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**Evaluation of HWVP Feed
Preparation Chemistry for an NCAW
Simulant--Fiscal Year 1991:
Evaluation of Offgas Generation,
Reductant Requirements and
Thermal Stability: Technical Report**

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

March 1996

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

Pacific Northwest National Laboratory
Richland, Washington 99352



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Summary

The Hanford Waste Vitrification Plant (HWVP) is being designed for the Department of Energy to immobilize pretreated radioactive high-level waste and transuranic waste as glass for permanent disposal. Laboratory studies were conducted to characterize HWVP slurry chemistry during selected processing steps, using pretreated Neutralized Current Acid Waste (NCAW) simulant. Laboratory tests were designed to provide bases for determining the potential for hazardous gas generation, making chemical adjustments for glass redox control, and assessing the potential for rapid exothermic reactions of dried NCAW slurry. Offgas generation rates and the total moles of gas released as a function of selected pretreated NCAW components and process variables were measured. An emphasis was placed on identifying conditions that initiate significant H_2 generation. Glass redox measurements, using $Fe^{+2}/\Sigma Fe$ as an indicator of the glass oxidation state, were made to develop guidelines for HCOOH addition. Thermal analyses of dried NCAW simulant were conducted to assess the potential of a rapid uncontrollable exothermic reaction in the chemical processing cell tanks.

Twelve laboratory-scale tests were completed using a FY 1991 pretreated NCAW basecase simulant. Process steps investigated were HCOOH addition, digestion, recycle waste stream addition, and slurry concentration. On-line offgas composition/generation rate, slurry temperature, and pH measurements were collected while processing a slurry simulant. Slurry samples were analyzed for cation solubility, plus selected anions and NH_4^+ . Condensate samples from offgas condensers were analyzed for NH_4^+ and anions. Melter feed simulants comprised of treated slurry and glass frit were prepared for rheology and glass redox measurements. Test variables were the amount of HCOOH added, HCOOH addition rate, NO_2 and NO_3 concentration, duration of the digestion period, noble metals content (with and without noble metals), and processing interrupts during H_2 release.

Chemical reactions which partially account for slurry preparation chemistry related to offgas generation and reductant requirements are proposed. Primary reactants are HCOOH, NO_3^- , NO_2^- , and CO_3^{2-} . Noble metals have been identified as reaction catalysts. Offgases observed were CO_2 , NO, NO_2 , N_2O , H_2 , and H_2O . No CO or N_2 was observed. Some NH_4^+ was detected in the slurry and condensate. Significant H_2 generation was observed only in the presence of noble metals and after a threshold molar ratio for HCOOH/ NO_2^- was reached. Maximum H_2 generation rates ranged from 0.31 to 1.12 mmole/min from a slurry volume of $\sim 1.5L @ 125 g WO/L$ (waste oxide/liter). In the absence of noble metals or below the HCOOH/ NO_2^- threshold, the maximum H_2 generation rate was a factor of ten lower. Ammonia generation increased with increasing H_2 generation, simulant NO_3^- loading, and process time. The maximum amount of NH_4^+ observed was 0.197 moles $NH_3/1.5 L @ 125 g WO/L$ slurry. The volume ratio of N_2O/NO_x decreased by a factor of 100 in the absence of noble metals.

While trends and basecase values for offgas generation are reported, several operating variables to which offgas generation rate and composition are believed to be sensitive require further study to support the proposed bounding conditions for source terms. These operating variables include noble metal concentration, slurry pH, temperature, slurry agitation rates, and the presence of organics.

The glass oxidation state was obtained within acceptable processing limits, $Fe^{+2}/\Sigma Fe = 0.005$ to 0.23, by balancing the major reductant (HCOOH) addition and oxidant (NO_3) loading. For all test cases, the $Fe^{+2}/\Sigma Fe$ was between 0.01 and 0.1. The minimum HCOOH addition was equivalent to a HCOOH/ NO_3 molar ratio of 2.2 (using 27 mL of 87 wt% HCOOH/L @ 125 g WO/L slurry at the FY 1991 pretreated NCAW basecase composition). Two process guidelines for HCOOH addition developed by the Savannah River Technology Center (SRTC) for the Defense Waste Processing Facility slurries were compared with HWVP feed preparation chemistry. The correlation of formate and nitrate in melter feed with glass redox (Ramsey 1991) was consistent with HWVP data. The SRTC empirical formula for minimum HCOOH addition to Defense Waste Processing Facility slurries^(a) was not directly applicable to HWVP NCAW forming chemistry.

Thermal analysis of dried slurry simulant samples showed a lower than expected initiation temperature (124°C) for an exothermic reaction in formatted Slurry Receipt and Adjustment Tank (SRAT) slurry. The maximum energy release measured for this exotherm was -354 J/g dried formatted simulant. No sharp exotherm was observed. Further thermal sensitivity studies may be required to assess the concern identified in the Preliminary Safety Analysis Report (Herborn and Smith 1990).

(a) Hsu, C. W. 1990. Formic Acid Requirement in the DWPF Chemical Processing Cell. WSRC internal memo to J. R. Knight, 5 July 1990. WSRC-RP-90-0554.

Acronyms

ALO	analytical laboratory operations
BFP	backscatter fundamental parameter
CPC	chemical processing cell
DOE	Department of Energy
DSC	differential scanning calorimetry
DWPF	Defense Waste Processing Facility
gpm	gallons per minute
HLW	high-level waste
HWVP	Hanford Waste Vitrification Plant
IC	ion chromatography
ICP	inductively-coupled plasma
ICP-ES	inductively-coupled plasma-emission spectroscopy
ICP-MS	inductively-coupled plasma-mass spectroscopy
IDMS	integrated DWPF melter system
IFO	index of feed oxidation
IR	infrared
LFL	lower flammability limit
M	molarity
NCAW	neutralized current acid waste
PHA	precipitate hydrolysis aqueous (DWPF waste stream)
PHTD	PNL HWVP Technology Development
PNL	Pacific Northwest Laboratory
ppb	part per billion
ppm	part per million
PSAR	Preliminary Safety Analysis Report
PSCM	pilot-scale ceramic melter
PUREX	plutonium/uranium recovery via extraction
QA	quality assurance
R	correlation coefficient
redox	reduction-oxidation
RSD	relative standard deviation
SAIC	Science Applications International Corporation
SEM	scanning electron microscopy
SIE	selective ion electrode
SIPT	slurry integrated process tank
slpm	standard liters per minute
SME	slurry mix evaporator
SMECT	slurry mix evaporator condensate tank
SRAT	slurry receipt and adjustment tank

SRL	Savannah River Laboratory
SRS	Savannah River Site
SRTC	Savannah River Technology Center
TC	total carbon
TGA	thermogravimetric analysis
TIC	total inorganic carbon
TO/L	total oxide/liter
TOC	total organic carbon
TRU	transuranic
WDXRF	wavelength dispersive x-ray fluorescence
WHC	Westinghouse Hanford Company
WO/L	waste oxide/liter
WSRC	Westinghouse Savannah River Company
WVDP	West Valley Demonstration Project
WVNS	West Valley Nuclear Services
XRF	x-ray fluorescence

Contents

Acknowledgments	iii
Summary	v
Acronyms	vii
1.0 Introduction	1.1
2.0 Conclusions and Recommendations	2.1
3.0 Objectives and Approach	3.1
3.1 Simulant Preparation	3.2
3.2 Laboratory-Scale Testing	3.2
3.3 Thermal Stability of Dried NCAW Simulant (Nitrate Salt-Organic Reactions)	3.7
4.0 Test Methods	4.1
4.1 Simulant Preparation	4.1
4.1.1 NCAW Simulant Preparation	4.1
4.1.2 Recycle Waste Stream Simulant Preparation	4.9
4.1.3 Melter Feed Simulant Preparation	4.10
4.2 Laboratory-Scale Testing Equipment Description	4.10
4.3 Test Procedure	4.14
4.4 Sampling Strategy/Analytical Methods	4.16
4.5 Methods Used for Thermal Analysis of Dried NCAW Simulant	4.20
5.0 Results	5.1
5.1 Physical Properties of the NCAW Simulant	5.1
5.2 Rheology of NCAW Melter Feed Simulant	5.1
5.3 Offgas Generation Data	5.5

5.4	Slurry and Condensate Composition	5.10
5.5	Glass Redox	5.10
5.6	Results of Dried NCAW Simulant Thermal Analyses	5.10
6.0	Discussion	6.1
6.1	Evaluation of Offgas Generation Data	6.2
6.1.1	Hydrogen Generation	6.2
6.1.2	N ₂ O and NO _x Generation	6.6
6.1.3	Ammonia Generation	6.14
6.2	Assessment of Alternative Redox Indicators and Application of an SRTC Formula for Minimum Formic Acid Addition to HWVP Using Cation Solubility	6.21
6.2.1	Summary of Observed Cation Solubility Trends During Titration of NCAW Simulant with Formic Acid	6.21
6.2.2	Potential Alternatives Considered for Monitoring Glass Redox	6.22
6.2.3	Assessment of the Applicability of the SRTC Minimum Formic Acid Addition Formula to the HWVP	6.28
6.3	Bases for HCOOH Addition to Control Glass Redox	6.30
6.4	Summary of Process Data	6.42
6.4.1	Offgas Generation	6.43
6.4.2	Glass Redox Control	6.47
6.5	Evaluation of NCAW Simulant Thermal Analyses	6.48
7.0	References	7.1
Appendix A -	Comparison of Analytical Methods for NCAW Slurry Simulant Characterization	A.1
Appendix B -	Full-Scale Operation Steps for HWVP Feed Preparation	B.1

Appendix C - Rheograms for NCAW Melter Feed Simulant Containing 500, 550, or 600 g Total Oxide/Liter	C.1
Appendix D - Offgas Profile as a Function of Process Time and Key Events Related to Offgas Generation During FY 1991 Laboratory-Scale Feed Preparation Tests	D.1
Appendix E - Comparison of H ₂ , N ₂ O, NO _x and CO ₂ Generation Rates During Processing with FY 1991 Laboratory-Scale Feed Preparation Test Variables	E.1
Appendix F - Hydrogen and CO ₂ Generation as a Function of Time During Cool Down and Heat Up Cycles for Selected FY 1991 Laboratory-Scale Feed Preparation Tests	F.1
Appendix G - Thermogravimetric and Differential Scanning Calorimetry Thermograms of NCAW Slurry, Formated NCAW Slurry, and Formated NCAW Slurry Plus Recycle Waste Stream Simulant	G.1
Appendix H - Total Amount of NH ₄ ⁺ in NCAW Slurry Simulant as a Function of Process Time for FY 1991 Laboratory-Scale Feed Preparation Tests	H.1

Figures

4.1.1 Flowsheet for FY 1991 Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Stock Simulant Preparation	4.8
4.2.1 Schematic of the Laboratory-Scale Apparatus for FY 1991 Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Simulant Feed Preparation Tests	4.12
4.2.2 Schematic of the Laboratory-Scale Offgas Equipment Configuration for FY 1991 Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Simulant Feed Preparation Tests	4.13
5.1.1 Correlation of Weight Percent Solids and Waste Oxide/Liter for Initial NCAW Simulant, Formated Simulant Prior to Recycle Addition and Formated Simulant after Recycle Waste Stream Addition	5.3
5.2.1 Apparent Viscosity as a Function of Shear Rate for Three Melter Feed Simulants Prepared from Test 7.1 at 500, 550 and 600 g TO/L	5.4
5.3.1 Activation Energies for Steady-State H ₂ Release for Tests 1.1: Maximum Amount of HCOOH and 6.2: HCOOH and Heat Interrupted	5.9
5.3.2 Dependence of CO ₂ Offgas Generation Rate on Temperature Cycling of NCAW Simulant	5.9
6.1.1 Estimated Boundary Region for Initiation of Significant H ₂ Release as a Function of HCOOH and NO ₂ Content in NCAW Simulant	6.3
6.1.2 Comparison of Peak H ₂ Generation Rates with Quantity of HCOOH for SRTC and PHTD Simulants	6.5
6.1.3 Hydrogen and N ₂ O Generation Rates and NO ₂ Concentration in NCAW Simulant (Test 3.2) as a Function of Process Time Showing the Initiation of the Second H ₂ Release and the Decrease of N ₂ O Production with NO ₂ Depletion	6.7
6.1.4 Estimated Amount of HCOOH Consumed by Reaction with NO ₂ (reduction to N ₂ O) for Selected NCAW Slurry Tests	6.12
6.1.5 Total Amount of N ₂ O and NO ₂ , Generated by the NCAW Slurry as a Function of Initial NO ₂	6.13
6.1.6 Distribution of Total NH ₄ ⁺ in Slurry and Condensate Collected During Processing of NCAW Simulant for FY 1991 Feed Preparation Tests	6.16

6.1.7	Distribution of NH_4^+ in Slurry and Condensate Collected During Processing of NCAW Simulant for FY 1991 Test 7.1.	6.17
6.1.8	Correlation Between H_2 Present in the Offgas and $\text{NH}_4^+ / \text{NO}_3^-$ Present in the NCAW Slurry Simulant and Collected Condensate for FY 1991 Tests 1.1, 1.2, 1.3, 3.1, 3.2, 4.1 and 7.1.	6.20
6.2.1	Representative Solubility Profiles for Selected Elements in Hanford Waste Vitriification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Feed Simulant During Testing	6.23
6.2.2	Potential-pH Equilibrium Diagram for the System Molybdenum-Water at 25°C	6.25
6.2.3	Potential-pH Equilibrium Diagram for the System Manganese-Water at 25°C	6.26
6.2.4	Potential-pH Equilibrium Diagram for the System Iron-Water at 25°C	6.27
6.3.1	PHTD Integrated System Considerations in Developing Reductant Addition Guidelines	6.30
6.3.2	Correlation of $\text{HCOOH} / \text{NO}_3^-$ with $\text{Fe}^{+2} / \Sigma \text{Fe}$ for NCAW Waste Glasses Showing $\text{HCOOH} / \text{NO}_3^-$ Threshold Value of 3	6.31
6.3.3	Amount of HCOOH Consumed in Individual SRAT Reactions Defined by FY 1991 NCAW Simulant Laboratory-Scale Tests	6.36
6.3.4	Quantity of HCOOH Consumed During the Formating of HWVP NCAW Noble Metal and Non-Noble Metal (Test 5) Slurry Simulants as a Function of HCOOH Added to the Slurry	6.37
6.3.5	Comparison of FY 1991 PHTD Laboratory-Scale Glass Redox Data with the SRTC Maximum HCOOH Envelope	6.40
6.3.6	Comparison of FY 1991 PHTD Laboratory-Scale Glass Redox Data with the WVDP Model	6.43
6.4.1	Correlation of Peak Offgas Generation Rate (CO_2 , NO_x , N_2O , total gas) with HCOOH Addition Rate.	6.45
6.4.2	Correlation of Offgas Generation (CO_2 , NO_x , N_2O , total gas) with Amount of HCOOH Added to NCAW Slurry Simulant.	6.46

