.944	94	-	-	-	Add rate 2g/min. Increase flow.
10:47	-	-	-	-	-	Add rate 2.02g/min. Increased flow.
10:57	-	-	-	-	-	Increased pump setting.
10:59	5.918	94	27	32	24	-
11:08	5.594	95	-	-	-	Add rate 2.13g/min. Increased flow.
11:09	-	-	-	-	-	Black residue around center shaft.
11:11	-	-	-	-	-	Add rate 2.25g/min. Increase flow.
11:19	5.116	94	-	-	-	Add rate 2.4g/min. Decrease flow.
11:23	-	-	-	-	-	Add rate 2.4g/min. Decrease flow.
11:26	4.98	95	-	-	-	Add rate 2.3g/min.
11:50	4.421	95	-	-	-	Island of black bubbles floating on surface.
12:00	4.067	95	27	32	25	Slight foam on surface.
12:20	3.514	95	28	32	25	Foam is gone.
12:40	3.054	95	-	-	-	
13:05	2.582	95	-	-	-	No floating residue or foam. Citric acid addition complete.
13:20	-	-	-	-	-	Removed 17.6g slurry T94-CITRIC-1-1-2.

Activity Log - Test T94-CITRIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/22/93</u>						
13:23	2.448	95	-	-	-	Increased heating for digestion.
13:47	2.39	101	-	-	-	Boiling.
14:02	2.324	102	-	-	-	Removed 77.9g condensate T94-CITRIC-1-2-3. Add 77.9g DIW.
14:10	2.379	102	-	-	-	Smooth surface no foam.
14:20	-	-	-	-	-	Removed 79.3g condensate T94-CITRIC-1-2-3. Add 79.3g DIW.
14:50	-	-	-	-	-	Removed 78.8g condensate T94-CITRIC-1-2-3. Add 78.8g DIW.
14:52	2.304	95	-	-	-	Add 150g DIW to adjust gWO/L.
15:26	2.400	102	-	-	-	Removed 75.7g condensate T94-CITRIC-1-2-3.
15:33	2.588	98	-	-	-	Removed 76.4g condensate T94-CITRIC-1-2-3. Add 76.4g DIW.
15:52	2.395	102	-	-	-	Removed 75.2g condensate T94-CITRIC-1-2-3. Add 75.2g DIW.
16:00	2.401	101	-	35	25	Removed 78.4g condensate T94-CITRIC-1-2-3. Add 78.4g DIW.
16:30	2.411	101	29	36	25	Removed 78.8g condensate T94-CITRIC-1-2-3. Add 78.8g DIW.
17:17	2.407	101	-	-	-	Removed 78.3g condensate T94-CITRIC-1-2-3. Add 78.3g DIW.

Activity Log - Test T94-CITRIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/22/93</u>						
17:35	2.422	102	-	-	-	Removed 77.9g condensate T94-CITRIC-1-2-3. Add 77.9g DIW. Heating and agitation off. Argon off. Note* Secondary condensates are a light yellow in color. pH probe put in buffer 4 to read 4.32 and buffer 7 to read 6.74.
17:46	-	-	-	-	-	Removed 15.1g slurry T94-CITRIC-1-1-3.

Activity Log - Test T94-GLYCOLIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>12/2/93</u>						
6:30	-	22	22	22	21	Start heating and agitation. Argon on.
7:31	-	97	78	28	24	Increased heat.
7:58	-	101	-	-	-	Boiling.
8:21	-	100	-	-	-	Decreased heat.
8:22	-	-	-	-	-	Removed 130.2g initial condensate T94-GLYCOLIC-1-2-1.
8:33	-	-	-	-	-	Removed 1.4g initial secondary condensate T94-GLYCOLIC-1-2-1a.
8:52	-	-	-	-	-	Removed 15.6g initial slurry T94-GLYCOLIC-1-1-1.
9:00	-	-	-	-	-	Start Glycolic acid addition. Target rate 1.46g/min.
9:06	-	-	-	-	-	Add rate 2.3g/min. Decrease flow.
9:08	8.839	95	-	-	-	-
9:16	-	-	-	-	-	Add rate 1.7g/min. Decrease flow.
9:26	-	-	-	-	-	Add rate 1.5g/min. Decrease flow.
9:35	7.026	95	-	-	-	Foaming.
9:48	-	-	-	-	-	Add 10ml DIW with 0.17g antifoam .
9:49	6.319	94	-	-	-	Add rate 1.4g/min.
9:51	5.825	95	-	-	-	Gray residue on surface.
10:09	-	-	-	-	-	Add rate 1.4g/min.
10:24	4.674	95	75	31	24	-

Activity Log - Test T94-GLYCOLIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>12/2/93</u>						
11:05	-	-	-	-	-	Removed 186.4g acid addition condensate T94-GLYCOLIC-1-2-2.
11:27	3.200	95	77	32	25	Gray residue on smooth surface.
12:01	2.700	95	-	-	-	Glycolic acid addition complete.
12:05	-	-	-	-	-	Removed 17g acid addition slurry T94-GLYC-1-1-2.
12:10	-	-	-	-	-	Removed 14.3g acid addition secondary condensate T94-GLYCOLIC-1-2-2a.
12:16	2.700	95	-	-	-	Increased heat for digestion. Grayish white residue on surface.
12:22	-	101	-	-	-	Boiling. Increased heat.
13:01	2.888	100	-	-	-	Removed 150.1g condensate T94-GLYC-1-2-3. Add 150.1g DIW.
13:29	2.98	98	-	-	-	Removed 78.4g condensate T94-GLYC-1-2-3. Add 78.4g DIW.
13:53	-	-	-	-	-	Removed 80.6g condensate T94-GLYC-1-2-3. Add 80.6g DIW.
14:10	-	-	-	-	-	Removed 75.7g condensate T94-GLYC-1-2-3. Add 75.7g DIW.
14:38	3.064	102	-	-	-	Removed 78.8g condensate T94-GLYC-1-2-3. Add 78.8g DIW.
14:54	-	-	-	-	-	Removed 77.1g condensate T94-GLYC-1-2-3. Add 77.1g DIW.
15:29	3.149	98	-	-	-	Removed 84.5g condensate T94-GLYC-1-2-3. Add 84.5g DIW.

Activity Log - Test T94-GLYCOLIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>12/2/93</u>						
15:55	3.107	102	-	-	-	Removed 86.0g condensate T94-GLYC-1-2-3. Add 86.0g DIW.
16:18	3.109	102	-	-	-	Heat off.
16:20	-	-	-	-	-	Removed 17.9g secondary condensate T94-GLYC-1-2-3s.
16:27	-	-	-	-	-	Removed 13.7g slurry T94-GLYC-1-1-3.
16:37	-	88	-	-	-	Argon off.

Activity Log - Test T94-FPGLYC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>2/23/94</u>						
6:30	11.72	24	24	23	24	Start agitation. Argon on.
6:40	11.77	25	25	24	24	Start heating. Reflux condensate.
6:45	11.60	33	23	24	24	No apparent change in density.
6:55	11.49	52	28	25	25	No apparent change in density.
7:00	10.77	66	34	20	25	No apparent change in density.
7:10	10.12	-	-	25	25	No apparent change in density.
7:20	9.5	97	81	26	25	No apparent change in density.
7:25	9.27	97	83	26	26	Increased heat.
8:00	8.63	101	89	25	24	Boiling.
8:02	-	-	-	-	-	Removed pH probe for calibration.
8:03	-	-	-	-	-	Slurry appears to be fluid.
8:15	-	101	91	25	24	Decreased heat.
8:38	-	-	-	-	-	Removed 16.0g of slurry T94-FPGLYC-1-1-1.
8:44	9.36	-	-	-	-	Added 5ml DIW with 0.19g antifoam. Placed pH probe in slurry.
8:51	9.45	95	79	26	25	Hooked up gas analyzer.
9:10	-	-	-	-	-	Started Glycolic acid addition. Target rate 1.7g/min.
9:13	9.55	94	81	32	26	Add rate 2.3g/min. Decreased flow.
9:14	-	-	-	-	-	Add rate 2.0g/min. Decreased flow.
9:16	-	-	-	-	-	Add rate 2.0g/min. Decreased flow.

Activity Log - Test T94-FPGLYC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>2/23/94</u>						
9:18	9.14	94	-	-	-	Add rate 1.6g/min.
9:25	-	-	-	-	-	Removed 34.9g condensate T94FPGLYC-1-2-1.
9:39	-	-	-	-	-	Removed 38.1g condensate T94FPGLYC-1-2-1.
9:55	6.82	94	81	30	24	Add 77.8g DIW.
10:02	-	-	-	-	-	Slight foam covering 65 to 70% of surface.
10:11	-	-	-	-	-	Add rate 1.5g/min.
10:15	-	-	-	-	-	Glycolic acid addition complete.
10:17	-	-	-	-	-	Removed 34.8g condensate T94-FPGLYC-1-2-1.
10:24	-	-	-	-	-	Removed 6g secondary condensate T94-FPGLYC-1-2-1s.
10:30	-	-	-	-	-	Removed 17.5g slurry T94-FPGLYC-1-1-2. Nitrogen analyzer pressures 3.7psi for flow balance. 23psi for ozone. Should be 4 and 30.
10:37	6.23	94	-	-	-	Increased heat.
10:45	6.23	97	89	32	25	Sample T94-FPGLYC-1-1-2 appears to have noticeable black granules.
10:57	6.35	98	89	33	25	Increased heat.
11:05	6.41	100	91.3	34.2	25.1	Increased heat.
11:15	6.41	101	91.2	35	25	Slurry appears fluid.
11:22	6.46	101	91	36	25	FTIR failure.

Activity Log - Test T94-FPGLYC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>2/23/94</u>						
11:24	-	-	-	-	-	Removed 155.4g condensate T94-FPGLYC-1-2-2.
11:28	-	-	-	-	-	Slight foaming.
11:35	6.51	102	91	35	23	Removed 39.5g condensate T94-FPGLYC-1-2-2.
11:47	-	-	-	-	-	Removed 39.4g condensate T94-FPGLYC-1-2-2.
11:53	-	-	-	-	-	Removed 38.4g condensate T94-FPGLYC-1-2-2.
11:55	6.6	103	91	37	25	Slight foaming.
11:58	-	-	-	-	-	Removed 30.2g condensate T94-FPGLYC-1-2-2.
12:07	-	-	-	-	-	Foam covering about 70% of surface area.
12:09	-	-	-	-	-	Removed 38.9g of condensate T94-FPGLYC-1-2-2.
12:12	-	-	-	-	-	Removed 18.4g of condensate T94-FPGLYC-1-2-2.
12:18	6.76	103	-	-	-	Removed 10.7g secondary condensate T94-FPGLYC-1-2-2s. Started refluxing.
12:24	-	-	-	-	-	Add 17g DIW.
12:34	6.84	103	91	40	26	Slight foaming.
12:46	6.85	103	92	41	26	Slight foaming.
12:55	6.87	103	91	39	24	Slight foam. Black residue on surface. Decreased heat.

Activity Log - Test T94-FPGLYC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>2/23/94</u>						
14:03	-	97	-	-	-	Retitrating with Glycolic acid to obtain a pH~5.5.
14:21	5.71	97	-	-	-	Glycolic acid addition complete.
14:27	5.51	97	80.4	30.1	23.4	Heat off.
14:36	5.73	91	-	-	-	Stirrer on.
14:44	5.87	85	-	-	-	Argon off. Removed pH probe.

Activity Log - Test T94-LACTIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/17/93</u>						
6:55	9.872	22	24	24	25	Start heating and agitation. Argon on.
7:25	9.796	71	36	24	24	Increased heat.
7:44	-	90	-	-	-	Increased heat a little.
8:06	10.913	102	-	-	-	Boiling. Ph probe removed. Slurry appears to be thicker than in previous tests.
8:21	-	103	50	25	25	Decreased heating.
8:34	-	98	-	-	-	Removed 28.6g initial condensate T94-LACTIC-1-2-1. Add 28.6g DIW.
8:44	-	-	-	-	-	Removed 14.3g initial slurry T94-LACTIC-1-1-1.
9:14	9.719	92	-	-	-	Off gas system set-up.
9:35	9.619	94	-	-	-	Lactic acid addition started. Target addition rate 1.4g/min.
9:38	9.607	94	-	-	-	Add rate 0.7g/min.
9:45	9.39	94	-	-	-	Add rate 1.3g/min.
9:51	8.975	94	-	-	-	Add rate 1.5g/min.
9:57	-	-	-	-	-	Removed acid addition condensate T94-LACTIC-1-2-2.
10:12	7.18	94	69	29	21	Frothy surface foam.
10:22	6.779	94	-	-	-	Add rate 1.44g/min.
10:38	5.749	94	-	-	-	Removed 31.8g condensate T94-LACTIC-1-2-2.
11:02	4.883	95	68	29	21	Light frothy surface foam.

Activity Log - Test T94-LACTIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/17/93</u>						
11:03	-	-	-	-	-	Removed condensate T94-LACTIC-1-2-2.
11:16	4.522	95	-	-	-	Foam settling and slowly collapsing. A cinnamon colored residue left on vessel wall.
11:32	4.241	95	-	-	-	Removed 35.5g condensate T94-LACTIC-1-2-2. Add 35.5g DIW.
11:42	4.094	94	70	29	21	Small amount of surface foam.
11:53	3.968	95	72	31	24	Moderate foaming.
11:58	3.926	95	-	-	-	Removed 38.7g condensate T94-LACTIC-1-2-2. Add 38.7g DIW.
12:20	-	-	-	-	-	Removed 38.8g condensate T94-LACTIC-1-2-2. Add 38.8g DIW.
12:36	3.579	94	-	-	-	Lactic acid addition completed. Per H.D Smith phone conversation.
12:45	3.604	94	-	-	-	Removed 30.8g condensate T94-LACTIC1-2-2. Add 30.8g DIW.
13:00	-	-	-	-	-	Removed 13.3g secondary condensate T94-LACTIC-1-2-2a.
13:04	-	-	-	-	-	Removed 17.6g Slurry T94-LACTIC-1-1-2.
13:10	3.608	94	-	-	-	Start heating.
13:37	3.657	101	-	-	-	Boiling.
13:38	-	-	-	-	-	Removed 76.0g condensate T94-LACTIC-1-2-3. Add 76.0g DIW.
14:08	3.645	102	-	-	-	Smooth surface. No foaming.