Tables

3.1.1	FY 1991 Reference Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Composition	3.3
3.1.2	FY 1991 Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Target Glass Composition	3.4
3.2.1	Summary of Test Variables and Test Conditions for the FY 1991 Laboratory-Scale Feed Preparation Tests	3.5
3.2.2	Details of Test Variables and Test Conditions for the FY 1991 Laboratory-Scale Feed Preparation Tests	3.6
4.1.1	FY 1991 Neutralized Current Acid Waste (NCAW) Reference and Simulant Target Compositions	4.2
4.1.2	Source Chemicals for FY 1991 Laboratory-Scale Neutralized Current Acid Waste (NCAW) Simulant Preparation	4.4
4.1.3	Sodium Nitrate, NO ₂ , and CO ₂ Additions to Stock Neutralized Current Acid Waste (NCAW) Feed Simulant for FY 1991 Laboratory-Scale Feed Preparation Testing	4.7
4.1.4	Target Recycle Waste Stream Simulant Composition, Recycle Simulant Source Chemicals and Frit Composition for FY 1991 Laboratory-Scale Feed Preparation Tests	4.11
4.2.1	Normal Offgas Concentration Range and Offgas Analyzer Specifications for FY 1991 Laboratory-Scale Feed Preparation Tests of Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Simulant	4.15
4.2.2	Process Step Sampling Strategy for FY 1991 Laboratory-Scale Feed Preparation Tests of Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Simulant	4.17
4.2.3	Total Organic Carbon and Total Carbon Analysis for NCAW Slurry Simulant	4.19
5.1.1	Density, Weight Percent Solids and Waste Oxide/Liter for Initial NCAW Simulant, Formated Simulant Prior to Recycle Addition and Treated Simulant at End of Test	5.2
5.2.1	Yield Stress and Apparent Viscosity of Three Melter Feed Simulants Prepared from Test 7.1 NCAW Simulant Measured at Shear Rates of 183, 383 and 451 s ⁻¹	5.3

5.3.1 Peak Generation Rates (mmoles/minute) of H ₂ , CO ₂ , NO _x and N ₂ O Measured During FY 1991 Laboratory-Scale Feed Preparation Tests	5.6
5.3.2 Quantities of CO ₂ , N ₂ O, NO _x and H ₂ Released During HCOOH Addition, Digestion, Recycle Waste Stream Addition, and for Test Duration for FY 1991 Laboratory-Scale Feed Preparation Tests	5.7
5.4.1 Quantities of HCOO ⁻ , NO ₂ ⁻ , and NO ₃ ⁻ at the End of HCOOH Addition, Digestion and Recycle Waste Stream Addition Processing Steps Determined by Slurry and Condensate Concentrations for the FY 1991 Laboratory-Scale Feed Preparation Tests	5.11
5.4.2 Average, Maximum and Minimum Amounts of HCOO ⁻ , NO ₂ ⁻ , NO ₃ ⁻ and NH ₄ ⁺ Measured in Condensate for the FY 1991 Laboratory-Scale Feed Preparation Tests	5.12
5.5.1 Glass Redox (Fe ⁺² /ΣFe) Before and After Recycle Addition and Selected Test Variables for Glasses Prepared from FY 1991 Melter Feed Simulant	5.13
5.6.1 Thermal Stability of NCAW Simulant, Formated NCAW Simulant and Formated NCAW Simulant Plus Recycle Simulant Measured from 40 to 700°C by DSC and TGA	5.14
6.1.1 Comparison of N ₂ O/NO _x Ratios for NCAW and DWPF Slurry Simulants After Treatment with HCOOH	6.8
6.1.2 Comparison of NCAW Slurry Target Amount of NO ₂ ⁻ , Measured N ₂ O and NO _x Offgas and Related Molar Ratios and HCOOH Addition (amount and rate) for FY 1991 Laboratory-Scale Feed Preparation Tests	6.10
6.1.3 Amount of NH ₄ ⁺ in Slurry and Condensate Samples Collected During FY 1991 Laboratory-Scale Feed Preparation Tests	6.15
6.1.4 Comparison of Times for NO ₂ ⁻ Depletion, Initiation of the Second H ₂ Release, and Measurable NH ₄ ⁺ Production for FY 1991 Laboratory-Scale Feed Preparation Tests (1.1, 3.1, 3.2, 6.1, 6.2, 7.1)	6.18
6.3.1 Comparison of HCOO ⁻ , NO ₃ ⁻ and HCOO ⁻ /NO ₃ ⁻ Before and After Recycle Waste Stream Addition with Glass Redox (Fe ⁺² /ΣFe)	6.33
6.3.2 Percent HCOOH Consumed After HCOOH Addition, After Digestion and Total for the Duration of the Test for FY 1991 Laboratory-Scale Feed Preparation Tests	6.38
6.3.3 Amounts of HCOO ⁻ and NO ₃ ⁻ in Melter Feed; HCOO ⁻ minus NO ₃ ⁻ in Melter Feed; and Glass Redox (Fe ⁺² /ΣFe) Before and After Recycle Waste Stream Addition for FY 1991 Laboratory-Scale Feed Preparation Tests	6.41

1.0 Introduction

The Hanford Waste Vitrification Plant (HWVP) is being designed for the Department of Energy (DOE) to immobilize pretreated radioactive high-level waste (HLW) and transuranic waste (TRU) as glass for permanent disposal. In support of the HWVP effort, laboratory-scale studies were conducted by Pacific Northwest Laboratory (PNL)^(a) to characterize HWVP slurry chemistry during selected processing steps, using simulated pretreated Neutralized Current Acid Waste (NCAW). Laboratory tests were designed to provide bases for determining the potential for hazardous gas generation, making chemical adjustments for glass redox control, and assessing the potential for rapid exothermic reactions of dried NCAW slurry.

Three Fluor Daniel, Inc., technical data needs^(b) were addressed in the FY 1991 studies:

- item 1.9a: measure H₂ generation during forming
- item 1.10a: nitrate salt reaction
- item 1.11a: determine HCOOH/sugar consumption range

Generation of H₂ during treatment of NCAW simulant was first reported by Wiemers (1988)^(c) and later confirmed during large-scale testing at Savannah River Laboratory (SRL).^(d) Hydrogen concentration in the process tanks must be kept below the lower-flammability-limit (LFL) to prevent an explosion that could damage equipment and result in extended plant down time. An estimate of the maximum H₂ generation rate as a function of operating parameters and slurry composition is required to develop a basis for plant design.

The HWVP Preliminary Safety Analysis Report (PSAR) (Herborn and Smith 1990) identified a potential hazard created by radiolytic drying of the slurry followed by energetic reactions between NO₂

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- (a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.
 - (b) Letter report R. A. Smith to J. M. Creer, "Information Needed for Detailed Design," November 4, 1991. WHC letter #9156641.
 - (c) Also refer to Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (d) Hutson, N. D. 1992. "Integrated DWPF Melter System (IDMS) Campaign Report." *Hanford Waste Vitrification Plant (HWVP) Process Demonstration*. WSRC-TR-0403, Rev. 0, UC-721.

and organics. A paper study conducted by Science Applications International Corporation (SAIC) concluded that the chemical processing cell (CPC) tanks could dry out from radiolytic decay heat in 234 days.^(a) However, the maximum steady-state temperature in the CPC tanks, 282°C, would be below the minimum ignition temperature (325°C) for an explosive mixture of NaNO₂/organic. As a check, calorimetry studies were performed on dried NCAW simulant to examine the magnitude and energy/temperature profile.

Formic acid is added to pretreated HLW in the CPC before vitrification to adjust the slurry rheology and to provide a reductant that maintains the glass oxidation state in the melter within an acceptable range. Sufficient reducing agent is needed to assure that the glass will not foam in the melting process, thereby decreasing process rates. But excess reducing agent may result in the reduction of metal oxides to their metallic state. Reduced metals can form a conductive sludge on the bottom of the melter, thus shorting the melter electrodes and causing the melter to fail prematurely. Iron is used as an indicator of the glass oxidation state (also referred to as the "glass redox"). The acceptable glass redox range for HWVP is $0.005 \leq \text{Fe}^{+2}/\Sigma\text{Fe} \leq 0.23$. Correlations between the components of the HWVP slurry and glass redox were measured to provide guidelines for adding reductant. The reductant capacity of sugar was not investigated per priorities set by Westinghouse Hanford Company (WHC).^(b)

In addition to the three technical data needs given above (items 1.9a to 1.11a), the issue of NH₃ generation during forming is important because NH₄NO₃ has safety implications. Ammonia in the presence of NO_x can form potentially explosive NH₄NO₃ in the vessel ventilation system. Ammonium nitrate deposition is of particular concern in the presence of organics that may act as a sensitizer for the detonation. The potential for NH₃ generation during treatment of NCAW with HCOOH was identified by Wiemers et al.^(c) Buildup of NH₄NO₃ in the presence of organics has recently been observed in the Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS) by SRL.^(d) The quantity of NH₃ generated during the slurry preparation process steps was measured during the PNL HWVP Technology Development (PHTD) FY 1991 laboratory-scale feed preparation tests to provide preliminary data for evaluating possible NH₄NO₃ hazards.

-
- (a) Dukas, S. and D. Slaughterbeck. 1991. *Potential For Reactions of Nitrate and Nitrite in the Hanford Waste Vitrification Process Feed*. Prepared for WHC by Science Applications International Corporation, Idaho Falls, ID.
 - (b) A change request by Creer (1991) entitled "Redox Rheology Control Scope Revisions," HWVP-0578.
 - (c) Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company, HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (d) Chang, B., P. Shriner and B. Nguyen. 1992. *Ammonium Nitrate Mitigation in the CPC*. WSRC-TR-92-379.

This FY 1991 PHTD study addresses the "Statement of Work for Applied Technology Tasks to be Performed by PNL in Support of the HWVP Project" (Kruger 1991) under work breakdown structure 1.2.2.03.02. This report satisfies the requirements for the deliverable C93-03.02A, key milestone K-899, "Issue Report on FY 1991 Feed Chemistry Laboratory Studies"^(a) and provides the technical basis for the Detailed Design Data Package, 1.2.2.03.02B^(b) defined in Kruger (1991).

The test objectives, approach, methods, results, discussion and conclusions are provided in this report. Reported data are based on a limited number of data points representing nominal and bounding conditions for NCAW processing and applies specifically to current HWVP processing steps. Interactions between variables and the effects of minor NCAW slurry constituents (e.g., organics, Cr, PO_4^{3-} , and SO_4^{2-}), additional HWVP slurry type components, radiolytic reactions, and slurry receipt and adjustment tank/slurry mix evaporator (SRAT/SME) heel are not included in this testing. Correlations between laboratory-scale data and large-scale tests will be evaluated in future studies when such data become available.

-
- (a) FY 1993 Pacific Northwest Laboratory Hanford Waste Vitrification Plant Technology Development (PHTD) Project Work Plan. Draft. December 1992. PHTD-93-002-REV 0.
 - (b) Wiemers, K. D., M. H. Langowski and M. R. Powell. 1991. *Detailed Design Data Package, 1.9a Measure Hydrogen Generation During Formating, 1.10a Nitrate Salt Reaction.* PHTD-91-03.02-K898.

2.0 Conclusions and Recommendations

A reaction scenario which begins to account for the HWVP feed preparation chemistry related to offgas generation and reductant requirements has been proposed. Primary reaction components are the noble metals (as catalysts), HCOOH, NO₃⁻, NO₂⁻, and CO₃²⁻.

- Formic acid is consumed in the reduction of NO₂⁻ and NO₃⁻, and in the production of H₂. Other relatively minor reactions with respect to HCOOH consumption are believed to take place, such as reduction of MnO₂ and perhaps the noble metals. In general, 40% of the HCOOH added was consumed, independent of the test variables and conditions investigated in the FY 1991 study.
- Nitrite is consumed by reaction with HCOOH being reduced to gaseous oxides of nitrogen (NO, NO₂, and N₂O) and through disproportionation to NO and NO₃⁻. The reduction to N₂O appears to be favored under alkaline conditions and in the presence of noble metals; the disproportionation reaction occurs primarily in acid.
- The greatest fraction of NH₃ was observed after significant H₂ generation and after adding a recycle waste stream. It is proposed that the primary source of NH₃ is NO₃⁻.
- Carbonate releases CO₂ upon acidification of the slurry. Carbon dioxide is also a product of redox reactions involving HCOOH. A major fraction of the offgas was CO₂.

If changes are proposed in the process flowsheet and/or slurry composition, further evaluation will be required. Some of the variables that have not been thoroughly investigated and that may control the offgas generation and potentially HCOOH consumption are pH, temperature, and noble metal concentration. In addition, correlations with large-scale tests are necessary. The following trends are representative of the conditions tested.

An H₂ release of relative significance was observed only in the presence of noble metals and when a HCOOH/NO₂⁻ threshold was reached. The maximum H₂ generation rates ranged from 0.31 to 1.12 mmole/min above a slurry volume of ~1.5 L at 125 g WO/L. In the absence of noble metals or below the threshold, the maximum H₂ generation rates were a factor of ten lower.

The N₂O generation depended on the initial amount of NO₂⁻, the amount of HCOOH added, the HCOOH addition rate, and the presence of noble metals. The maximum N₂O generation rates ranged from 0.15 to 3.35 mmoles N₂O/min for ~1.5 L at 125 g WO/L simulatant. The maximum NO_x generation rates ranged from 0.09 to 3.89 mmoles NO_x/min for ~1.5 L at 125 g WO/L simulatant. The

molar ratio, N_2O/NO_x , varied between tests from 0.08 to 7.^(a) The lowest ratios were observed in the absence of noble metals and at higher HCOOH addition rates. Higher values were observed in tests with lower amounts of NO_2 or HCOOH addition.

The NH_3 generation was observed to increase in the presence of noble metals and H_2 and with increase in NO_3^- concentration and digestion time. The amount of NH_3 measured during these tests ranged from 0.0001 to 0.2 moles per 1.5 L NCAW simulant plus associated recycle waste stream simulant addition.

The CO_2 maximum generation rate was relatively constant varying from 6.2 to 8.6 mmole CO_2 /min per ~1.5 L NCAW simulant, except in the case of a high HCOOH addition rate (equivalent to 8 gpm full-scale) in which the rate was higher. Decomposition of carbonic acid and NO_2^- reduction by HCOOH to N_2O are two primary sources of CO_2 .

It is desirable to provide a general correlation, based on slurry composition and process variables, for predicting maximum offgas generation rates. General trends and key process parameters related to offgas generation have been identified. Applying these results to a generic formula for HWVP design is restricted because of the limited number of tests and large number of variables (eg., pH, temperature, noble metal, NO_2^- , NO_3^- , and HCOOH concentrations, duration, and HCOOH addition rate) affecting the offgas generation.

Using the reference FY 1991 NCAW simulant composition,^(b) significant H_2 releases were not observed with the addition of sufficient HCOOH (27 mL 87 wt% HCOOH/L at 125 g WO/L slurry) to obtain an acceptable glass redox. Based on the threshold value for H_2 release, more than double this amount of HCOOH addition would be required to initiate significant H_2 releases at the reference FY 1991 NCAW NO_2^- loading (20 g NO_2^- /L at 125 g WO/L slurry). In the presence of high NO_3^- , such a HCOOH demand may be required to obtain an acceptable glass redox.

Significant H_2 releases are predicted to occur at ~30 mL 87 wt% HCOOH/L at 125 g WO/L slurry if the NO_2^- concentration is decreased by a factor of four from the reference FY 1991 NCAW simulant composition.

The total offgas generation rate will be at a maximum during the initial HCOOH addition, equivalent to the $N_2O + NO_x + CO_2$ generation rates. The maximum generation rates observed during significant H_2 release and recycle waste stream addition were conservatively governed by the CO_2 maximum generation rate. The generation of N_2O and NO_x during significant H_2 release was not observed.

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- (a) Higher values are reported; however, these values have a large uncertainty because the amount of gas generated is near the detection limits.
- (b) Smith, R. A. 1991. Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing--Errata Correction. Letter to J. M. Creer. #9150151.