Activity Log - Test T94-LACTIC-1

Date/ Time	Ph	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/17/93</u>						
14:09	-	-	-	-	-	Removed 80.7g condensate T94-LACTIC-1-2-3. Add 80.7g DIW.
14:28	-	-	-	-	-	Removed 78.6g condensate T94-LACTIC-1-2-3. Add 78.6g DIW.
14:48	-	-	-	-	-	Removed 77.1g condensate T94-LACTIC-1-2-3. Add 77.1g DIW.
15:08	3.62	102	-	-	-	
15:22	-	-	-	-	-	Removed 81.5g condensate T94-LACTIC-1-2-3. Add 81.5g DIW. Removed Ph probe. A 4 to 5g slurry loss occurred due to pressure loss.
15:36	3.642	103	87	33	24	
15:42	-	-	-	-	-	Removed 75.5g condensate T94-LACTIC-1-2-3. Add 75.5g DIW.
16:07	-	-	-	-	-	Removed 84.5g condensate T94-LACTIC-1-2-3. Add 84.5g DIW.
16:29	3.631	103	88	34	23	Bubbling and surface foam.
16:31	-	-	-	-	-	Removed 78.5g condensate T94-LACTIC-1-2-3. Add 78.5g DIW.
16:44	3.634	103	-	-	-	No more surface foam.
17:00	3.641	103	90	36	25	Slight surface foam.
17:05	-	-	-	-	-	Removed 85.9g condensate T94-LACTIC-1-2-3. Add 85.9g DIW.
17:18	3.636	103	88	33	22	No more surface foam.
17:24	3.636	103	-	-	-	Removed 77.0g condensate T94-LACTIC-1-2-3. Add 77.0g DIW.

Activity Log - Test T94-LACTIC-1

Date/ Time	Ph	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>11/17/93</u>						
17:26	-	-	-	-	-	Stopped heating. Removed 18.2 secondary condensate T94-LACTIC-1-2-3a.
17:42	3.55	87	-	-	-	Agitator off.
17:44	-	-	-	-	-	Argon off.
17:50	-	-	-	-	-	Removed 15.2g Slurry post digestion T94-LACTIC-1-1-3.

Activity Log - Test T94-HNO3-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
3/8/94						
6:30	11.632	25.4	26	25	25	Start heating and agitation. Argon on.
7:05	-	97	66	23	23	Increased heating.
7:15	-	101	78	21	24	Boiling
7:30	-	101	78	26	25	Removed condensate T93-HNO3-1-2-1, decreased heating. Add 35.0g DIW.
8:00	-	-	-	-	-	Removed 18g initial slurry T94-HNO3-1-1-1.
8:25	-	95	71	25	25	-
9:19	-	-	-	-	-	Add 5ml of DIW with 0.14 g antifoam.
9:32	9.763	94	-	-	-	HNO3 addition starts. Target addition rate 1.22g/min.
9:48	9.513	-	-	-	-	Add rate 1.30g/min. Decrease flow
9:53	9.217	95	-	-	-	Add rate 1.2g/min.
9:56	-	-	-	-	-	Slight foaming.
10:02	8.49	95	69	30	24	-
10:12	-	-	-	-	-	Slight foaming.
10:15	6.762	95	-	-	-	Foaming.
10:20	6.523	96	32	26	-	Removed 38.8g condensate T94-HNO3-1-2-2. Foam to top of heating mantle.
10:30	-	-	-	-	-	Add rate 1.5g/min. Decreased flow.
10:35	5.385	96	-	-	-	Foam 1/4" below mantle top.
10:42	4.712	96	-	-	-	Foam on surface.

Activity Log - Test T94-HNO3-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>3/8/94</u>						
10:47	4.423	96	-	-	-	Foam approximately 1/2".
10:51	4.019	96	-	-	-	Foam breaking up.
11:02	3.502	95	-	29	23	Removed 39.8g of condensate T94-HNO3-1-2-2.
11:06	3.43	-	-	-	-	HNO3 addition stopped. Island of foam around center shaft.
11:16	3.645	-	-	-	-	HNO3 addition started.
11:23	3.204	95	-	-	-	HNO3 addition stopped.
11:34	-	-	-	-	-	Removed 37.7g of condensate T94-HNO3-1-2-2.
11:30	3.437	-	-	-	-	HNO3 addition started.
11:37	3.038	96	-	-	-	Slight surface foam.
11:41	2.866	-	-	-	-	Nice red brown color and fluid.
11:45	2.742	95	65	29	24	HNO3 addition completed. Increased heating. Grayish colored surface foam around center shaft. Refluxing condensate. Removed 91.3g condensate T94-HNO3-1-2-2.
11:50	-	-	-	-	-	Removed 10.7g secondary condensate T94-HNOS-1-2-2s.
12:05	-	-	-	-	-	Removed 17g acid addition slurry T94-HNO3-1-1-2.
12:15	3.163	99	73	30	30	-
12:45	3.343	102	80	23	23	-
13:00	3.38	102	81	29	23	Collecting condensate.

Activity Log - Test T94-HNO3-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>3/8/94</u>						
13:10	3.421	102	-	-	-	No foam. White streaks on surface.
13:35	-	-	-	-	-	Removed 110.5g post acid addition condensate.
13:38	3.453	103	-	31	26	Note* Slurry T94-HNO3-1-1-1 has brown coloring and smooth appearance. Slurry T94-HNO3-1-1-2 reddish brown color with obvious granular particles.
13:46	3.458	102	82	29	25	Slight surface foam.
13:57	3.446	102	83	28	23	Light brown color.
14:10	-	-	-	-	-	Stopped heating. Removed 18.2g slurry T94-HNO3-1-1-3. Removed 9.2g secondary condensate T94-HNO3-1-2-3s.
14:22	3.462	85	-	-	-	Agitator off. Argon off.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
7:35	-	11.3	24	Stirrer on 6. Set point temperature to 93 degrees (C). Argon on.
8:09	-	10.4	92	No change.
8:31	-	9.0	100	Set point to 90 degrees (C).
9:05	-	9.2	88	Set point to 92 degrees (C).
9:29	-	9.2	91	Set Point to 93 degrees (C). Connecting off-gas system. Preparing for acid addition.
9:36	-	9.2	91	Added 0.24 g Dow Corning 544 anti foam compound with 10 g deionized water.
9:56	-	9.2	91	Waiting for off-gas system to start.
10:10	-	9.3	92	Detected small air leak from acid addition line. Sealed leak.
10:34	-	9.3	93	Possible air leak in off-gas system. No leak found.
10:36	-	9.3	92	Removed 18 g of T95-FPHNO3-1-2-1 condensate.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
10:38	0	9.3	93	Started HNO3 addition. Initial acid weight 1111.2 g. Target addition rate, period #1 - 1.04 g/min. for 14 minutes. Period #2 - 1.53 g/min. for 10 minutes. Period #3 - 1.94 g/min. until pH of < 4.9 is met.
10:40	2	9.2	93	Addition rate 1.0 g/min. Pump rate set at 1.6.
10:45	7	8.9	93	No change.
10:47	9	8.8	92	Addition rate 1.1 g/min. Pump rate decreased to 1.4.
10:49	11	8.8	93	Addition rate 0.9 g/min.
10:51	13	8.7	93	Increased pump rate to 2.4 for period #2 of acid addition . Target rate of 1.53 g/min for ~10 minutes.
10:54	16	8.5	92	Addition rate 1.2 g/min. Increased pump rate to 2.8.
10:55	17	8.4	92	Addition rate 1.5 g/min.
10:59	21	8.1	92	Increased stir speed to 8 per phone call H.D. Smith and Test Instructions.
11:01	23	7.9	92	Increase pump rate to 4 for period #3. Target addition rate 1.95 g/min until pH of <4.9 obtained.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
11:04	26	7.5	92	Addition rate 1.5 g/min. Increased pump rate to 4.4.
11:07	29	6.9	92	Decrease pump rate to 4.2. Addition rate 1.9 g/min.
11:11	33	6.3	93	Slight foaming.
11:12	34	6.2	93	Stirrer increased to 9.
11:14	36	6.0	93	Foam covering surface.
11:18	40	5.8	94	Heavy foaming.
11:21	43	5.7	93	Still foaming.
11:24	46	5.5	93	Increased stirrer speed to 10.
11:25	47	5.3	93	Foaming.
11:28	50	5.1	93	Foaming.
11:30	52	4.9	93	Foaming.
11:33	55	4.7	93	Acid addition completed. Final weight 1031.2 g a total of 80 g acid added.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
12/6/94				
11:36	58	4.6	92	Removed 33.3 g of T95-FPHNO3-1-2-2 condensate.
11:38	60	-	-	Removed 4.0 g of T95-FPHNO3-1-2-2s secondary condensate.
11:41	63	4.7	92	Good surface movement. No foam.
11:42	64	4.7	92	Increased temperature set point to 95 degrees (C) for beginning of digestion heat up phase.
11:45	67	4.7	92	Removed 14.4 g of T95-FPHNO3-1-1-2 slurry.
11:49	71	4.7	93	No change.
11:54	76	4.7	94	No change.
12:00	82	4.8	95	Increased temperature set point to 96 degrees (C).
12:05	87	4.8	95	No change.
12:06	88	4.8	95	Removed 33.0 g of T95-FPHNO3-1-2-1 condensate.
12:11	93	4.8	95	Good surface movement.
12:14	96	4.8	95	Increased temperature set point to 97 degrees (C).