A measured glass redox, $Fe^{+2}/\Sigma Fe$, between 0.01 and 0.1, was obtained with a mole ratio of the major reductant (HCOOH) to oxidant (NO_3^-) of 2.2 to 12.6. The lower end corresponds well with previously predicted HCOOH needs, $HCOOH/NO_3^- = 3$ to 4. A $HCOOH/NO_3^-$ molar ratio of 2.2 is equivalent to 27 ml 87 wt% HCOOH/L FY 1991 NCAW simulant at 125 g WO/L. Correlations of glass redox with other test variables were not observed. This is attributed to the lack of sensitivity of the glass redox measurement in the more oxidized range, $Fe^{+2}/\Sigma Fe \leq 0.1$, and to a complete set of feed preparation reactions which result in similar formate and nitrate melter feed concentrations independent of the initial composition over the range tested. Savannah River Laboratory correlations of the reductant and oxidant in the melter feed with glass redox were also observed to fit the PHTD data well. Correlations of glass redox with melter feed composition may greatly simplify an analytical requirement in the plant.

A lower than expected initiation temperature ($124^\circ C$) for an exothermic reaction in dried formed SRAT simulant was observed. Because $124^\circ C$ is below the maximum steam coil temperature, further thermal sensitivity studies may be required to assess this concern identified in the PSAR (Herborn and Smith 1990).

3.0 Objectives and Approach

Specific test objectives of the FY 1991 laboratory-scale feed preparation study were to:

- measure offgas generation rates and total moles of gas released as a function of selected NCAW components and process variables
- develop process guidelines for the amount of HCOOH required to provide an acceptable glass redox based on the established range for $Fe^{+2}/\Sigma Fe$, 0.005 to 0.23
- provide thermal analysis data that may be used to assess the potential for a rapid exothermic reaction in dried formated NCAW slurry simulant.

To support the three test objectives, the following approach was taken:

- preparing an NCAW simulant closely resembling the predicted composition of actual waste in composition, speciation, and physical properties; measuring simulant physical properties (density, percent solids, WO/L); and evaluating uncertainties associated with analytical methods used for measuring the simulant composition
- conducting laboratory-scale tests to
 - evaluate reaction mechanisms and predict reaction products by preparing slurry chemistry profiles related to generation of gases and glass redox control [The profiles include 1) selected soluble slurry anion concentrations ($HCOO^-$, NO_3^- , and NO_2^-), 2) selected slurry cation concentrations (Al, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Si, Sr, Zn, and Zr), 3) soluble NH_4^+ concentrations in the slurry, 4) condensate composition (NO_3^- , NO_2^- , $HCOO^-$, and NH_4^+), and 5) slurry pH and temperature.]
 - determine the total amount of gases released specifically related to permitting and safety concerns (H_2 , N_2O , NO_x , CO_2 , CO) and their respective generation rates as a function of selected compositional and operational variables
 - determine the glass redox, as represented by $Fe^{+2}/\Sigma Fe$, of melter feed simulants vitrified in closed crucibles and evaluate analytical uncertainties in the glass $Fe^{+2}/\Sigma Fe$ measurement, measure melter feed rheology.
- evaluate the thermal stability of dried, formated NCAW simulant (nitrate salt/organic reactions).

3.1 Simulant Preparation

Three simulants were prepared for the FY 1991 laboratory-scale feed preparation test activities: a stock NCAW, a recycle waste stream, and melter feed. A HWVP NCAW slurry simulant was prepared by co-precipitation of component hydroxides from nitrate solutions. A few of the minor components were added as salts other than nitrates or as oxides. Sodium carbonate, NO_2^- , and NO_3^- slurry loadings were adjusted as required for individual test objectives. The recycle waste stream simulant was a new addition to the laboratory-scale process. Recycle waste stream simulant was added as a slurry to the formatted NCAW simulated waste at a ratio of 0.12 g recycle oxide/g waste oxide. This is equivalent to ~375 mL recycle waste stream slurry per ~1.5 L initial NCAW simulant. The FY 1991 reference NCAW composition provided by Smith (1991)^(a) is given in Table 3.1.1. Simulant preparation steps are discussed in Section 4.1, and measured compositions for the NCAW simulant are discussed in Appendix A.

Melter feed simulants were prepared by adding dry frit to formatted simulated NCAW waste for glass redox and rheology measurements. A new frit composition and waste loading for the melter feed was developed for FY 1991 testing.^(b) Unlike previous HWVP frits, this frit contains no Na. The target glass composition is given in Table 3.1.2. Melter feed simulants prepared without recycle waste stream addition had a waste/frit loading of 0.29/0.71 based on weight of glass forming oxide components. Melter feed simulants prepared with formatted slurry containing recycle waste stream components had a waste/recycle/frit loading of 0.28/0.034/0.686 based on oxide weight.

3.2 Laboratory-Scale Testing

Twelve tests were completed for the FY 1991 laboratory-scale feed preparation study. The individual test variables and test conditions are summarized in Table 3.2.1. The maximum and minimum labels in Table 3.2.1 refer to the test matrix used in laboratory-scale FY 1991 tests, not necessarily to plant boundary conditions. Test 5.1 listed in Table 3.2.1 was conducted for slurry integrated performance testing and was not part of the present work scope. However, selected data for test 5.1 have been included for future reference only. A more detailed listing of test variables is provided in Table 3.2.2.

Laboratory-scale testing of simulated NCAW included HCOOH addition, digestion, addition of recycle waste simulant, and slurry concentration. Monitoring offgas generation rates and concentrations, online measurement of slurry pH, and characterization of slurry and condensate samples

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- (a) Smith, R. A. 1991. Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing—Errata Correction. Letter to J. M. Creer. #9150151.
 - (b) Hrma, P. and M. J. Schweiger. 1991. Frit for NCAW-91 Glass. Letter Report from PNL HWVP Technology Development Project to WHC.

Table 3.1.1. FY 1991 Reference Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Composition^(a)

Component	weight% *	Feed Molarity, moles element/ feed **	Component	weight% *	Feed Molarity, moles element/ feed **
Ag2O	1.20E-01	1.29E-03	Nb2O3	1.01E-02	1.08E-04
Al2O3	9.04E+00	2.22E-01	Ni2O3	5.78E-01	4.29E-03
Am2O3	7.22E-02	5.98E-07	NO	2.90E+00	3.65E-02
As2O3	4.25E-05	3.41E-04	NpO2		
B2O3	5.75E-03	2.06E-04	P2O5	8.72E-01	1.53E-02
BaO	1.78E-01	1.43E-03	PbO2	7.00E-01	3.66E-03
BeO	1.01E-01	5.94E-03	PdO	1.20E-01	1.23E-03
Br			Pm2O3	4.60E-02	3.32E-04
CaO	7.91E-01	1.76E-02	Pr2O3	1.53E-01	1.16E-03
CdO	3.02E+00	2.94E-02	PuO2	6.00E-02	2.77E-04
CoO2	6.05E-01	4.98E-03	Rb2O3	5.75E-02	6.55E-04
Co2O3			Re2O7		
Cr2O3	2.62E-01	4.30E-03	Rh2O3	1.04E-01	1.02E-03
Ca2O	6.05E-01	5.32E-03	Ru2O3	3.80E-01	3.77E-03
CuO	2.45E-01	3.85E-03	SO3	6.55E-01	1.02E-02
Oy2O3	1.04E-04	6.98E-07	Sb2O3	5.88E-03	5.00E-05
Er2O3	3.08E-06	2.02E-06	SeO2	1.59E-02	1.78E-04
Eu2O3	2.02E-02	1.42E-04	SiO2	4.03E+00	8.38E-02
F	9.70E-02	6.38E-03	Sm2O3	7.50E-02	5.42E-04
Fe2O3	2.62E+01	4.42E-01	SnO	1.08E-02	9.78E-05
Gd2O3	3.70E-03	2.57E-05	SO	1.19E-01	1.43E-03
GeO2	1.57E-04	1.82E-06	Ta2O5	3.33E-03	1.68E-05
HgO			Tb2O3	2.26E-04	1.54E-06
Ho2O3	5.32E-06	3.52E-08	Te2O7	1.52E-01	1.23E-03
I	4.50E-06	4.38E-08	TeO2	1.07E-01	7.77E-04
In2O3			ThO2		
K2O	1.98E-01	5.21E-03	TiO2	6.52E-01	1.02E-02
La2O3	6.53E-01	3.91E-03	Tm2O3	1.68E-10	1.09E-12
Li2O	1.84E-04	5.92E-06	U3O8	4.74E+00	2.11E-02
MgO	2.02E-01	6.25E-03	Y2O3	7.99E-02	8.65E-04
MnO2	2.14E+00	3.08E-02	ZnO	3.34E-01	5.13E-03
MoO3	5.59E-01	4.85E-03	ZrO2	1.51E+01	1.53E-01
Ni2O	2.14E+01	8.84E-01			
			Sum	100	2.02

Anions for NCAW Feed Simulant		
	g/100g total oxides	Feed Molarity, moles/L
NO3-	5.78E+00	1.18E-01
NO2-	1.90E+01	4.39E-01
CL-	3.00E-01	1.08E-02
OH-		
SO4--	7.98E-01	1.02E-02
PO4--	7.84E-02	1.03E-03
CO3--	6.00E+00	1.25E-01
F-	9.70E-02	6.38E-03
TOC***	1.34E-01	1.39E-02
I-	4.50E-06	4.36E-08

* Normalized to 100g waste oxide/filter
 **Based on 125g waste oxide/filter
 ***Organic carbon source was sodium oxalate

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

Table 3.1.2. FY 1991 Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Target Glass Composition^(a)

Component	Plant Feed Concentration (Wt%)	Recycle Feed Concentration (Wt%)	Frit Concentration (Wt%)
Ag ₂ O	0.03		
Al ₂ O ₃	2.60	0.14	
B ₂ O ₃	2.00E-03		14.03
BaO	0.05		
CaO	0.23	0.01	
CaO	0.87	0.11	
CaO ₂	0.18		
Cl	0.08		
Cr ₂ O ₃	0.07		
Cs ₂ O	0.17		
CoO	0.07		
F	0.03		
Fe ₂ O ₃	8.12	0.04	
GeO ₂	4.00E-05		
K ₂ O	0.06	0.01	
La ₂ O ₃	0.19		
Li ₂ O			5
MgO	0.10	0.01	
MnO ₂	0.61	0.03	
MoO ₃	0.16		
Na ₂ O	6.15	1.45	
Nb ₂ O ₃	3.00E-03		
Nd ₂ O ₃	1.00		
NiO	0.66		
P ₂ O ₅	0.25	0.11	
PbO ₂	0.20		
Pr ₂ O ₃	0.04		
Rb ₂ O ₃	0.02		
Sb ₂ O ₃	2.00E-03		
SeO ₂	5.00E-03		
SiO ₂	1.15	1.49	49.57
Sm ₂ O ₃	0.02		
SrO	3.00E-03		
SO ₃	0.19		
SrO	0.03		
Ta ₂ O ₅	1.00E-03		
TeO ₂	0.03		
TiO ₂	0.19	4.00E-03	
Y ₂ O ₃	0.02		
ZrO	0.10		
ZrO ₂	4.35		
Total	28.0	3.4	68.6

(a) Hrma, P. and M. J. Schweiger. 1991. Frit for NCAW-91 Glass. Letter Report from PNL HWVP Technology Development Project to WHC.

Table 3.2.1. Summary of Test Variables and Test Conditions for the FY 1991 Laboratory-Scale Feed Preparation Tests

<u>Test Variable</u>	<u>Test</u>	<u>Description of Test Conditions</u>
Amount of HCOOH	1.1	Maximum amount of HCOOH added (74 ml 87 wt% HCOOH/L slurry at 125 g WO/L)
	1.2	Minimum amount of HCOOH added (27 ml 87 wt% HCOOH/L slurry at 125 g WO/L)
	1.3	Nominal amount of HCOOH added (49 ml 87 wt% HCOOH/L slurry at 125 g WO/L)
HCOOH Addition Rate	2.1	Maximum rate, 4 times reference (2 ml/min, equivalent to 8 gpm plant-scale)
	2.2	Mid rate, 2 times reference (1 ml/min, equivalent to 4 gpm plant-scale)
Amount of NO ₂	3.1	Lowest amount of NO ₂ , 30% reference (0.13 moles NO ₂ /L slurry at 125 g WO/L)
	3.2	Mid amount of NO ₂ , 60% reference (0.27 moles NO ₂ /L slurry at 125 g WO/L)
Extended Digestion	4.1	Digestion period extended from 4 to 8 hrs
Noble Metals Absent	5.1	Conducted for Slurry Integrated Performance Test (SIPT)
	5.2	Excessive amount of HCOOH (68 ml 87 wt% HCOOH/L slurry at 125 g WO/L)
H ₂ Quenching	6.1	Formic acid addition discontinued at onset of hydrogen spike
	6.2	Formic acid addition and power supply to heating mantle discontinued at onset of hydrogen spike
Amount of NO ₃ /NO ₂	7.1	Maximum amount of NO ₃ , 3 times reference (0.40 moles NO ₃ /L slurry at 125 g WO/L) Minimum amount of NO ₂ , 30% reference (0.13 moles NO ₂ /L slurry at 125 g WO/L)

Table 3.2.2. Details of Test Variables and Test Conditions for the FY 1991 Laboratory-Scale Feed Preparation Tests

Test No.	Target Composition Initial Nitrate in Slurry (NO ₃ ⁻)			Target Composition Initial Slurry Nitrite (NO ₂ ⁻)			Target Composition Initial Slurry Carbonate (CO ₃ ⁻)			Contains Noble Metals	Target Initial Conc. gWO ₃ /L	Slurry Density g/ml
	(mol)	(mol/L)	(g/L)	(mol)	(mol/L)	(g/L)	(mol)	(mol/L)	(g/L)			
1.1	0.20	0.13	8.23	0.65	0.43	19.60	0.19	0.12	7.38	yes	125	1.08
1.2	0.20	0.13	8.23	0.65	0.44	20.13	0.19	0.13	7.58	yes	125	1.08
1.3	0.19	0.13	8.23	0.65	0.46	20.54	0.19	0.13	7.72	yes	125	1.08
2.1	0.20	0.13	8.23	0.65	0.43	19.88	0.19	0.12	7.48	yes	125	1.08
2.2	0.20	0.13	8.23	0.65	0.44	20.28	0.19	0.13	7.61	yes	125	1.08
3.1	0.20	0.13	8.23	0.20	0.13	6.10	0.19	0.13	7.51	yes	118	1.08
3.2	0.20	0.13	8.23	0.40	0.27	12.23	0.19	0.13	7.58	yes	120	1.08
4.1	0.20	0.13	8.23	0.65	0.43	19.73	0.19	0.12	7.41	yes	125	1.08
5.2	0.20	0.13	8.23	0.65	0.45	20.54	0.19	0.13	7.72	no	125	1.1
6.1	0.20	0.13	8.23	0.65	0.44	20.13	0.19	0.13	7.58	yes	125	1.08
6.2	0.19	0.13	8.23	0.65	0.45	20.88	0.19	0.13	7.77	yes	125	1.08
7.1	0.61	0.40	24.82	0.20	0.13	6.07	0.19	0.12	7.39	yes	124	1.08

Test No.	Forming Amount			HCOOH addition rate (ml/min)	Amount of Recycle (ml)	HCOOH in recycle (mol)	NO ₃ in recycle amount (mol)	Carrier Gas	Comments
	HCOOH (mol)	HCOOH (mol/L)	HCOOH (ml 88.7wt%/L)						
1.1	2.59	1.87	74.1	0.6	297.3	0.06	0.19	Ar/O ₂	Maximum HCOOH amount tested.
1.2	0.91	0.61	27.1	0.6	292	0.06	0.19	Ar/O ₂	Minimum HCOOH amount tested. Addition of HCOOH was interrupted for 10 minutes.
1.3	1.60	1.10	48.8	0.57	277.7	0.05	0.18	Ar/O ₂	Medium HCOOH amount tested.
2.1	1.52	1.11	49.2	2, 1, 0.62	251.8	0.04	0.18	Ar/O ₂	Maximum HCOOH addition rate tested. Rate was decreased twice due to excess foaming.
2.2	1.51	1.07	47.5	0.99	280.3	0.05	0.18	Ar/O ₂	Medium HCOOH addition rate tested.
3.1	1.58	1.10	48.8	0.64	251.8	0.05	0.18	Ar/O ₂	Minimum nitrite tested.
3.2	1.51	1.04	46.1	0.57	237.3	0.05	0.18	Ar/O ₂	Medium nitrite tested.
4.1	1.53	1.01	44.8	0.58	270.9	0.05	0.18	Ar/O ₂	Reflux during digestion. Extended digestion period.
5.2	2.17	1.43	68.0	0.57	not added	not added	not added	air	HCOOH added in one batch to w/o noble metals feed.
6.1	2.03	1.46	64.7	0.49	not added	not added	not added	Ar/O ₂	Terminated HCOOH addition when 2nd H ₂ peak initiated.
6.2	2.05	1.51	67.0	0.49	not added	not added	not added	Ar/O ₂	Monitored offgases at temperature of 95C-100C. Terminated HCOOH addition and shut off temperature controller when 2nd H ₂ peak initiated. Monitored offgases through cool down (63C), reheat to 100C, and cool down (73C).
7.1	1.88	1.24	55.0	0.48	258.6	0.05	0.17	Ar/O ₂	Maximum nitrate and minimum nitrite tested.

provided the basis for determining offgas productivity and elucidating slurry chemistry. Reductant requirements were estimated based on a glass redox measurement, $\text{Fe}^{+2}/\Sigma\text{Fe}$. Cation solubility data were also collected to compare results with the Savannah River Technology Center (SRTC) reductant formulation for minimum HCOOH addition (see Section 6.2). Process steps, test equipment, and sampling strategy are described in detail in Section 4.0.

3.3 Thermal Stability of Dried NCAW Simulant (Nitrate Salt-Organic Reactions)

The potential for NO_3^- and HCOOH to react exothermically was evaluated using differential scanning calorimetry, thermogravimetric analysis, and Henkin tests on dried NCAW simulant (described in Section 4.3). The thermal tests provide only limited information on potential explosion hazards and minimum reaction temperatures. Larger sample size and additional initiators such as spark, friction and impact may need to be tested to satisfy a safety analysis review.

4.0 Test Methods

This section on test methods includes descriptions of waste simulant preparation, testing equipment, test procedures, the nominal test sampling strategy and associated analytical methods, and thermal analyses performed on dried NCAW simulant.

4.1 Simulant Preparation

Three simulants were prepared: stock pretreated NCAW, recycle waste stream, and melter feed. The simulant preparation steps are discussed below.

4.1.1 NCAW Simulant Preparation

The FY 1991 reference NCAW composition^(a) and the target stock NCAW composition for simulant preparation are listed in Table 4.1.1. Table 4.1.2. lists the source chemicals for NCAW simulant preparation. As additional information about the HWVP feed preparation chemistry became available, several elements previously deleted from the target simulant composition were added to more closely represent the actual waste (designated with an asterisk in Table 4.1.1). Substitutions were limited to radioactive and toxic elements, and to expense considerations. Substitutions were made on a mole element/L basis rather than by weight percent. Stoichiometric substitution is important to the redox and glass chemistries. Newly included as either direct additions (dir add) or compensated for by substitution (sub) are Ag (dir add), Be (sub), Dy (sub), Er (sub), Eu (sub), Gd (sub), Ho (sub), K (dir add), La (dir add), Nb (dir add), Pb (dir add), Pu (sub), Sb (dir add), Se (dir add), Sm (dir add), Sn (dir add), Ta (dir add), Tb (sub), Tc (not added),^(b) Te (dir add), Th (sub), Ti (dir add), Tm (sub), U (sub), and Zn (dir add). Lithium, Ge, and I were included in the slurry preparation calculations, but were not added to the simulant due to the relatively small amount required. Newly accounted-for components, substitutions, deletions, and corresponding justifications are noted in Table 4.1.1. Listed below are a few comments regarding the NCAW simulant composition:

- Oxalate was included in earlier laboratory-scale studies^(c) and in the pilot-scale ceramic melter test simulant (Goles and Nakaoka 1990); however, it was not included in subsequent PNL laboratory-scale studies in order to simplify the chemical system while studying H₂

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- (a) Smith, R. A. 1991. Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing--Errata Correction. Letter to J. M. Creer. #9150151.
 - (b) Tc was not added. No substitution was made for Tc. Re was originally chosen to substitute for Tc but WHC and PNL decided not to make the substitution based on potential Re oxide catalytic properties.
 - (c) Farnsworth R. K. 1987. *The Effect of Feed Composition and Formic Acid Addition on Glass Redox State*. Letter Report to Westinghouse Hanford Company, HWVP-87-V110203A.

Table 4.1.1. FY 1991 Neutralized Current Acid Waste (NCAW) Reference^(a) and Simulant Target Compositions

FY 1991 Reference NCAW Composition ^{**}				FY 1991 NCAW Simulant Target Composition		
Component	Component wt%	moles element/ L feed (125 gWOL)	Substitution/ Deletion	Component wt%	moles element/ L feed (125 gWOL)	
Ag2O	1.20E-01	1.29E-03		1.22E-01	1.32E-03	
Al2O3	9.04E+00	2.22E-01		9.25E+00	2.27E-01	
Am2O3	7.22E-02	5.38E-07	DEL 1			
As2O3	4.25E-05	3.41E-04	DEL 2			
B2O3	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 2*			
Br			N/A 3			
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	
CeO2	6.05E-01	4.39E-03		6.56E-01	4.77E-03	
Co2O3			3			
Cr2O3	2.62E-01	4.30E-03		2.67E-01	4.39E-03	
Cs2O	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	
Dy2O3	1.04E-04	6.98E-07	SUB Nd 4*			
Er2O3	3.08E-06	2.02E-08	SUB Nd 4*			
Eu2O3	2.02E-02	1.42E-04	SUB Nd 4*			
F	9.70E-02	6.38E-03		9.90E-02	6.52E-03	
Fe2O3	2.82E+01	4.42E-01		2.88E+01	4.51E-01	
Gd2O3	3.70E-03	2.57E-05	SUB Nd 4*			
GeO2	1.57E-04	1.82E-06	6	1.56E-04	1.86E-06	
HgO			N/A 3			
Ho2O3	5.32E-06	3.52E-08	SUB Nd 4*			
I	4.50E-06	4.36E-06	5, 6	4.60E-06	4.53E-06	
In2O3			N/A 3			
K2O	1.96E-01	5.21E-03		2.00E-01	5.32E-03	
La2O3	6.53E-01	5.01E-03		6.67E-01	5.12E-03	
Li2O	1.84E-04	5.92E-06	6	7.23E-05	6.05E-06	
MgO	2.02E-01	6.25E-03		3.72E-01	1.15E-02	
MnO2	2.14E+00	3.08E-02		2.19E+00	3.15E-02	
MoO3	5.59E-01	4.85E-03		5.70E-01	4.95E-03	
Na2O	2.14E+01	8.64E-01		2.19E+01	8.82E-01	
Nb2O3	1.01E-02	1.08E-04		1.03E-02	1.10E-04	
Nd2O3	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	
NpO2			3			

Notes Regarding Substitution/Deletion
 1 RADIOACTIVE
 2 TOXIC
 3 NONE IN REFERENCE FEED COMPOSITION
 4 EXPENSIVE
 5 The amount of I in the reference feed is below that required for detection by the gas chromatograph. Iodine was not added to the feed simulant due to the small amount required for the batch size prepared.
 6 Not added to the 1991 stock simulant. However, oxide is included in wt% values.
 7 A substitution was not made for Tc.
 * New addition to simulant. Note: All substitutions are based on the addition of amount of mole element/L.

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

Table 4.1.1. (contd)

FY 1991 NCAW Reference Composition				FY 1991 NCAW Simulant Target Composition	
Component	Component wt%	moles element/ L feed (125 gWOL)	Substitution/ Deletion	Component wt%	moles element/ L feed (125 gWOL)
P2O5	8.72E-01	1.53E-02	•	8.87E-01	1.56E-02
PbO2	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
Pm2O3	4.60E-02	3.32E-04	SUB Nd 4*		
Pr2O3	1.53E-01	1.16E-03		1.56E-01	1.18E-03
PuO2	6.00E-02	2.77E-04	SUB Ce 1*		
Rb2O3	5.75E-02	6.56E-04		5.87E-02	6.70E-04
Re2O7			3		
Rh2O3	1.04E-01	1.02E-03		1.06E-01	1.04E-03
Ru2O3	3.80E-01	3.77E-03		3.87E-01	3.85E-03
SO3	6.55E-01	1.02E-02		6.69E-01	1.04E-02
Sb2O3	5.88E-03	5.00E-05		5.95E-03	5.11E-05
SeO2	1.59E-02	1.78E-04	•	1.61E-02	1.82E-04
SiO2	4.03E+00	8.38E-02		4.11E+00	8.56E-02
Sm2O3	7.50E-02	5.42E-04	•	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
Ta2O5	3.33E-03	1.88E-05	•	3.39E-03	1.92E-05
Tb2O3	2.26E-04	1.54E-06	SUB Nd 4*		
Te2O7	1.52E-01	1.23E-03		1, 7	
TeO2	1.07E-01	7.77E-04	•	1.01E-01	7.94E-04
ThO2			SUB Zr 1*		
TiO2	6.52E-01	1.02E-02	•	6.66E-01	1.04E-02
Tm2O3	1.68E-10	1.09E-12	SUB Nd 4*		
U3O8	4.74E+00	2.11E-02	SUB Nd 1*		
Y2O3	7.99E-02	8.85E-04		8.17E-02	9.04E-04
ZnO	3.34E-01	5.13E-03	•	3.41E-01	5.24E-03
ZrO2	1.51E+01	1.53E-01		1.54E+01	1.56E-01
sum	1.00E+02	2.02E+00		1.00E+02	2.06E+00

Notes Regarding Substitution/Deletion

1 RADIOACTIVE

2 TOXIC

3 NONE IN REFERENCE FEED COMPOSITION

4 EXPENSIVE

5 The amount of I in the reference feed is below that required for detection by the gas chromatograph. Iodine was not added to the feed simulant due to the small amount required for the batch size prepared.

6 Not added to the 1991 stock simulant. However, oxide is included in wt% values.

7 A substitution was not made for Tc.

* New addition to simulant. Note: All substitutions are based on the addition of amount of mole element/L.

Note 1: Simulant target compositions for Cl⁻, SO₄²⁻, PO₄³⁻, and CO₃²⁻, and total organic carbon (TOC) are listed in Table 3.1.1. The NO₂⁻ and NO₃⁻ concentrations used for each test are given in Table 3.2.2. Simulant composition based on the amounts of source chemicals added to prepare the simulant are listed in Table A1 in Appendix A.

Note 2: Due to a calculation error 25% more noble metals (Pd, Ru and Rh) were added to the simulant than the target values shown in Table 4.1.1. See Table A1 in Appendix A.

Table 4.1.2. Source Chemicals for FY 1991 Laboratory-Scale Neutralized Current Acid Waste (NCAW) Simulant Preparation

Major Component Element	Major Component Source	Minor Component	Minor Component Nitrates, Insolubles & Noble Metals Source	Soluble and Slightly Soluble Component	Soluble and Slightly Soluble Minor Components Source
Al#	Al(NO ₃) ₃ ·6H ₂ O	Ag	AgNO ₃	B	H ₃ BO ₃
Fe#	Fe(NO ₃) ₃ ·9H ₂ O	Ce*	Ce(NO ₃) ₂ ·4H ₂ O*	Ba	Ba(OH) ₂ ·8H ₂ O
Mn	Mn(NO ₃) ₂ and KMnO ₄	Cd	Cd(NO ₃) ₂ ·4H ₂ O	Ca*	
Ni ₁ ,#	Ni(NO ₃) ₂ ·6H ₂ O	Co	Co(NO ₃) ₂ ·6H ₂ O	Cs*	
Zr#	Zr(NO ₃) ₂ ·2H ₂ O	Cr	Cr(NO ₃) ₃ ·6H ₂ O	Cu	CuSO ₄ ·5H ₂ O
		Ge*	GeO ₂ **	K	KOH
		La	LaF ₃	Mg	MgCO ₃
		Li	Li(OH) ₂	Mo	NaCl
		Mg	LiO ₂ **	Nb	NbF ₅
		Nb	Mg(NO ₃) ₂ ·6H ₂ O		
		Ni	Nb ₂ O ₅		
		Pb	Md(NO ₃) ₃ ·6H ₂ O		
		Pr	NbF ₅		
		Rb**	Po(NO ₃) ₂		
		Si	Pr(NO ₃) ₃ ·6H ₂ O		
		Sm	RbNO ₃ *		
		Sr*	SiO ₂		
		Te	Sm(NO ₃) ₃ ·6H ₂ O		
		Ti	Sr(NO ₃) ₂ *		
		Y	Ta ₂ O ₅		
		Zn	TaO ₂		
			TiO ₂		
			Y(NO ₃) ₃ ·6H ₂ O		
			Zr(NO ₃) ₂ ·6H ₂ O		
		Ru	RuNO(NO ₃) ₃		
		Rh	Rh(NO ₃) ₃		
		Pd	Pd(NO ₃) ₂		

Footnotes:

#Note: Fe, Ni, and Zr hydroxides were co-precipitated and blended with an Al hydroxide slurry to produce the mixed hydroxide slurry. The mixed hydroxide slurry was the source of these elements in laboratory-scale preparation. ** Ni(NO₃)₂·6H₂O was added to the minor component slurry because analysis results showed Ni to be below target concentration.

*Ca and Sr were added as nitrates and co-precipitated as hydroxides in the Minor Component Nitrate/Insolubles/Noble Metals Slurry (Column 4). It was determined by analysis of the supernatant and final slurry that the hydroxides from these elements were sufficiently soluble to be washed out in various proportions during the washing steps employed to reduce the nitrate concentration of the Minor Component Nitrate/Insolubles/Noble Metals Slurry. It is recommended that for future simulant preparation Rb, Ca, Ce, and Sr be added in the Soluble Slurry.

^ Addition of these elements in the form of their respective hydroxides is suggested. -- GeO₂, LiO₂, and Nb were present in such small amounts (i.e. .001-.0001g) in laboratory-scale feed that they were not added. In large scale simulant preparation these compounds should be added if possible.

generation and glass redox behavior.^{(a)(b)} In the present study, as complete a slurry matrix as possible was desired. Consequently, $C_2O_4^{2-}$ is present in both the slurry and recycle waste stream simulants.