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
12:19	101	4.8	96	Good surface movement.
12:24	106	4.8	96	No change. Increased temperature set point to 98 degrees (C).
12:28	110	4.8	97	Removed 27.6 g of T95-FPHNO3-1-2-3 condensate. Increased temperature set point to 99 degrees (C).
12:34	116	4.8	98	No change.
12:39	121	4.8	99	Increased temperature set point to 102 degrees (C).
12:42	124	4.8	100	Thick surface foam not much action.
12:45	127	4.8	101	Boiling.
12:50	132	4.9	102	Small amount of foam, thick slurry with not much stirring action.
12:55	137	4.9	102	Thick boiling action.
13:00	142	4.9	102	Removed 37.5 g of T95-FPHNO3-1-2-3 condensate.
13:05	147	4.9	102	Slurry thick, boiling with little stirring action.
13:15	157	4.9	102	No change.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
13:25	167	5.0	102	Removed 33.1 g of T95-FPHNO3-1-2-3 condensate. 13:20 temperature dropped to 97 degrees (C) then back up to 102.
13:30	172	5.0	102	Temperature erratic.
13:32	174	5.0	100	Fluke thermometer reads a constant 102.2 degrees (C) on slurry temperature.
13:37	179	5.0	102	Temperature appears to be holding.
13:41	183	5.0	102	Removed 30.3 g of T95-FPHNO3-1-2-3 condensate.
13:48	190	5.0	102	Very little surface movement.
13:50	192	5.0	102	Temperature bouncing between 102.7-103.1 degrees (C).
13:55	197	5.0	102	Surface appearance suggests slurry has elevated viscosity (i.e. thick).
14:03	205	5.0	102	No change.
14:09	211	5.0	102	Removed 37 g of T95-FPHNO3-1-2-3 condensate. No noticable motion on surface with the exception of stationary surface bubbles.
14:21	223	5.0	102	No change.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
14:26	228	5.0	101	No change.
14:30	232	5.0	100	Slight temperature decrease. Removed 29.2 g of T95-FPHNO3-1-2-3 condensate.
14:36	238	5.0	101	Temperature bouncing between 101-100 degrees (C).
14:41	243	5.0	103	No surface movement.
14:47	249	5.0	103	No change.
14:55	257	5.0	103	Removed 39.4 g of T95-FPHNO3-1-2-3 condensate.
15:00	262	5.0	102	No surface movement.
15:06	268	5.0	103	No change.
15:09	271	5.0	103	Hard to see surface movement due to slurry spatter on reaction vessel lid and sides.
15:17	279	5.0	103	Removed 32.6 g of T95-FPHNO3-1-2-3 condensate.
15:25	287	5.0	103	Still unable to see slurry movement in reaction vessel.
15:32	294	5.0	103	No change.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
15:43	305	5.0	103	Removed 32.1 g of T95-FPHNO3-1-2-1 condensate.
15:47	309	5.0	103	No change.
15:52	314	5.0	103	No change.
16:01	323	5.0	104	Increased temperature set point to 101 degrees (C).
16:10	332	5.0	103	No change.
16:24	346	5.0	103	Removed 35.3 g of T95-FPHNO3-1-2-3 condensate.
16:30	352	5.0	103	Removed 12.6 g of T95-FPHNO3-1-2-3 secondary condensate.
16:42	364	5.0	102	No change.
16:48	370	5.0	103	Temperature erratic and fluctuated between 100-105 in 3 minutes.
16:55	377	5.0	103	No change.
17:12	394	5.0	101	No change.
17:19	401	5.0	102	Removed 29.9 g of T95-FPHNO3-1-2-3 condensate.
17:24	406	5.0	102	No change.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
<u>12/6/94</u>				
17:29	411	5.0	102	No change.
17:33	415	5.0	102	No change.
17:40	422	5.0	102	No change.
17:46	428	5.0	102	Unable to view slurry surface.
17:54	436	5.0	102	No change.
18:00	442	5.0	102	Removed 28.9 g of T95-FPHNO3-1-2-3 condensate. Removed 2.9 g of T95-FPHNO3-1-2-3s secondary condensate.
18:06	448	5.0	101	No change.
18:16	458	4.9	101	No change.
18:20	462	-	-	Removed 12.7 g of T95-FPHNO3-1-2-3 condensate.
18:28	470	4.9	101	Refluxing started.
18:34	476	4.9	100	Increased temperature set point to 102 degrees (C).
18:43	485	4.9	101	No change.

Laboratory-Scale Melter Feed Preparation Activity Log

Nitric Acid Addition, Test-T95-FPHNO3-1

Date/ Time	Cumulative Time (min) (1)	pH	Temperature Slurry (C)	Activity/Observations
12/6/94				
18:50	492	4.9	101	No change.
19:00	502	4.9	103	No change.
19:07	509	4.9	103	No change.
19:22	524	4.9	101	Slurry appears to be thick with no surface movement. Little visibility.
19:28	530	4.9	103	No change.
19:35	537	4.9	103	No change.
19:45	547	4.9	101	Decreased temperature set point to 0.
19:59	561	4.9	98	Off-gas data collection stopped at this time, therefore, the cumulative time log is discontinued. Test completed at this time.
20:09	-	4.8	86	Argon off. Stirrer left on.
12/7/94				
9:12	-	4.1	-	Removed 21.9 g of T95-FPHNO3-1-1-3 slurry.