- The P_2O_5 and PO_4^{3-} mole element/ L values listed in the FY 1991 NCAW reference composition are 1.53 E-02 and 1.03 E-03 mole element/L for P_2O_5 and PO_4^{3-} , respectively. It has been recommended by WHC that the P_2O_5 value be used as a basis for adding Na_3PO_4 .
- A small amount of Th (0.2 wt% oxide in the slurry) was detected in the 101AZ core 1 sample.^(c) This core sample was primarily supernate. The 101AZ core 2 sample was more representative of the sludge fraction, but did contain some supernate. Thorium in the 101AZ core 2 sample existed primarily in the supernate phase and was removed to below the analytical detection limits during washing. These data suggest that the Th species is soluble and will not be present in significant amounts in a pretreated (washed) NCAW slurry. However, Scanning Electron Microscopy (SEM) analysis of the 102AZ core 1 washed solids indicated the presence of Th (possibly as fluoride) particles. The Th particles have the potential to be active catalytically (Colmenares 1984) and should be considered for future research.
- It has been postulated that noble metals exist as hydroxides in the NCAW. Discrete noble metal particles were not detected by SEM characterization of the washed 102AZ core 1 sample. The noble metals may be interdispersed among other crystalline or amorphous phases. However, it has also been suggested that the noble metals may exist as discrete particles in a metallic state distributed in the undisturbed sludge layer not yet sampled. The speciation and particle size of the noble metals is expected to significantly impact their respective catalytic activity.
- A major constituent, uranium (4.74 wt% U_3O_8), is not included in the FY 1991 NCAW simulant. The effect of uranium on slurry and glass redox chemistry and slurry/melter feed rheology is not known.

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- (a) Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company, HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (b) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (c) An internal memo to R. A. Smith from C. R. Allen, 1991, PNL-90-460. Core Sample Status Deliverables of NCAW: HWVP-90-1.2.2.05.04A, HWVP-90-1.2.2.05.04B, HWVP-90-1.2.2.05.07A, and HWVP-90-1.2.2.05.07B.

- Just before starting a feed preparation test, Na_2CO_3 , NaNO_2 and NaNO_3 were added as shown in Table 4.1.3. The NaNO_2 and NaNO_3 were compositional variables. The Na_2CO_3 was a potential variable, but due to limited time and expense, tests were not conducted to evaluate the effects of varying the Na_2CO_3 content on offgas generation.

A flowsheet for the HWVP NCAW stock slurry simulant preparation is given in Figure 4.1.1. Most simulant components were co-precipitated as hydroxides from nitrate solutions to simulate the NCAW treatment history. This process is believed to provide a more accurate representation of the waste component speciation. For the laboratory-scale tests, NCAW stock slurry simulant was prepared by the following steps:

- step 1 - mixed hydroxide slurry was obtained from pilot-scale ceramic melter test (PSCM-23) (Goles and Nakaoka 1990)
- step 2 - the MnO_2 was precipitated from KMnO_4 and $\text{Mn}(\text{NO}_3)_2$; the supernate was decanted^(a)
- step 3 - the MnO_2 and mixed hydroxide slurry were blended, washed, settled and decanted twice (the slurry from step 3 is designated major component slurry)
- step 4 - minor constituent hydroxides (including noble metals) were co-precipitated in the presence of the insoluble components via NaOH ; the mixture was washed, settled and decanted
- step 5 - a soluble component solution was prepared
- step 6 - batches from steps 3 to 5 were blended.

To facilitate simulant preparation, a vendor-prepared co-precipitated mixed hydroxide slurry was obtained from the pilot-scale ceramic melter test (PSCM-23). This slurry contained Al, Fe, Ni and Zr hydroxides and approximately five times the nominal NO_3^- concentration of the NCAW target simulant. The mixed hydroxide slurry had been prepared in 1989. Some chemical and/or physical changes could have occurred during this time, and the impact of these possible changes is unknown.

(a) The revised procedure for HWVP NCAW preparation specifies addition of the hydrous MnO_2 to the dissolved major nitrate salts before co-precipitation with NaOH . A previously precipitated slurry of Al, Fe, Ni, Zr was used for FY 1991 laboratory-scale testing to minimize waste. The hydrous MnO_2 was blended with the hydroxide slurry.

Table 4.1.3. Sodium Nitrate, NO₂, and CO₃²⁻ Additions to Stock Neutralized Current Acid Waste (NCAW) Feed Simulant for FY 1991 Laboratory-Scale Feed Preparation Testing

Test	Amount of Component Added to Obtain Given Slurry Molarity*		
	NaNO ₃ (mole/L)	NaNO ₂ (mole/L)	Na ₂ CO ₃ (mole/L)
1.1	Note 1	0.43	0.12
1.2	Note 1	0.44	0.13
1.3	Note 1	0.45	0.13
2.1	Note 1	0.43	0.12
2.2	Note 1	0.44	0.13
3.1	Note 1	0.13	0.13
3.2	Note 1	0.27	0.13
4.1	Note 1	0.43	0.12
5.2	Note 2	0.45	0.13
6.1	Note 1	0.44	0.13
6.2	Note 1	0.45	0.13
7.1	0.27 Note 3	0.13	0.12

Notes

*The listed sodium salts were added to each test aliquot (1.5 L of NCAW simulant) just prior to forming. Nitrate and Nitrite were test variables. Carbonate was a potential test variable but due to limited time and funding it was not evaluated and therefore a relatively constant amount of carbonate was added to each test aliquot.

1 NaNO₃ not added to stock simulant.

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

2 Non-noble metal stock simulant at 125 g WO/L contained 0.12 mol NO₃⁻/L.

3 This is the quantity(concentration) of NaNO₃ added to the stock simulant for test 7.1. The total NO₃⁻ concentration for test 7.1 includes the NaNO₃ added plus NO₃⁻ which was present in the stock simulant. For Test 7.1--> Total NO₃⁻= 0.27 mol/L+0.13 mol/L=0.40 mol/L

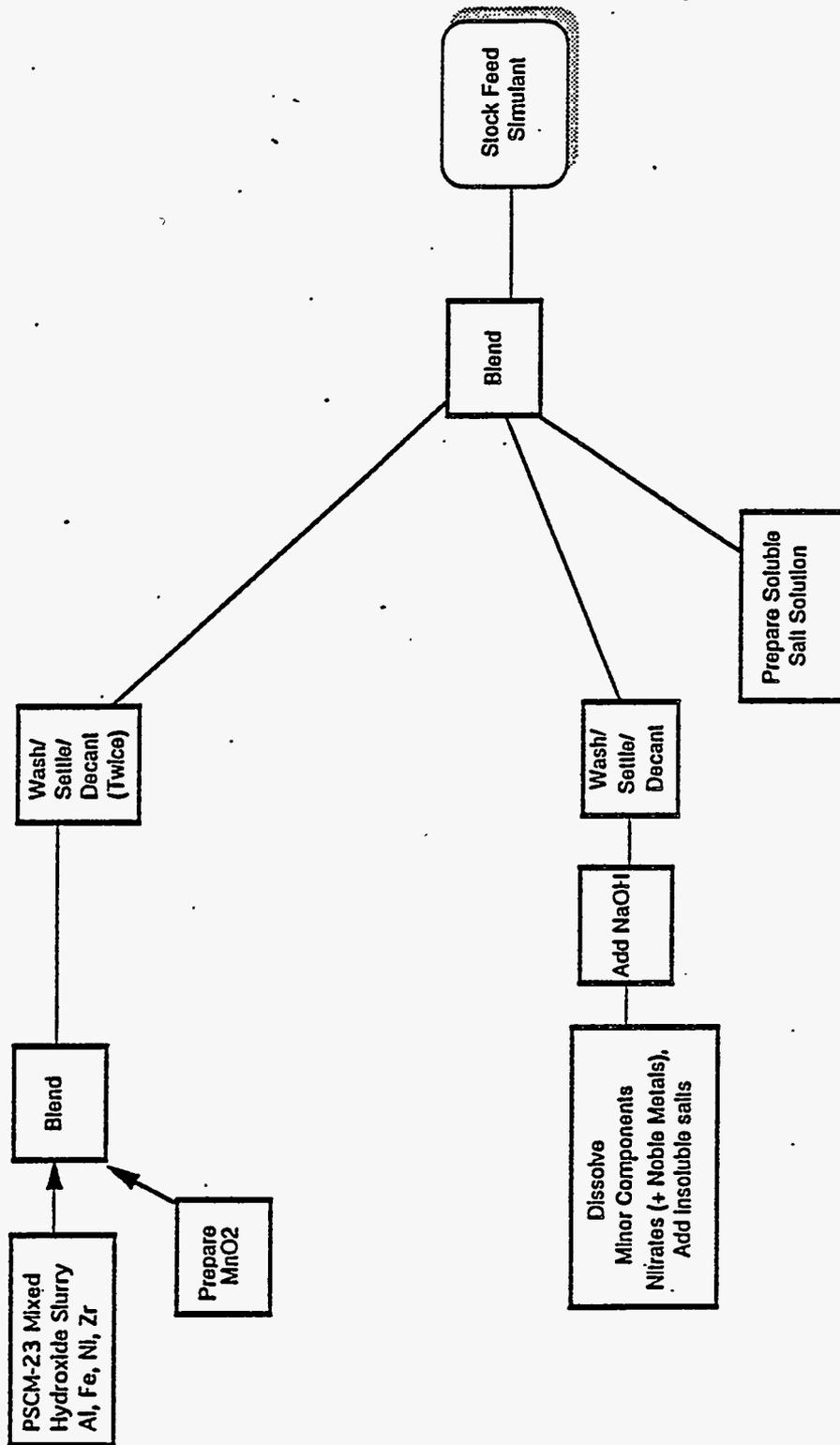


Figure 4.1.1. Flowsheet for FY 1991 Hanford Waste Vitriification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Stock Simulant Preparation

A 3:1 volume wash (water:simulant) was conducted twice on the major component slurry (Al, Fe, Mn, Ni, and Zr) to remove excess NO_3^- . The initial batch contained 35 g NO_3^-/L slurry. The washing efficiency for NO_3^- was 75-80%. The NO_3^- concentration after washing was approximately 2 to 3 g NO_3^-/L .^(a) The elements Cd, Si, Nd and Na were not included in the major component slurry, even though they are present in the NCAW simulant in appreciable quantities (see target compositions in Table 3.1.1). Adding Cd, Si, and Nd with the other major components (Zr, Fe, Ni, Mn, Al) may be recommended pending further consideration of their respective solubility behavior. Sodium salts are soluble and would be lost during the co-precipitation and wash preparation steps.

Manganese was precipitated separately as MnO_2 from a solution of KMnO_4 and $\text{Mn}(\text{NO}_3)_2$. This step was added to the NCAW slurry simulant preparation procedure to accommodate the increase in Mn concentration. Previously, Mn was considered a minor constituent and was added as calcined MnO_2 .^(b) The supernate from the MnO_2 slurry was decanted before blending the slurry with the mixed hydroxide batch because it contained high concentrations of NO_3^- but very little Mn (<200 ppm).

Most of the minor constituents were co-precipitated as hydroxides from the respective nitrates. With the exception of Cd, Na, Nd, and Si, those elements in the slurry at <1 wt% oxides were considered minor constituents. The noble metals were co-precipitated with the minor nitrates and insoluble constituents. Ruthenium was added as the ruthenium nitrosyl nitrate species. Nitric acid solutions were used as the source for palladium nitrate and rhodium nitrate. One 3:1 volume wash with 0.1M NaOH was completed on the precipitated hydroxides to remove excess NO_3^- . A second wash was not completed to minimize loss of Cs, Sr, Rb, and Ca. In the future, Cs, Sr, Rb, and Ca components will be added to the soluble component batch in their hydroxide form. Two washes may be implemented for the co-precipitated minor elements in future batches where low NO_3^- levels (<8 g NO_3^-/L @ 125 g WO/L slurry) are required in the NCAW simulant.^(c) Soluble species that could be removed during the washing steps were added to the simulant after blending of the major and minor components was completed. The stock NCAW simulant target oxide loading was 125 g waste oxide/liter (WO/L).

4.1.2 Recycle Waste Stream Simulant Preparation

Recycle waste stream simulant constituents represent materials that would be waste products from the vitrification process. The target recycle waste stream composition and chemical sources,

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- (a) The 3:1 washes (water:simulant) were performed to simulate potential pretreatment steps.
 - (b) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (c) The slurry was washed with 0.1M NaOH instead of water to reduce the possibility of washing/removing metal cations. The lathanide hydroxides are predicted to become more soluble as the pH decreases below 9 (Pourbaix 1974).

provided by WHC,^(a) are shown in Table 4.1.4. Recycle constituents include equipment decontamination chemicals, filter materials such as diatomaceous earth, melter offgas condensate, spent frit from canister decontamination, and miscellaneous waste streams.

A summary relating recycle simulant source chemicals to process source follows. In the recycle simulant, HNO_3 , KMnO_4 , $\text{Na}_2\text{C}_2\text{O}_4$, and Na_3PO_4 represent equipment decontamination chemicals. The base used to neutralize process condensates and equipment decontamination chemicals is represented by NaOH ; NaCl is an impurity often found in NaOH . Melter offgas condensate contains Cs , Cd , Cl , and PO_4^{3-} . In the simulant, CdO , NaCl , and Na_3PO_4 represent these elements. Process waste treatment materials were represented by zeolite IE-96 and diatomaceous earth. The Cs , Sr and transuranic (TRU) elements removed during a waste treatment process^(b) were not included by WHC in the reference composition. Frit was not added to the recycle simulant because it was determined (by WHC) to be a potentially unreactive material.^(a) However, HCOOH , (15 g HCOOH /100 g of recycle oxide) which is present in the spent frit, was added to the stock recycle simulant immediately before recycle waste stream addition to slurry simulant. Recycle waste stream chemicals were blended with water to produce a 60 g recycle oxide/L recycle slurry.

4.1.3 Melter Feed Simulant Preparation

Melter feed was prepared by adding dry frit to formatted slurry simulant. For glass redox measurements, the formatted slurry was first concentrated; then frit was added to yield a target oxide loading of 500 g total oxide/liter (TO/L). Melter feed rheology samples were prepared by preconcentration of the formatted simulant to give target loadings after frit addition of 500, 550, and 600 g TO/L. No further processing was conducted.

4.2 Laboratory-Scale Testing Equipment Description

The testing 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 thermocouple, HCOOH 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. Formic acid was introduced below the surface of the simulant through a Teflon tube using a peristaltic pump to control the addition rate. The sweep gas composed of either 4.4% O_2 in Ar or air (refer to Table 3.2.2) carried offgases from the reaction vessel plenum, through condensers at a rate of

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- (a) Smith, R. A. 1991. Revision of Pretreated Neutralized Current Acid Waste Composition for FY 1991 Pilot Testing--Errata Correction. Letter to J. M. Creer. #9150151.
- (b) Eakin, D. E. 1991. *Results of HWVP Transuranic Process Waste Treatment Laboratory and Pilot-Scale Filtration Tests Using Specially Ground Zeolite*. HWVP-91-1.2.2.03.06A.

Table 4.1.4. Target Recycle Waste Stream Simulant Composition, Recycle Simulant Source Chemicals and Frit Composition for FY 1991 Laboratory-Scale Feed Preparation Tests

Reference and Target Oxides In Recycle Simulant			Sources of Recycle Simulant for NCAW Slurry Simulant			Frit Composition	
Oxide	Reference* g Recycle Oxide per g Oxide In SRAT Slurry	Target Value** g Recycle Oxide per L of Recycle Simulant	Source	←-----target value-----→ g Source per 1L of Recycle Simulant	g Source per 1L of NCAW Slurry#	Frit Oxide ##	Oxide wt%
CdO	0.004	2.01	CdO	2.01	0.50	B2O3	20.45
MnO2	0.0012	0.60	KMnO4	1.10	0.27	Li2O	7.29
Na2O	0.05	25.17	NaOH	24.50	6.08	SiO2	72.26
P2O5	0.004	2.01	Na3PO4	4.65	1.15		
NO3-	0.08	40.27	HNO3	40.92	10.16		
Cl-	0.00008	0.04	NaCl	0.07	0.02		
TOC	0.0027	1.36	Na2C2O4	7.59	1.88		
Diatomaceous Earth	0.04	20.13	Diatomaceous Earth	20.13	5.00		
Zeolite (IE-95)	0.02	10.07	Zeolite (IE-95)	10.07	2.50		
sum of nonvolatiles	0.1192	60	sum***	111	28	sum	100

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

The sum of nonvolatiles includes all components except nitrate, chlorine and total organic carbon.