1. Time after initiation of acid addition (min).

Activity Log - Test T94-OXALIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>3/10/94</u>						
6:20	10.736	28	-	23	23	Start heating and agitation. Argon on.
6:50	10.657	82	46	23	25	Increased heating.
7:18	9.212	100	84	25	24	Boiling.
7:33	-	102	-	27	29	Reduced heating.
7:35	-	-	-	-	-	Removed 75.1g initial condensate T94-OXALIC-1-2-1.
7:47	-	-	-	-	-	Add 75.1g DIW.
8:30	-	94	-	-	-	Removed 16.9g initial slurry T94-OXALIC-1-1-1.
9:36	9.52	94	-	-	-	Started Oxalic acid addition. Target rate 2.2g/min. 48g Oxalic acid added over 11 min.
9:47	8.345	94	-	-	-	Minimum pH rebound.
9:48	-	-	-	-	-	Off gas leak detected. System fixed.
10:03	8.045	94	-	-	-	Add 11.5g Oxalic acid.
10:12	-	-	-	-	-	Fuse blew on off gas equipment. Fixed. Attached flow valve for acid addition.
10:17	7.658	94	-	-	-	11.1g Oxalic acid addition.
10:23	7.242	94	-	-	-	11.4g Oxalic acid addition. Foaming.
10:28	7.013	94	-	-	-	14.4g Oxalic acid addition. Foaming.
10:32	7.223	94	-	-	-	No foam.
10:37	7.006	94	-	-	-	10.1g Oxalic acid addition.

Activity Log - Test T94-OXALIC-1

Date/ Time	pH	Slurry	Temperatures (C)			Activity/Observations
			Con.#1	Con.#2	Con.#3	
<u>3/10/94</u>						
10:42	7.121	94	-	-	-	12.8g Oxalic acid addition.
10:48	6.672	94	-	-	-	11.8g Oxalic acid addition.
10:53	6.873	94	-	-	-	13.8g Oxalic acid addition. Foaming.
10:57	6.586	94	75	31	25	12.3g Oxalic acid addition.
11:03	5.858	94	-	-	-	12.5g Oxalic acid addition.
11:08	5.887	94	-	-	-	12.9g Oxalic acid addition.
11:10	6.038	94	77	31	26	10.5g Oxalic acid addition.
11:16	5.973	94	-	-	-	Removed 36.8g condensate T94-OXALIC-1-2-2.
11:18	5.516	94	-	-	-	11.0g Oxalic acid addition.
11:24	5.434	94	-	-	-	10.1g Oxalic acid addition.
11:28	5.289	94	-	-	-	10.7g Oxalic acid addition.
11:33	5.152	94	-	-	-	10.1g Oxalic acid addition.
11:39	4.994	94	-	-	-	9.8g Oxalic acid addition.
11:44	4.908	94	-	-	-	12.3g Oxalic acid addition.
11:51	4.725	95	-	-	-	12.8g Oxalic acid addition.
11:59	4.41	94	-	-	-	11.7g Oxalic acid addition. Slight foaming on addition.
12:04	4.288	94	-	-	-	11.6g Oxalic acid addition.
12:09	3.965	94	-	-	-	12.5g Oxalic acid addition. Grayish and white granular surface scum.
12:13	3.965	94	-	-	-	11.5g Oxalic acid addition.

Activity Log - Test T94-OXALIC-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
3/10/94						
12:18	3.845	94	-	-	-	13.6g Oxalic acid addition.
12:19	3.858	94	-	-	-	12.7g Oxalic acid addition.
12:29	3.615	95	-	-	-	12.6g Oxalic acid addition. Grayish colored slick around center shaft.
12:34	3.618	95	-	-	-	12.4g Oxalic acid addition.
12:38	3.470	94	-	-	-	11.5g Oxalic acid addition. Grayish colored surface scum.
12:43	3.924	95	-	-	-	12.7g Oxalic acid addition.
12:48	3.25	95	-	-	-	11.5g Oxalic acid addition.
12:53	3.64	94	-	-	-	11.8g Oxalic acid addition.
12:58	2.98	-	-	-	-	11.5g Oxalic acid addition. Gray residue on surface.
13:04	3.18	-	-	-	-	10.3g Oxalic acid addition.
13:09	2.75	-	-	-	-	11.9g Oxalic acid addition.
13:14	2.42	-	-	-	-	Note* Adding 10.9g extra Oxalic acid- see strong decrease in max. NOx generation. Oxalic acid addition complete.
13:18	-	-	-	-	-	Removed 365.7g total acid addition condensate T94-OXALIC-1-2-2.
13:21	-	-	-	-	-	Removed 7.7g acid addition secondary condensate T94-OXALIC-1-2-2s.

Activity Log - Test T94-OXALIC-1

Date/	Time	pH	Slurry	Con.#1	Con.#2	Con.#3	Activity/Observations
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3/10/94	13:23	2.62	-	-	-	-	Increased heat. Removed 17.9g slurry T94-OXALIC-1-1-2. Sample red brown color. Small black to dark brown particles.
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13:32	2.654	99	86	31	26	26	Slurry reddish brown color very fluid.
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13:43	2.609	100	-	-	-	-	Boiling. Gray white surface scum.
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14:18	2.678	102	86	31	25	25	Increased heat.
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14:40	2.645	103	91	32	25	25	-
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15:10	-	-	-	-	-	-	Removed 349.5g post acid addition, concentration condensate T94-OXALIC-1-2-3. Removed 7.7g post acid addition, concentration secondary condensate T94-OXALIC-1-2-3s.
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15:15	-	-	-	-	-	-	Heat off.
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15:20	-	-	-	-	-	-	Removed 17.9g post acid addition, concentration slurry T94-OXALIC-1-1-3.
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15:30	-	-	-	-	-	-	Argon off.
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Note: Sample T94-OXALIC-1-2-2 slight cloudy appearance. All other condensate samples clear. T94-OXALIC-1-1-1 slurry, fast supernate separation. Supernate greenish yellow coloring. T94-OXALIC-1-1-2 slurry, supernate separation. Supernate dark green coloring. T94-OXALIC-1-1-3 slurry, supernate separation. Supernate dark greenish brown.

Activity Log - Test T94-FPOXAL-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>5/19/94</u>						
7:00	-	25	25	25	25	Start heating and agitation. Argon on.
7:45	-	90	25	21	25	Increased heating.
8:01	-	101	-	-	-	Boiling.
8:25	9.505	102	80	23	25	-
8:29	-	102	-	-	-	Removed 19.0g initial slurry T94-FPOXAL-1-1-1.
8:30	-	-	-	-	-	Decreased heating.
9:17	-	93	-	26	26	Slurry is a light-brown color.
9:54	-	94	61	24	23	Decreased heating.
10:02	-	-	-	-	-	Condensate collection per phone call Harry D. Smith.
10:24	-	102	-	-	-	Boiling. Decreased heating.
10:26	-	-	73	27	25	Slurry thickening and darkening in color.
10:42	-	101	69	27	24	Removed 39.6g pre-addition condensate.
11:07	-	101	69	26	22	Slurry has a pudding like consistence. A noticeable thickening and loss in volume.
11:15	-	102	-	-	-	Removed 33.2g pre-addition condensate.
11:31	-	-	-	-	-	Increased heating.
11:53	-	102	-	-	-	Removed 39.4g pre-addition condensate.