**The target concentration for the recycle slurry is 60 g oxide/L of recycle. Actual composition was not measured.
To convert from column 2 to 3: (g recycle oxide)/(sum of nonvolatiles)*(60 g total recycle oxide/L of recycle)

*** The sum values have been rounded to the ones place.

#1L of NCAW slurry is @ 125 g WO/L of NCAW slurry. The approximate amount of recycle simulant necessary
for addition to 1 L of NCAW simulant is 250ml of recycle simulant (@ 60 g recycle oxide/L of recycle simulant).

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

The amount of gram waste oxides was determined by subtracting the waste oxides contained in slurry samples (which were removed
during formic acid addition and digestion) from the initial gram waste oxides.

(initial gram waste oxides=1.5L of slurry*125gWO/L of slurry=187.5gWO)

Hirma, P. and M. J. and Schwelger. 1991. Frit for NCAW-91 Glass. Letter Report from
PNL HWVP Technology Development Project to WHC.

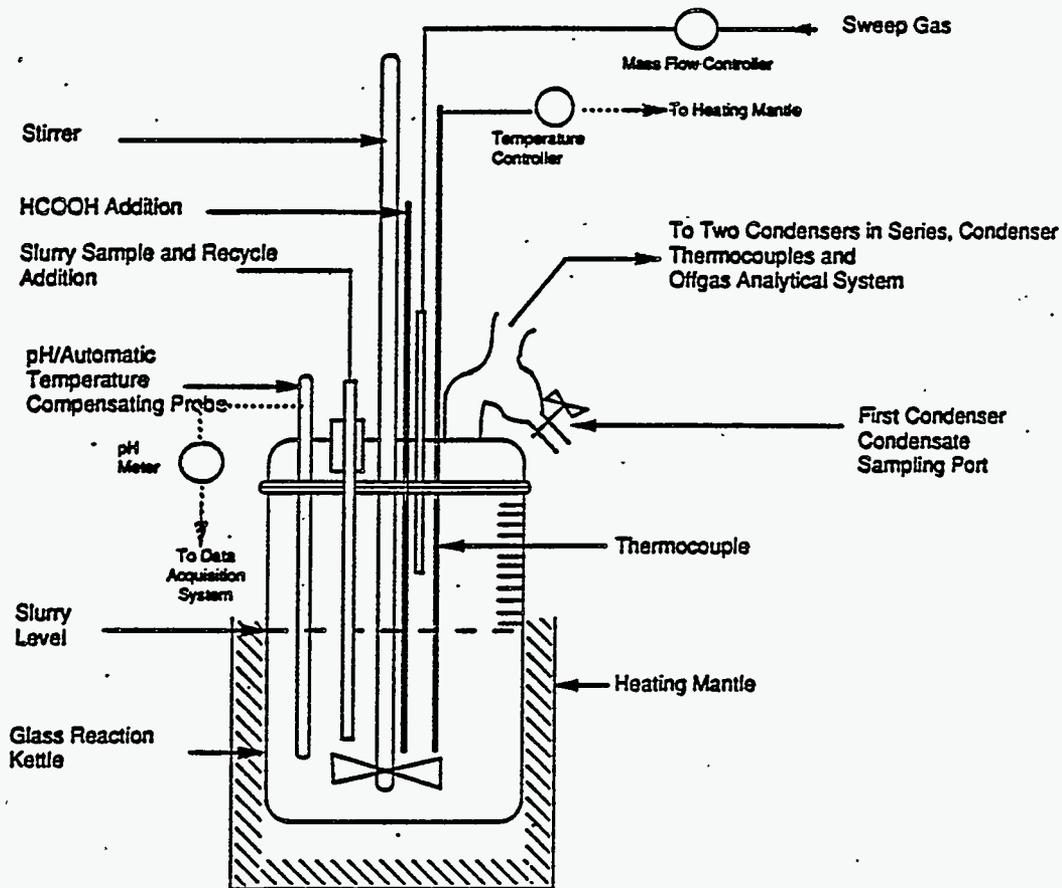


Figure 4.2.1. Schematic of the Laboratory-Scale Apparatus for FY 1991 Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Simulant Feed Preparation Tests

~0.6 slpm. The sweep gas was diluted downstream from the condenser with a gas composed of 4.39% CH_4 in Ar. The flow rate of the dilution gas was ~0.3L/min. Slurry pH was collected at ~15 sec intervals on the data acquisition system. Slurry and gas temperatures were recorded manually.

Figure 4.2.2 is a schematic of the offgas equipment configuration. Because of the dynamic nature of the reduction reaction rates and resultant gaseous generation rates, real time monitoring capabilities were employed to characterize the generation rates of the major gaseous reaction products. The emission rate behavior of N_2O , CO , and CO_2 was monitored with specific infrared gas analyzers. A chemiluminescent NO/NO_x analyzer was used to measure primarily NO_x . Concentrations of NO were monitored intermittently during selected tests. An electrochemical sensor was employed to detect gas phase concentrations of O_2 . The H_2 and N_2 concentrations were measured using gas chromatography.

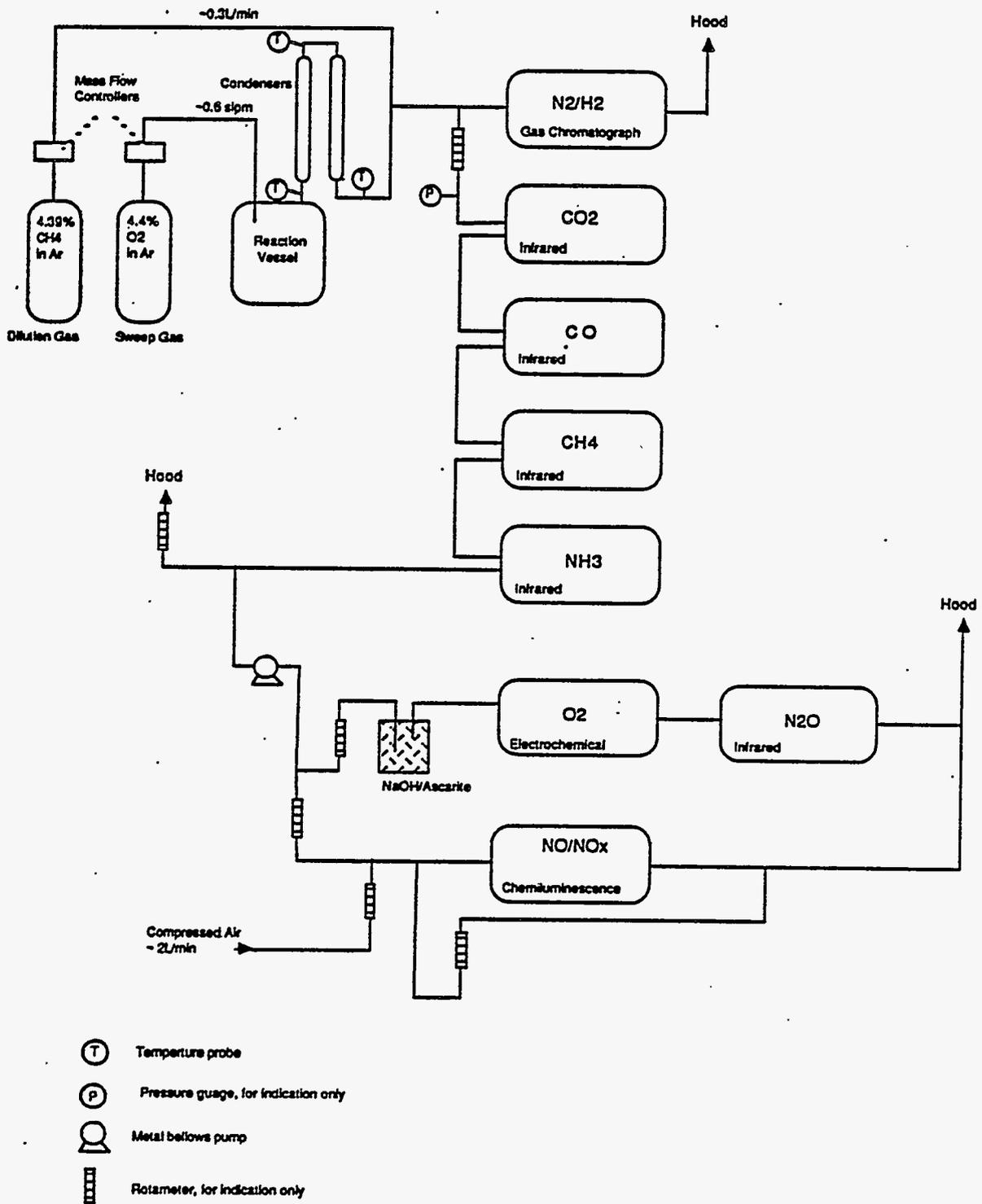


Figure 4.2.2. Schematic of the Laboratory-Scale Offgas Equipment Configuration for FY 1991 Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Simulant Feed Preparation Tests (detection method given for each gas detector)

The nominal gas sampling rate to measure H_2 and N_2 via the gas chromatograph was ~ 1 sample/2 min. Every 15 sec, N_2O , NO_x , CO , CO_2 , and O_2 were sampled. The total offgas flowrate versus time was monitored via a CH_4 tracer in the dilution gas added downstream from the condenser. A separate infrared analyzer provided analysis of the CH_4 . Table 4.2.1 lists additional details concerning the offgas analyzers.

Attempts to monitor NH_3 via the infra-red (IR) detector failed because the detector was sensitive to several gases including the carrier gas ($Ar/O_2/CH_4$) and CO_2 . Ammonia is predicted to be trapped in the condensate until the condensate reaches a fairly alkaline pH. Soluble NH_4^+ was measured in the slurry and condensate samples by selective ion electrode.

4.3 Test Procedure

Laboratory tests on the NCAW simulant consisted of the following steps:

- step 1 - $HCOOH$ addition
- step 2 - digestion (concentration 1)
- step 3 - recycle addition
- step 4 - concentration 2
- step 5 - dry frit addition to make melter feed (also completed for samples collected after step 3)
- step 6 - crucible melting of melter feed simulant for glass redox measurement.

Steps 1 and 2 simulate activities in the SRAT, while steps 3 and 4 simulate processing in the SME (full-scale operation steps used for development of the laboratory procedure are given in Appendix B). The laboratory steps did not include concentration of the NCAW simulant slurry prior to $HCOOH$ addition or boiling of melter feed. A summary of the laboratory-scale procedure follows:

- A tared 2 L reaction vessel was filled with approximately 1.5 L of stock NCAW simulant @ 125 g WO/L. The weight of the simulant was determined. The initial volume was calculated using the density of the simulant (1.08 g/mL of stock NCAW simulant).
- The vessel was placed in the heating mantle, configured per Figure 4.2.1 and heated to $95^\circ C$. Sodium nitrite, $NaNO_2$, and Na_2CO_3 compounds were added to the simulant during initial heat up via a port in the reaction vessel lid.
- Formic acid was added after the vessel was sealed and sweep-gas started. Temperature and pH were monitored. Formic acid addition was conducted under reflux conditions (i.e., condensate was returned to the vessel). Slurry samples were collected during $HCOOH$ addition.

Table 4.2.1. Normal Offgas Concentration Range and Offgas Analyzer Specifications for FY 1991 Laboratory-Scale Feed Preparation Tests of Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste Waste (NCAW) Simulant

Analyzer	Model/ Manufacturer	Method of Measurement	Normal Concentration Range During Test	Analyzer Range	Approximate Minimum Detection Limits	Approximate Accuracy
CO ₂	IR 703D-355/Optical Filter Corp. Infrared Instr.	Infrared Absorbance	0-15%	0-50%	0.05%	3% relative
N ₂ O	IR 703D-845/Optical Filter Corp. Infrared Instr.	Infrared Absorbance	0-5%	0-5%	0.05%	3%
CH ₄	IR 703D-145/Optical Filter Corp. Infrared Instr.	Infrared Absorbance	1-2%	0-5%	0.05%	3%
CO*	IR 703D-445/Optical Filter Corp. Infrared Instr.	Infrared Absorbance	0%	0-5%	0.03%	3%
NH ₃ **	IR 703D-245/Optical Filter Corp. Infrared Instr.	Infrared Absorbance	0%	0-1.5%	0.05%	3%
NO _x	951 A/ Beckman Industrial	Chemiluminescent	0-2%	0-5%	50 ppm	7%
O ₂	IR 2200-3052-6/Optical Filter Corp. Infrared Instr.	Electrochemical	0-15%	0-25%	50 ppm	2%
H ₂	M2OOD/Microsensor Technology Inc.	Gas Chromatograph	0-2%	0-4%	2 ppm	2%
N ₂	M2OOD/Microsensor Technology Inc.	Gas Chromatograph	0-80%	0-100%	100 ppm	2%
O ₂ #	M2OOD/Microsensor Technology Inc.	Gas Chromatograph	0-20%	0-50%	100 ppm	2%
CO*#	M2OOD/Microsensor Technology Inc.	Gas Chromatograph	0%	0-50%	200 ppm	2%
CH ₄ #	M2OOD/Microsensor Technology Inc.	Gas Chromatograph	1-2%	0-50%	100 ppm	2%

*The CO Infrared analyzer exhibits a linear response to N₂O as well as CO. After correcting for the N₂O interference, no CO was observed during testing. CO was also monitored by the gas chromatograph (GC). No CO was detected by the GC which confirmed the CO Infrared analyzer results.

**The NH₃ analyzer exhibits a linear response to NH₃, CO₂, and CH₄ gases along with a strong non-linear response to N₂O. The total complex response function makes the data from the NH₃ Infrared analyzer questionable. Any NH₃ present in the offgas was likely obscured by the interferences. All reported ammonia data represents soluble ammonium ion in the slurry and condensate as measured by selective ion electrode.

#Even though the GC measured O₂, CO, and CH₄ gases, the data from the specific Infrared analyzers were used.

- For digestion, the temperature was increased to 100°C (near boiling), and both condensate and slurry samples collected to allow monitoring of the extent of reaction as a function of time, pH, and gas composition. Digestion time was 4 h except for test 4.1 that was digested for 8 h (4 h under reflux conditions and 4 h during condensate collection). About 80 mL/h of condensate was removed during digestion from the first condenser (coolant temperature = 10°C, capacity of collector = 40 mL). The second, downstream condenser (coolant temperature = 25 to 29°C, capacity of collector = 10 mL) generally produced less than 10 mL during testing. The NCAW simulant was allowed to cool to room temperature overnight after digestion.
- The vessel plus the digested NCAW simulant were weighed prior to heat up and recycle waste stream simulant addition. The NCAW simulant was heated to 100°C prior to recycle addition. The recycle waste stream was added via tygon tubing and a peristaltic pump at a rate of approximately 10 mL/min. Settling within the tubing occurred during recycle waste stream addition, so the tubing was turned constantly by hand to prevent build up of solids. Condensate was allowed to reflux back into the vessel during heat up and recycle waste stream addition.
- After recycle waste stream addition, the slurry was concentrated at 100°C (near boiling), and the condensate collected for ~1 h. Final weight of the vessel and slurry was then determined after sample removal.

Slurry samples were removed for redox and physical property measurements, plus thermal and chemical analyses before and after recycle addition. For redox and rheology measurements dry frit was added to a concentrated slurry sample that had been cooled to room temperature. The resultant melter feed simulant was vitrified in a sealed crucible for $\text{Fe}^{+2}/\Sigma\text{Fe}$ analysis.

4.4 Sampling Strategy/Analytical Methods

The sampling strategy is summarized in Table 4.2.2. Samples were removed during testing for chemical analyses, glass redox, and physical characterization. Slurry and supernate samples were analyzed routinely by inductively coupled plasma-emission spectroscopy (ICP-ES) for metal cations (Wagner 1991)^(a) and ion chromatography (IC) (Urie 1991)^(b) for HCOO^- , NO_3^- and NO_2^- . Inductively Coupled Mass Spectroscopy (ICP-MS) and x-ray fluorescence (XRF) were only used to compare analytical methods (refer to Appendix A), not routine simulant characterization. Measurements of IC and pH were performed on condensate samples. Concentration of NH_4^+ in the slurry supernate and condensate was measured by selective ion electrode (SIE).^(c) A procedure for sealed crucible melts

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- (a) Wagner, J. J. 1991. PNL-ALO-211, rev. 0. Determination of Elements by Inductively Coupled Argon Emission Spectroscopy.
 - (b) Urie, M. W. 1992. PNL-ALO-212. Determination of Inorganic Anions by Ion Chromatography.
 - (c) Burt, M. C. 1991. PNL-ALO-226. Ammonia (nitrogen) in Aqueous Samples.

Table 4.2.2. Process Step Sampling Strategy for FY 1991 Laboratory-Scale Feed Preparation Testing of Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Simulant

Sample/ Analysis Type	Process Step			
	Untreated NCAW (Initial)	HCOOH Addition	Digestion	Recycle Addition/ Concentration
Proposed Number of Analyses				
<u>Slurry Chemical Analyses</u>				
ICP slurry	1	0	0	0
ICP supernate	1	3	1	1
IC supernate	1	3	1	1
TOC slurry	1	0	1	1
TC slurry	1	0	1	1
SIE for NH ₄ ⁺ slurry	1	3	1	1
XRF (optional)	1	0	0	0
<u>Glass Redox</u>				
Fe+2/ΣFe	0	0	1	1
<u>Physical Properties</u>				
density	1	0	1	1
wt% solids	1	0	1	1
TO/L	1	0	1	1
Rheology for selected tests with emphasis on melter feed.				
Thermal Analysis for selected tests with emphasis on formatted feed.				
<u>Condensate</u>				
IC	0	3	3	3
pH	0	3	3	3
SIE for NH ₄ ⁺	0	3	3	3
<u>Offgas</u>	0	on-line	on-line	on-line
Online measurement performed for H ₂ , O ₂ , NO _x , N ₂ O, N ₂ (except with air purge), CO, CO ₂				
NO was monitored intermittently for selected tests.				
Monitoring of gas phase NH ₃ and HCOOH concentrations was not successful.				

Acronyms

ICP: Inductively Coupled Plasma
 IC: Ion Chromatography
 TOC: Total Organic Carbon
 TC: Total Carbon

SIE: Selective Ion Electrode
 XRF: X-Ray Fluorescence
 TO/L: Total Oxides/Liter

was developed and used for preparation of samples for glass redox measurements ($\text{Fe}^{+2}/\Sigma\text{Fe}$) based on SRTC experience.^(a) The $\text{Fe}^{+2}/\Sigma\text{Fe}$ ratio in the glass samples was used as an indicator of the glass oxidation state and was measured using the 1,10 phenanthroline spectrophotometric method.^(b)

Carbon analysis^(c) of the NCAW slurry simulant was unacceptable. In Table 4.2.3 the total organic carbon (TOC) and total carbon (TC) analytical results for NCAW slurry simulant (eight FY 1991 tests) are shown. From comparing the analytical results with the target values, it is apparent that further analytical development is required for measuring carbon in the NCAW simulant. The values for TOC are 12 to 15 times higher than the known source quantity addition of 0.17 g of carbon/L of slurry that was added as $\text{Na}_2\text{C}_2\text{O}_4$. The values for TC are 1 to 2.5 times higher than the known source quantities of $\text{Na}_2\text{C}_2\text{O}_4$ and Na_2CO_3 . Consequently, the calculated inorganic carbon values range from -0.3 to 2 g of carbon/L of slurry. The TOC procedure was performed by heating the slurry to 600°C to drive off the carbon as CO_2 that was then measured. The TC procedure was performed at 1000°C. Specific factors or slurry matrix effects for carbon analysis have not been identified to explain the results. Similar results were experienced during previous tests.^(d) Further analytical development is required, perhaps using spiked matched matrix standards for calibration. Accurate determination of carbon in the slurry was not possible.

Weight percent solids of the NCAW slurry was determined by weight loss after drying for 24 h at 105°C. Weight percent solids were also measured by a microwave oven drying method. The microwave method was investigated because it decreased turn around time from 24 h to 1 h. Comparison of microwave oven-dried and conventional oven-dried results for weight percent solids showed the microwave oven-dried samples to be consistently higher by 3 to 5%. It is not known if the observed bias would be consistent for significantly different slurry types. Total oxide of the NCAW slurry was determined by weight loss after drying for 1 h at 1150°C. Density of the NCAW slurry was obtained by weighing the slurry in a calibrated graduated cylinder.

Rheograms (shear stress as a function of shear rate) were obtained using a Haake Rotovisco RV 100 viscometer driven by a M500 head with the MV II-standard sensor system. The MV II system is a rotating spindle and cup assembly. The measurements were collected at room temperature for 5 min over a shear rate range of 0 to 451 s^{-1} . The downward scan required an additional 5 minutes.

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- (a) Olson, K. M. August 1991. WTC-006-29, rev 0. Preparation of Feed Samples for $\text{Fe}^{+2}/\Sigma\text{Fe}$ analysis.
 - (b) Burt, M. C. August 1988. PNL Test Procedure 7-40.20, rev 0. Spectrophotometric Determination of Reduced and Total Iron in Glass with 1,10 Phenanthroline.
 - (c) Baldwin, D. August 1989. PNL-MA-597, 7-40.37. "Determination of Carbon in Solids Using the Coulometrics Carbon Dioxide Coulometer."
 - (d) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.

Table 4.2.3. Total Organic Carbon and Total Carbon Analysis for NCAW Slurry Simulant (Eight FY 1991 Tests)

	Test Number								
	Target Value†	1.1	1.2	1.3	2.1	2.2	3.1	3.2	4.1
Total Carbon (g/L of slurry)*	1.67	2.19	2.23	2.41	1.72	2.36	2.45	4.28	2.62
Total Organic Carbon (g/L of slurry)**	0.17	2.33	2.53	2.3	2	2.31	2.2	2.28	2.18
Inorganic Carbon (g/L of slurry)***	1.5	-0.14	-0.3	0.11	-0.28	0.05	0.25	2	0.44

*Total Carbon analysis was performed at approximately 1000°C

**Total Organic Carbon analysis was performed at approximately 600°C

***Inorganic Carbon values were determined by subtracting the Organic Carbon values from the Total Carbon values.

†Known source component quantities of NaC₂O₄ and Na₂CO₃.

Data reported from the analyses of initial slurry simulants that do not contain formic acid. Carbon analyses were not performed on the remaining tests based on the above data which was not representative of known slurry source carbon quantities:

4.5 Methods Used for Thermal Analysis of Dried NCAW Simulant

The thermal properties of explosives are important considerations in normal processing evaluations and accident investigations. Three types of tests were conducted to evaluate the thermal stability of dried NCAW simulant: differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Henkin Critical Temperature tests.

DSC is used to look for exothermic and endothermic changes that determine the temperature of phase changes and chemical reactions. The DSC analysis was performed on a Perkin-Elmer Model DSC 7 instrument. The TGA measures changes in weight associated with gas producing reactions or vaporization as a function of temperature. TGA was performed with a Perkin-Elmer Model TGA-7.

Slurry samples were not dried before the TGA analysis. Slurry samples for the DSC analysis were dried at 60°C for ~24 h before initiating thermal analyses to concentrate the solids, decrease volatile components (primarily water) and minimize potential risk to the equipment from foaming or splatter. For both TGA and DSC analyses, approximately 10 mg of sample were heated at a rate of 10°C/min over a temperature range of 40 to 700°C under an air purge. An air purge was used as a first approximation of the vessel plenum composition.

The Henkin Critical Temperature Test is a semi-routine test used to confirm the decomposition kinetic rate parameters determined from DSC measurements (Scheele and Cady 1992). The Henkin test is useful for a preliminary estimate of scale-up effects even when kinetic parameters are not available. The Henkin sample is larger than a DSC sample, and differences in cook-off temperature are an indication of the direction and magnitude of changes that might occur with even larger samples. The Henkin test is sometimes called the time-to-explosion test because events often do not occur until several minutes after the sample is placed in a preheated environment. The reason for the delay is that induction processes must often occur before the start of the exothermic reactions that cause the event. Rapid gas evolution that is indicated by sample displacement and/or noise is recorded as an "event."

Henkin tests^(a) were conducted on NCAW slurry samples at temperatures of 380, 450, and 550°C. Between 15 and 21 mg of slurry (not dried) were placed in a small test tube. The test tube was placed into a cavity within a preheated, temperature controlled metal block. Indications of an explosion by visual observation were made over a 20 min period.

(a) PNL Laboratory Procedure for the Measurement of Explosive Behavior, LCB-SSX-1, 1989.

5.0 Results

Section 5.0 describes laboratory data collected during FY 1991 laboratory-scale feed preparation tests. The data pertain to physical properties of the NCAW simulant, rheology of melter feed simulant, offgas and slurry chemistry, glass redox, and thermal stability of dried slurry simulant samples. A preliminary evaluation of the uncertainties and limitations of three analytical methods for determining elemental composition was performed using stock NCAW simulant and is discussed in Appendix A.

5.1 Physical Properties of the NCAW Simulant

Table 5.1.1 lists density, weight percent solids, and WO/L for initial NCAW slurry simulant (stock plus added NaNO_2 , NaNO_3 , and Na_2CO_3), formed simulant before recycle addition, and formed simulant after recycle addition and concentration (end of test). Correlations between the weight percent solids in slurries and the oxide loading measurements were developed for large-scale operations (Slurry Integrated Process Tank [SIPT]). The results indicate that for the simulant slurries tested, the weight percent solids can be used to predict the oxide loading provided the volatile anion loading is comparable. Correlations for initial NCAW simulant, formed simulant before recycle addition, and the formed simulant after recycle addition have been developed. A scatter plot showing the general relationship between wt% solids and WO/L is provided in Figure 5.1.1.

5.2 Rheology of NCAW Melter Feed Simulant

Rheograms were obtained for a melter feed simulant at three oxide loadings, 500, 550, and 600 g TO/L. The melter feed was prepared by adding frit to the formed simulant with recycle from test 7.1.^(a) No specific criteria were available to select an exact test simulant for rheology measurements.

The yield stress and apparent viscosity for three shear rates (183, 383, and 451s^{-1}) for the melter feed simulants at the three oxide loadings are given in Table 5.2.1. The flow behavior index, n , and consistency factor, K , are also provided in Table 5.2.1. The index and consistency factor were calculated from the slope and y-intercept, respectively, of a log-log plot of shear stress versus shear rate.

(a) Test 7.1 was conducted with a high nitrate, low nitrite simulate. Formic acid was added in the amount of 55 mL 87 wt% HCOOH/L slurry. The pH of the waste simulant at the end of the feed preparation steps was 7.2 (100°C). The pH of the simulant before and after frit addition is not known.

Table 5.1.1. Density, Weight Percent Solids and Waste Oxide/Liter^(a) for Initial NCAW Simulant, Formated Simulant Prior to Recycle Addition and Treated Simulant at End of Test

Test Number	Initial Slurry ^(b)				End Digestion ^(c)				End of Test ^(d)			
	Density (g/ml)	Wt. % Solids		WO/L	Density (g/ml)	Wt. % Solids		WO/L	Density (g/ml)	Wt. % Solids		WO/L
		CEM	Oven			CEM	Oven			CEM	Oven	
1.1	1.10	15.39	14.57	119.05	ND ^(e)	ND	ND	ND	1.12	18.76	16.89	134.02
1.2	1.14	16.13	14.94	131.20	1.11	19.23	17.85	147.98	1.11	16.89	15.76	125.80
1.3	1.08	16.16	15.05	120.11	1.13	20.20	18.40	153.38	1.20	20.86	19.30	168.19
2.1	1.09	15.50	14.51	117.70	1.14	18.02	19.44	166.55	1.11	16.05	14.79	119.12
2.2	1.11	16.27	15.10	124.32	1.13	19.84	18.04	150.97	1.13	18.36	19.96	187.38
3.1	1.09	14.53	13.45	112.84	1.14	20.24	18.54	160.51	1.14	20.39	18.57	157.07
3.2	1.10	15.28	14.05	117.29	1.17	21.13	19.64	172.65	1.14	23.01	19.59	160.75
4.1	1.09	15.75	14.93	121.01	1.14	20.45	18.73	159.36	1.14	18.90	17.49	149.39
5.2	1.12	16.06	15.23	126.60	1.04	22.51	21.31	143.26	ND	SD ^(f)	SD	SD
7.1	1.10	16.32	15.23	122.99	1.11	20.77	19.24	155.02	1.13	SD	SD	SD

- (a) Values for waste oxides (WO/L) represent results from "loss-on-ignition" determinations, made using a muffle furnace operating at 1150°C.
- (b) Values shown reflect sampling before HCOOH addition.
- (c) Values shown reflect sampling after digestion and before recycle waste stream addition.
- (d) Values shown reflect sampling after recycle addition at the end of testing.
- (e) Not determined.
- (f) Suspect data, not given.

NOTE: Two ovens were used for drying samples: CEM Instruments microwave oven and Blue M Instruments conventional oven.

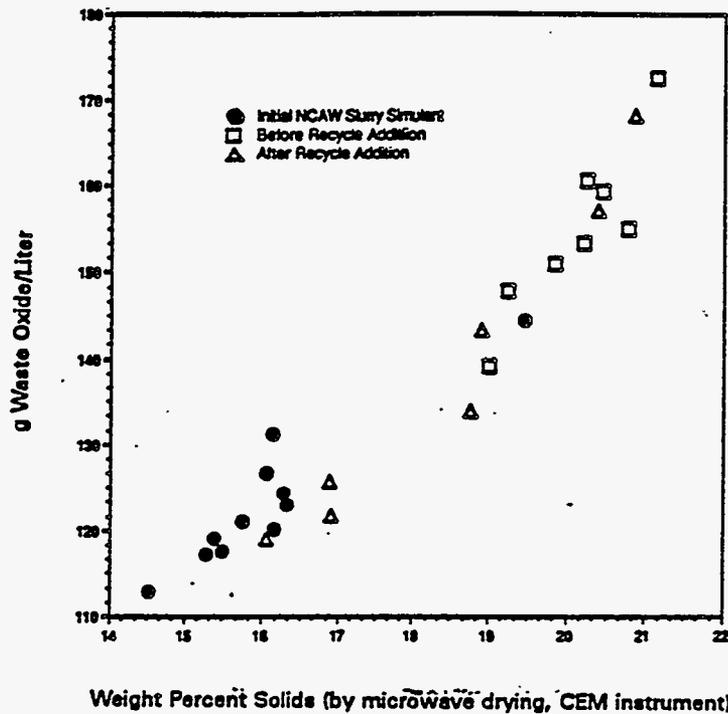


Figure 5.1.1. Correlation of Weight Percent Solids and Waste Oxide/Liter for Initial NCAW Simulant, Formated Simulant Prior to Recycle Addition and Formated Simulant after Recycle Waste Stream Addition

Table 5.2.1. Yield Stress and Apparent Viscosity of Three Melter Feed Simulants Prepared from Test 7.1 NCAW Simulant Measured at Shear Rates of 183, 383 and 451 s⁻¹

TO/L	Yield Stress, Pa	Apparent Viscosity, mPa S			Flow Index, n	Consistency Factor, K
		183 s-1	383 s-1	451 s-1		
500	13.5	110	67	60	1	0.09
550	20.0	159	98	88	1	0.09
600	17.3	142	88	79	0.9	0.09

The unexpected decrease in yield stress and viscosity (550 to 600 g TO/L) may be attributed to uncertainties in preparation and/or analysis or an unknown variable, such as aging, which was not controlled.