Activity Log - Test T94-FPOXAL-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>5/19/94</u>						
12:15	-	-	-	-	-	Removed 37g pre-addition condensate.
12:35	-	102	82	28	25	Removed 39.9g pre-addition condensate. Slurry appears to be thicker than in previous tests.
12:45	-	-	-	-	-	Decreased heating.
13:05	9.054	93	-	-	-	Add 10ml DIW with 0.2g antifoam.
13:10	-	-	-	-	-	Start Oxalic acid addition.
13:12	-	-	-	-	-	20.69g Oxalic acid addition.
13:23	-	-	-	-	-	11.9g Oxalic acid addition.
13:24	8.739	-	-	-	-	9.7g Oxalic acid addition.
13:34	-	-	-	-	-	10.0g Oxalic acid addition.
13:39	-	-	-	-	-	Acid addition chamber plugged. Unplugged chamber and added leftover acid.
13:49	-	-	-	-	-	10.8g Oxalic acid addition.
13:50	-	-	-	-	-	12.0g Oxalic acid addition.
13:55	-	94	56	24	23	10.8 Oxalic acid addition.
14:00	-	-	-	-	-	9.1g Oxalic acid addition.
14:05	-	-	-	-	-	10.0g Oxalic acid addition.
14:10	7.987	-	-	-	-	12.2g Oxalic acid addition.
14:17	7.81	-	-	-	-	11.0g Oxalic acid addition.
14:21	-	-	-	-	-	10.19g Oxalic acid addition.

Activity Log - Test T94-FPOXAL-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>5/19/94</u>						
14:23	7.569	-	-	-	-	Removed 34.0g condensate T94-FPOXAL-1-2-1.
14:26	-	-	-	-	-	10.8g Oxalic acid addition.
14:29	7.482	-	-	-	-	Slurry appears to have a consistency of yogurt.
14:31	-	-	-	-	-	11.8g Oxalic acid addition.
14:35	-	-	-	-	-	10.72g Oxalic acid addition.
14:40	-	-	-	-	-	Slight foaming.
14:42	-	-	-	-	-	9.20g Oxalic acid addition.
14:44	-	-	-	-	-	12.8g Oxalic acid addition.
14:46	7.22	94	-	-	-	13.1g Oxalic acid addition.
14:47	-	-	-	-	-	10.6g Oxalic acid addition.
14:50	7.15	-	-	-	-	Surface foaming.
14:51	-	-	-	-	-	12.7g Oxalic acid addition.
14:54	7.096	94	58	28	28	Surface foaming.
14:59	-	-	-	-	-	8.6g Oxalic acid addition. 13.2g Oxalic acid addition.
15:00	-	-	-	-	-	Added total in all 240g Oxalic acid to this point. Should be 242g for target rate.
15:03	-	-	-	-	-	Removed 14.2g secondary condensate T94-FPOXAL-1-2-1s 10.48g Oxalic acid addition.

Activity Log - Test T94-FPOXAL-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>5/19/94</u>						
15:11	7.07	-	-	-	-	12.0g Oxalic acid addition. Oxalic acid addition after 120min. should be 264g. Oxalic added to this point 262.5g total.
15:16	-	-	-	-	-	Removed 34.2g condensate T94-FPOXAL-1-2-1.
15:17	6.986	-	-	-	-	10.0g Oxalic acid addition.
15:22	-	-	-	-	-	9.02g Oxalic acid addition. Surface foam.
15:27	6.973	-	-	-	-	10.38g Oxalic acid addition. Increased agitator. Grayish white scum covering surface. Increased stirrer from normal 6 setting to 8.
15:31	-	94	-	-	-	10.0g Oxalic acid addition. Total acid addition to time is 292g. Total addition should be 308g.
15:32	-	-	-	-	-	10.02g Oxalic acid addition.
15:35	6.915	-	-	-	-	Foaming. Noticeable thickening.
15:36	-	-	-	-	-	9.08g Oxalic acid addition.
15:41	-	-	-	-	-	7.6g Oxalic acid addition.
15:44	-	-	-	-	-	9.0g Oxalic acid addition.
15:47	6.873	-	-	-	-	Total acid addition to time is 337.5g. Total addition should be 352g.
15:50	-	-	-	-	-	9.0 Oxalic acid addition.
15:54	6.755	95	-	-	-	9.3g Oxalic acid addition.

Activity Log - Test T94-FPOXAL-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>5/19/94</u>						
15:55	-	-	-	-	-	8.76g Oxalic acid addition. Removed 35.7g condensate T94-FPOXAL-1-2-1.
15:59	-	-	-	-	-	9.55g Oxalic acid addition.
16:00	6.694	94	-	-	-	9.65g Oxalic acid addition. Slight foaming.
16:05	6.635	-	-	-	-	7.68g Oxalic acid addition.
16:11	6.559	-	-	-	-	8.16g Oxalic acid addition.
16:16	6.523	-	-	-	-	7.22g Oxalic acid addition.
16:18	-	-	-	-	-	7.44g Oxalic acid addition.
16:20	6.477	-	-	-	-	3.87g Oxalic acid addition.
16:23	-	-	-	-	-	5.28g Oxalic acid addition. Total Oxalic acid addition 423.4g Oxalic acid addition complete.
16:30	6.408	94	-	-	-	Removed 38.3g condensate T94-FPOXAL-1-2-1.
16:31	-	-	-	-	-	Slurry appears to be more fluid.
16:34	-	-	-	-	-	Removed 19.0g slurry T94-FPOXAL-1-1-2.
16:40	6.434	-	-	-	-	Increased heating for digestion.
16:50	6.445	-	-	-	-	Foaming.
16:53	-	-	-	-	-	Removed 39.2g condensate T94-FPOXAL-1-2-2.

Activity Log - Test T94-FPOXAL-1

Date/ Time	pH	Temperatures (C)				Activity/Observations
		Slurry	Con.#1	Con.#2	Con.#3	
<u>5/19/94</u>						
17:09	6.618	99	-	-	-	Removed 38.9g condensate T94-FPOXAL-1-2-2. Reduced agitator. Slurry more fluid.
17:20	-	-	-	-	-	Reduced heating.
17:23	-	-	-	-	-	Removed 29.7g condensate T94-FPOXAL-1-2-2.

Melter Feed and Condensate Composition

The following tables summarize the results of the analyses of condensate and slurry samples taken during the slurry simulant processing into melter feed on the laboratory-scale. The time and date that the sample was taken is given by the activity log. The gWO/L and slurry density values allow the samples to be compared on the basis of a common gWO/L value.

gWO/L and density- Density was determined from the weight of a known volume of slurry under ambient conditions and the gWO/L was determined by firing the pre-weighed slurry to oxides in a furnace at 1050°C for two hours. The accuracy of these measurements is on the order of 2-3%.

pH- The pH measurements were made at ambient conditions using calibrated pH sensing electrodes "Orion" (PNL-ALO-501 Rev.1). The accuracy of these measurements is better than 0.1 pH unit.

Anions- The anions were determined by ion chromatography using PNL-ALO-212 Rev.1 for the laboratory samples. The estimated accuracy is ± 5 to 10%.

Ammonia- Ammonia is measured as the NH_4^+ ion with a standard ion electrode using procedure PNL-ALO-226 Rev.0. The accuracy is $\pm 15\%$ for concentrations < 1 ppm. For concentrations > 1 ppm the accuracy improves to $\pm 5\%$.

Analytical Laboratory Results
 Test T94-HCOOH-Base1
 Date: 11/15/93

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	HCOO- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
1-1-1	9:20	-65	Initial	21.68	1706	1558	127.6	1.1	11.5	0.00013	0.2	6.2	24
1-1-2	13:20	175	Formating	22.5	1572	1427	137.5	1.1	3.9	0.026	59.9	< 0.5	17.2
1-1-3	17:20	415	Digestion	21.5	1550	1407	137.5	1.1	5.39	0.34	35.4	0.182	26.7
Condensate													
1-1-1	9:35	-50	Pre-formating	75.3	1636	1488	133.7	1.1	9.15	0.0048	< 0.0002	0.0008	0.0026
1-2-1a	9:40	-45	Pre-formating	1.9	1595	1447	132.5	1.1		0.019	< 0.005	0.011	0.15
1-2-2	12:50	145	Formating	257					2.59	0.001	1.2	< 0.001	0.18
1-2-2a	13:17	172	Digestion	15.5					2.15	0.006	1.38	< 0.0025	0.73
1-2-3	17:30	425	Digestion	766.2					2.67	0.0007	2.03	< 0.0005	0.0052
1-2-3a	17:34	429	Digestion	19	1550	1407	137.5	1.1	2.53	0.0007	3.92	< 0.0025	0.048

● minutes after acid addition initiated.

Analytical Laboratory Results

Test: T94-HCOOH-Base2
Date: 11/30/93

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	HCOO- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
2-1-1	827	-99	Initial	31.2	1721	1550	127.6		11.63	0.00033	< 0.3	6.7	24.3
2-1-2	1322	196	Formating	16.1	1500	1350	144.8		3.96	0.0058	76.9	2.6	27.8
2-1-3	1501	295	Digestion	13.6	1433	1370	141.5		4.65	0.06	70.1	0.94	26.5
2-1-4	1750	464	Digestion	16.2	1404	1344	142.6		4.99	0.16	62.6	0.54	24.4
Condensate													
2-2-1	835	-91	Initial	101.9	1752	1578	127.6		8.74	0.007	< 0.0004	0.00092	0.0035
2-2-2	1151	105	Formating	187.6	1681	1513	130.7		2.73	0.0015	0.18	0.001	0.15
2-2-2a	1314	184	Digestion	17.1	1516	1365	144.9		2.3	0.006	1.0	0.0033	0.59
2-2-3	1501	295	Digestion	227.3	1447	1382	141.5		2.53	0.0002	3.6	< 0.005	0.035
2-2-3a	1502	296	Digestion	8.6	1447	1382	141.5		2.44	0.00071	6.1	0.0048	0.089
2-2-4	1747	461	NaNO2 add.	308.7	1433	1370	141.5		3.04	0.0027	0.64	0.042	0.069
2-2-4a	1748	462	NaNO2 add.	12	1421	1359	142.6		2.91	0.0028	1.3	0.004	0.029

a minutes after acid addition initiated.

Analytical Laboratory Results

Test T94-HCOOH-Base3
Date: 12/6/93

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	HCOO- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
3-1-1	820	-74	Initial	14	1738	1565	127.6		11.6	0.00032	2.6	6.1	22.5
3-1-2	1251	197	Formating	21.9	1509	1274	154.4		4.23	0.027	83.1	0.093	29.3
3-1-3	1430	296	Digestion	17.4	1687	1435	135.6		4.7	0.074	72.7	0.98	26.8
3-1-4	1754	500	Digestion	18.6	1653	1405	136.7		5.53	0.25	68.6	1.1	46.3
Condensate													
3-2-1	730	-124	Initial	67.2	1738	1565	127.6		7.56	0.007	1.9	0.0012	0.0041
3-2-2	1246	192	Formating	282	1501	1349	148.1		2.82	0.001	0.1	0.0027	0.14
3-2-2a	1247	193	Formating	15	1531	1294	154.4		2.28	0.006	0.14	< 0.005	0.6
3-2-3	1425	291	Digestion	117.7	1704	1451	135.6		2.64	0.00041	2.6	< 0.005	0.024
3-2-3a	1425	291	Digestion	5.1	1704	1451	135.6		2.52	0.0014	5.8	< 0.005	0.12
3-2-4	1743	489	HNO3 add.	372.6	1672	1422	136.8		4.2	0.079	0.36	0.0067	0.01
3-2-4a	1747	493	HNO3 add.	14.7	1653	1405	136.7		7.45	0.33	1	0.0047	0.03

• minutes after acid addition initiated.

Analytical Laboratory Results

Test T94- Citric-1
Date: 11/22/93

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	C6H5O7- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
1-1-1	838	-72	Initial	18.3	1654	1482	134.5		11.66	0.0006	< 0.5	6.4	23
1-1-2	1320	210	Citric add.	17.6	1424	1254	157		3.16	0.03	40	0.27	23
1-1-3	1746	476	Digestion	15.1	1541	1372	142.1		3.04	0.066	34	0.34	22
Condensate													
1-2-1	810	-100	Initial	80	1672	1498	134.5	1.14	9.34	0.0074	< 0.005	0.0011	0.0038
1-2-2	1315	205	Citric add.	395.7					3.79	~0.0003	< 0.01	0.002	0.006
1-2-2a	1316	206	Citric add.	16.9					3.83	0.008	< 0.02	0.0052	0.15
1-2-3	1735	465	Digestion	776.7					3.88	~0.0003	< 0.01	0.0011	0.038
1-2-3a	1738	468	Digestion	19.6					4.09	0.0011	< 0.05	0.0038	0.024

a minutes after acid addition initiated.

Analytical Laboratory Results

Test T94- Glycolic-1
Date: 12/2/93

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	C2H3O3- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
1-1-1	852	-8	Initial	15.6	1736	1564	127.6		11.61	0.001	0.97	6.2	22.3
1-1-2	1205	185	Glycolic add.	17	1533	1380	143.1		3.66	0.00019	107	< 0.5	26.7
1-1-3	1627	447	Digestion	13.7	1554	1400	139.8		3.77	0.00019	114	< 0.5	29.1
Condensate													
1-2-1	822	-38	Initial	130.2	1736	1564	127.6		8.9	0.0058	0.00076	0.00077	0.0026
1-2-1a	833	-27	Initial	1.4	1736	1564	127.6		8.19	0.0045	0.10	0.0021	0.0024
1-2-2	1105	65	Glycolic add.	186.4	1550	1395	143.1		2.27	0.0013	0.031	0.00058	0.53
1-2-2a	1210	190	Digestion	14.3	1518	1367	144.4		1.35	0.005	0.2	0.0025	4.5
1-2-3	1554	414	Digestion	740.2	1554	1400	139.8		3.18	< 0.0001	0.11	< 0.0005	0.044
1-2-3a	1624	444	Digestion	17.9	1554	1400	139.8		1.88	0.00038	0.25	0.0023	1.2

a minutes after acid addition initiated.

Analytical Laboratory Results

Test T94 - FPGLYC - 1

Date: 2/23/94

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	C2H3O3- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
1-1-1	2/23 838	-33	Initial	16	1960	1749	140.3		11.68	0.00033	0.37	19.4	7.7
1-1-2	1030	79	Glycolic add	17.5	1893	1684	144.4		7.55	0.00017	24	20	8.4
1-1-3	2/24 750	1359	Concentration	12.3	969	837	180		6.94	0.00017	37	19.1	9.6
1-1-4	1001	1490	Concentration	18.1	883	735	225		9.93	0.0009	44	20.4	9.8
									6.54	0.92			
Condensate													
1-2-1	2/23 1017	66	Glycolic add	141.1	1910	1699	144.4		4.17	0.0028	0.0052	0.0049	0.035
1-2-1a	1018	67	Glycolic add	6	1910	1699	144.4		3.12	0.0018	0.0223	0.004	0.28
1-2-2	1212	181	Concentration	360.2	1561	1352	180		3.55	0.0011	0.0104	0.0017	0.045
1-2-2a	1216	185	Concentration	10.8	1561	1352	180		2.9	0.0025	0.033	< 0.0005	0.18
1-2-3	2/24 935	1468	Concentration	101.6					2.8	0.0052	0.0078	< 0.0005	0.14
1-2-3a	935	1468	Concentration	2					3.07	0.0094		< 0.04	0.33
1-2-4	2/25 1124	3013	Concentration	100.5					2.01	0.00029	0.039	0.0004	0.71
Rheology	2/24 800	1369		575	986	852							
Rheology	2/25 1245	3094		83.6	817	680							

a minutes after acid addition initiated.

Analytical Laboratory Results
Test T94- Lactic-1
Date: 11/17/93

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	C3H5O3- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
1-1-1	844	-52	Initial	25.1	1738	1565	127.6		11.63	0.0008	<0.7	6.3	21.6
1-1-2	1304	208	Lactic add.	17.6	1567	1410	140.5		4.01	0.03	116	< 0.5	21.2
1-1-3	1750	518	Digestion	15.2	1534	1379	142.2		4.02	0.04	131	< 0.5	21.5
Condensate													
1-2-1	835	-61	Initial	28.6	1738	1565	127.6		7.75	0.0015	0.008	0.0009	0.0031
1-2-2	957	21	Lactic add.	324.4	1700	1530	130.5		2.46	0.0015	0.07	0.0008	0.28
1-2-2a	1300	204	Digestion	13.3	1580	1422	140.4		1.96	0.014	0.21	< 0.001	1.1
1-2-3	1722	466	Digestion	795.4	1567	1410	140.5		3.43	0.0001	0.15	< 0.0001	0.0028
1-2-3a	1726	494		18.2	1549	1393	142.2		2.78	0.0018	0.28	< 0.0025	0.14

a minutes after acid addition initiated.

Analytical Laboratory Results
Test T94- HNO3-1
Date: 3/8/94

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	C2O4- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
1-1-1	800	-103	Initial	18	1737	1538	140.5	1.12	11.86	0.00049	0.24	21.2	8.5
1-1-2	1205	142	Nitric add.	17	1580	1383	155.6	1.21	4.91	< 0.0001	0.005	3.1	75.8
1-1-3	1410	267	Digestion	18.2	1443	1248	169		5.34	< 0.0001	0.004	1.8	86.3
Condensate													
1-2-1	730	-133	Initial	35	1755	1554	140.5	1.12	8.05	0.008	(b)	0.00288	0.0188
1-2-1a	1145	122	Nitric add.	129	1597	1398	155.6		1.59	0.0018	(b)	0.00157	3.21
1-2-2	1150	127	Nitric add.	10.7	1738	1539	140.5	1.12	1.05	< 0.0001	(b)	< 0.01	13
1-2-2a	1335	232	Digestion	111.5	1401	1261	169	1.14	2.05	0.00014	(b)	< 0.01	0.86
1-2-3	1410	267	Digestion	9.2	1461	1264	169	1.14	1.3	0.018	(b)	< 0.01	5.54
1-2-3a													

a. minutes after acid addition initiated.

b. no data

Analytical Laboratory Results

Test T94-FPHNO3-1

Date: 12/6/94

Sample ID	Time (local Military)	Time (min)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (ppm)	C2O4- (g/L)	NO2- (ppm)	NO3- (ppm)
Slurry		12/6/94											
1-1-1	NA		Initial	na	1761	1518	172.5	1.154	11.44	1.3	na	24000	11000
1-1-2	11:46		post acid	14.4	1692	1450	180	1.16	6.6	<0.43	na	18000	43000
1-1-3	post test		concentration	21.9	1238	997	267	1.24	7.44	<0.41	na	28000	66000
Condensate		12/6/94											
1-2-1	10:36		pre-acid cond.	18	na	na	na	1	3.85	4.6	na	2.7	22
1-2-2	12:36		during acid add.	33.3	na	na	na	1	0.82	2	na	7.3	17500
1-2-3	18:20		concentration	437.7	na	na	na	1	2.09	<0.1	na	1.7	550

Analytical Laboratory Results
Test T94-Oxalic-1
Date: 3/10/94

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH (c)	NH3 (g/L)	C2O4- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
1-1-1	936	-106	Initial	17	1694	1485	146		11.48,11.74	0.0026	<0.239	25.5	8.7
1-1-2	1320	224	Acid add.	17	1505	1298	167		3.57,3.55	<0.0001	25.9	0.6	15.4
1-1-3	1520	344	Digestion	17.1	1165	960	223		3.64,3.42	<0.2	33	0.1	18.9
Condensate													
1-2-1	735	-121	Initial	209.4	1711	1500	146		8.92	0.0084	< 0.001	0.0021	0.0014
1-2-2	1318	222	Acid add.	402.5	(b)	(b)	(b)	(b)	1.85,1.48	0.00036	< 0.05	0.051	2.01
1-2-2a	1321	225	Acid add.	18.9	1523	1314	165		1.40,0.84	0.0084	< 0.1	< 0.1	8.5
1-2-3	1510	334	Digestion	349.5	(b)	(b)	(b)	(b)	2.41,2.17	0.00014	< 0.01	< 0.01	0.47
1-2-3a	1510	334	Digestion	7.7	1183	946	219		1.50,1.12	0.0011	< 0.1	< 0.1	4.2

a. minutes after acid addition initiated.
b. no data
c. two measurements made in some cases

Analytical Laboratory Results
Test T94- FPOxal-1
Date: 5/19/94

Sample ID	Time (local Military)	Time (min) (a)	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH	NH3 (g/L)	C2O4- (g/L)	NO2- (g/L)	NO3- (g/L)
Slurry													
	5/19/94												
1-1-1	829	-283	Initial	19	2164	1917	140	1.13	9.8	0.00025	0.46	20	7.7
1-1-2	1635	203	post acid	19	2109	1866	140	1.13	7.44	<0.000099	55	13	10.4
	5/20/94												
1-1-3	849	1177	concentration	20.4	1564	1328	176	1.17	7.74	<0.00010	63	18	14.6
Condensate													
	5/19/94												
1-pre add	1240	-32	pre-acid cond.	189.1	1975	1728	153	1.14					
1-2-1s	1315	3	secondary conc.	14.2	2108	1862	142	1.13	1.49	0.0033	< 0.0005	0.001	3.3
1-2-1	1630	192	during acid add.	143	2128	1893	140	1.13	1.83	0.002	< 0.0005	0.001	2.2
1-2-2	1723	251	concentration	107.8	2001	1758	149	1.13	2.86	0.0012	< 0.00005	0.00073	0.086
	5/20/94												
1s	1247	1415	secondary conc.	14.65	1751	1508	174	1.16					
1-conc	1512	1620	concentration	423	1560	1318	198	1.18					
1-2-3	1528	1636	concentration	37.8	1513	1271	205	1.18	4.24	0.0026	< 0.00005	0.01	0.0016

a minutes after acid addition initiated.