The index and consistency factor may be used in engineering models of pressure drop across slurry transfer lines. The change in apparent viscosity with shear rate is shown in Figure 5.2.1. Associated rheograms (shear stress versus shear rate) are provided in Appendix C. The reported values were derived from a second or third replicate viscosity measurement on the same sample.

The yield stress ranged from 13.5 to 20 Pa. The apparent viscosity over a shear rate range of 183 to 451 s^{-1} ranged from 60.1 to 159.5 mPa-s. The measured yield stress is of concern as it exceeds the current plant design criteria of 15 Pa. An unexpected decrease in yield stress was observed between samples containing 550 and 600 g WO/L. The decrease may reflect error in sample preparation or sensitivity limits of the associated sample preparation and rheological measurements.^(a) The largest change in yield stress was observed between samples containing 500 and 550 g WO/L.

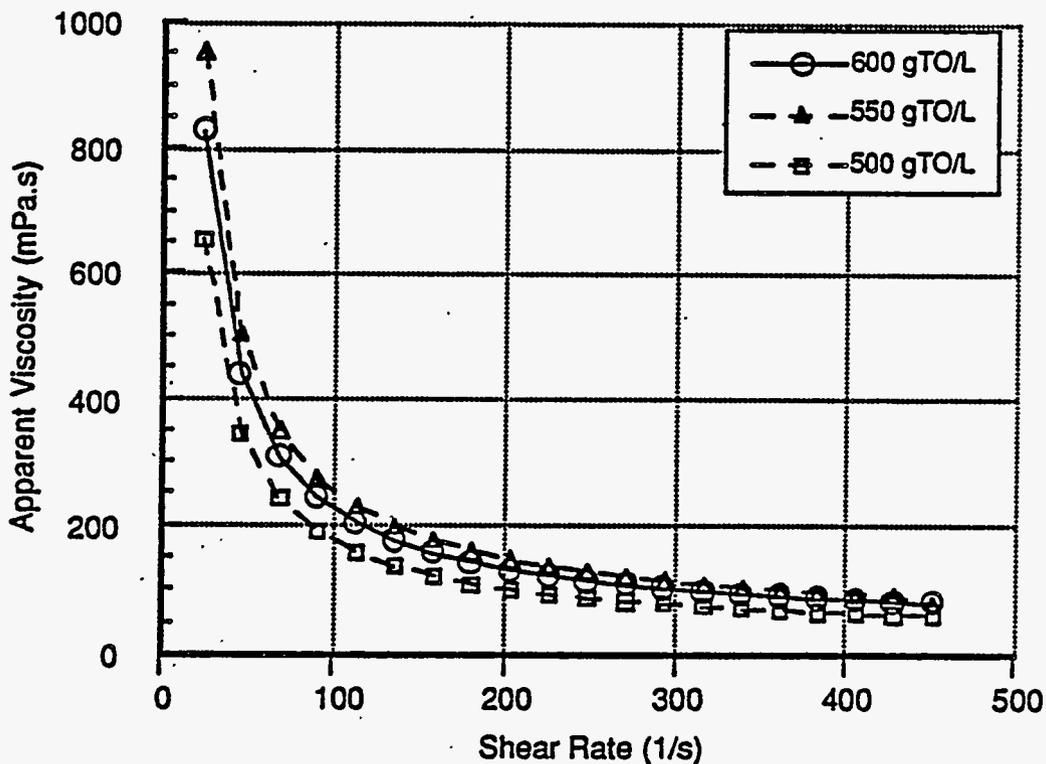


Figure 5.2.1. Apparent Viscosity as a Function of Shear Rate for Three Melter Feed Simulants Prepared from Test 7.1 at 500, 550 and 600 g TO/L

- (a) Attempt to verify the oxide loadings after receipt of the rheological data was not pursued, because the recovered simulant was visually more viscous than before the rheological measurement. Although the sample lids appeared to be tight, it is not certain whether the change in physical state was due to drying, aging resulting from chemical changes in waste and/or frit, or shearing during the rheological measurements.

The simulants demonstrated a very slight pseudoplastic to Bingham plastic behavior based on the calculated flow behavior index, n , being 0.9 to 1 (Fow et al. 1986). A time-dependent behavior (hysteresis) was observed for all oxide loadings. The simulated melter feed slurries were rheopectic, exhibiting an increase in shear stress with time.^(a) A preliminary evaluation of the data suggests that the melter feed simulant may experience some physical alterations due to shear effects or aging.

5.3 Offgas Generation Data

Process profiles and key events during the laboratory tests that pertain to offgas generation measurements for each feed preparation test are provided in Appendix D. Peak gas generation rates are listed in Table 5.3.1. Total moles of each gas released as a function of process step are given in Table 5.3.2.

Upon re-evaluation of the data it was realized that the availability of the reactants (i.e. HCOO^- and NO_2^-) was decreased by as much as 20% as a result of slurry sampling. The offgas data has not been corrected for removal of slurry samples. Although replicate tests have not intentionally been conducted to determine experimental error, review of offgas data as presented in Appendix E, provides an estimated error ranging from 10 to 20%. Based on this cursory evaluation, the error introduced by sample removal (maximum 20%) may be considered to be within the estimated experimental error. However, a 20% increase in the amount and peak gas generation rate should be applied as a conservative estimate of the maximum gas release.

The process profiles in Appendix D identify, as a function of process time, the offgas generation rate (mmole/min) for H_2 , CO_2 , N_2O , and NO_2 ; the slurry pH, volume and temperature; and the amount of HCOOH added during the test run. Carbon monoxide and N_2 are not reported because they were not detected during feed preparation tests. Analytical detection limits for the gases were 100 ppm for N_2 and 200 ppm for CO .^(b) The release of NO gas was monitored only on an intermittent basis for selected tests (refer to Section 6.1). For most of the tests, little change from nominal O_2 (3%) was observed. During test 5 (non-noble metal simulant) in which significantly greater amounts of NO_2 were observed, the O_2 concentration decreased to ~1%.

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- (a) Rheopectic behavior is observed on the rheogram as the shear rate is steadily increased from zero to a maximum value and then decreased steadily back to zero. The down-curve will be above the up-curve. This behavior results when the structural configuration and particle orientation of some slurries cannot adjust instantaneously to changes in shear stresses.
 - (b) However, the tracer gas, CH_4 , contained a small amount of N_2 , which raises the detection limit for N_2 to 200 ppm.

Table 5.3.1. Peak Generation Rates (mmoles/minute) of H₂, CO₂, NO_x and N₂O Measured During FY 1991 Laboratory-Scale Feed Preparation Tests

Test	Peak Gas Generation Rates (mmole/min)			
	H ₂	CO ₂	NO _x	N ₂ O
1.1	0.56	7.48	0.40	2.83
1.2	<0.05	8.60	0.37	2.11
1.3	<0.05	7.92	0.49	2.70
2.1	<0.05	7.25	2.18	1.79
2.2	<0.05	13.95	1.09	3.35
3.1	0.42	8.01	0.27	2.04
3.2	0.31	8.17	0.41	2.42
4.1	<0.05	8.41	0.48	2.23
5.1	<0.05	6.97	1.55	0.15
5.2	<0.05	6.65	3.89	0.28
6.1	1.12	7.33	0.65	2.40
6.2	0.73	6.23	0.51	2.59
7.1	0.31	6.28	0.093	1.34

Note: Approximate slurry volume was 1.5L (125 g WO/L).

Gas compositions were measured downstream of both condensers and therefore did not include any condensed gases (such as NO_x, NH₃, and HCOOH). Corrections for time delays between gas release from the slurry and injection into the detector were included in the offgas profiles. Step decreases in the slurry volume shown in the process profiles are due to sampling. Continuous decreases in slurry volume are a result of boil-off. Increases in slurry volume are due to HCOOH or recycle waste stream addition.

Comparisons of the offgas generation rates for the following test variables are provided in Appendix E:

Figure	Variable	Test
E1.a-d	Amount of HCOOH	1.1, 1.2, 1.3
E2.a-d	Rate of HCOOH Addition	1.3, 2.1, 2.2
E3.a-d	Amount of NO ₂	1.3, 3.1, 3.2
E4.a-d	Extended Digestion Period	1.3, 4.1
E5.a-d	Noble Metals	1.1, 5.2
E6.a-d	Low NO ₂ , High NO ₃	3.1, 7.1

Table 5.3.2. Quantities of CO₂, N₂O, NO_x and H₂ Released During HCOOH Addition, Digestion, Recycle Waste Stream Addition, and for Test Duration for FY 1991 Laboratory-Scale Feed Preparation Tests

Test No.	Offgas Species	Quantity of Gas Released During Specified Period, moles				Total for Test
		HCOOH Addition	Digestion	Recycle Waste Stream Addition		
1.1	CO ₂	8.76E-01	1.39E-01	5.50E-02	1.07E+00	
	N ₂ O	2.36E-01	1.50E-04	1.50E-04	2.36E-01	
	NO _x	3.00E-02	2.40E-04	5.30E-05	3.03E-02	
	H ₂	2.71E-02	2.98E-02	1.11E-02	6.80E-02	
1.2	CO ₂	2.76E-01	1.77E-02	8.20E-03	3.03E-01	
	N ₂ O	8.70E-02	5.75E-02	7.00E-03	1.53E-01	
	NO _x	1.20E-02	1.90E-03	9.20E-05	1.40E-02	
	H ₂	7.90E-04	2.40E-04	1.10E-04	1.10E-03	
1.3	CO ₂	5.85E-01	3.43E-02	2.30E-02	6.42E-01	
	N ₂ O	2.10E-01	3.24E-02	5.00E-04	2.43E-01	
	NO _x	3.40E-02	1.30E-03	0.00E+00	3.53E-02	
	H ₂	2.80E-03	4.00E-03	4.90E-03	1.16E-02	
2.1	CO ₂	4.52E-01	4.70E-02	NA	4.99E-01	
	N ₂ O	1.43E-01	1.90E-02	NA	1.62E-01	
	NO _x	1.08E-01	1.00E-02	NA	1.18E-01	
	H ₂	6.00E-04	Hydrogen data set incomplete for this test			
2.2	CO ₂	4.90E-01	6.60E-02	1.06E-02	5.67E-01	
	N ₂ O	1.45E-01	7.20E-02	2.50E-03	2.19E-01	
	NO _x	2.60E-02	5.50E-03	4.20E-05	3.20E-02	
	H ₂	1.60E-04	6.90E-05	2.70E-05	2.50E-04	
3.1	CO ₂	4.57E-01	1.02E-01	4.30E-02	6.02E-01	
	N ₂ O	7.70E-02	8.30E-04	6.20E-04	7.70E-02	
	NO _x	6.70E-03	5.25E-05	3.80E-05	6.70E-03	
	H ₂	1.07E-02	1.97E-02	6.00E-03	3.60E-02	
3.2	CO ₂	5.35E-01	8.10E-02	3.50E-02	6.52E-01	
	N ₂ O	1.46E-01	1.10E-03	5.00E-04	1.48E-01	
	NO _x	1.90E-02	2.00E-04	1.70E-05	1.92E-02	
	H ₂	5.00E-03	1.45E-02	2.00E-03	2.15E-02	
4.1	CO ₂	5.50E-01	4.30E-02	2.10E-02	6.14E-01	
	N ₂ O	1.90E-01	5.24E-02	4.00E-04	2.43E-01	
	NO _x	2.90E-02	3.40E-03	5.40E-05	3.23E-02	
	H ₂	8.30E-04	1.90E-04	9.00E-04	1.90E-03	
7.1	CO ₂	5.24E-01	1.80E-01	5.70E-02	7.61E-01	
	N ₂ O	8.00E-02	1.20E-04	0.00E+00	8.00E-02	
	NO _x	4.10E-03	1.10E-04	1.40E-04	4.34E-03	
	H ₂	1.27E-02	2.77E-02	4.50E-03	4.49E-02	

Table 5.3.2. (contd)

Test No.	Offgas Species	Quantity of Gas Released for Specified Period, moles					Total for Test
		First HCOOH Addition	First Digestion	Recycle Waste Stream Addition	Second HCOOH Addition	Second Digestion	
5.1	CO ₂	1.69E-01	3.40E-02	7.20E-03	9.30E-02	3.83E-02	3.40E-01
	N ₂ O	2.50E-04	2.10E-04	2.10E-04	6.20E-03	1.40E-03	8.30E-03
	NO _x	4.60E-03	1.60E-02	4.70E-03	6.59E-02	3.91E-02	1.30E-01
	H ₂	2.40E-06	3.30E-05	9.70E-05	3.60E-05	1.50E-04	2.30E-04

Test No.	Offgas Species	Quantity of Gas Released for Specified Period, moles		
		HCOOH Addition	Digestion	Total for Test
5.2	CO ₂	4.12E-01	3.60E-03	4.16E-01
	N ₂ O	2.00E-02	8.00E-04	2.10E-02
	NO _x	2.54E-01	1.17E-02	2.65E-01
	H ₂	1.00E-03	5.00E-04	6.00E-04
6.1	CO ₂	7.43E-01	9.93E-02	8.42E-01
	N ₂ O	2.39E-01	2.00E-03	2.41E-01
	NO _x	5.10E-02	6.00E-04	5.20E-02
	H ₂	2.60E-03	3.95E-02	4.20E-02

Test No.	Offgas Species	Quantity of Gas Released for Specified Period, moles						
		1	2	3	4	5	6	7
6.2	CO ₂	0.00E+00	7.20E-01	4.90E-02	1.00E-02	2.60E-02	6.00E-03	8.12E-01
	N ₂ O	0.00E+00	2.22E-01	7.00E-04	0.00E+00	0.00E+00	0.00E+00	2.23E-01
	NO _x	0.00E+00	4.60E-02	0.00E+00	0.00E+00	0.00E+00	0.00E+00	4.60E-02
	H ₂	0.00E+00	6.00E-04	1.20E-02	2.70E-03	7.30E-03	3.60E-03	2.60E-02

Test 6.2: Process Step Key (Reference Figure D12)
 Time 0 min = Onset of Formic Acid Addition
 1 = Heat up (-57 min to 0 min)
 2 = HCOOH Addition (0 min to 190 min)
 3 = Cool Down (190 min to 275 min)
 4 = Heat Up (275 min to 308 min)
 5 = Temp = 100°C (308 min to 340 min)
 6 = Cool Down (340 min to 394 min)
 7 = Total moles evolved

Changes in H₂ and CO₂ generation rate with temperature are shown in Appendix F. Measurements at steady state H₂ generation were used to calculate activation energies (refer to Figure 5.3.1). Activation energies of 59.2 kJ/mole for test 1.1 and 82.5 kJ/mole for test 6.2 were calculated for the H₂ generation reaction. The significant temperature dependence of CO₂ generation is demonstrated in Figure 5.3.2, in which cycling of the CO₂ generation rate (+/-10%) with cycling of the slurry temperature is uniformly traced.

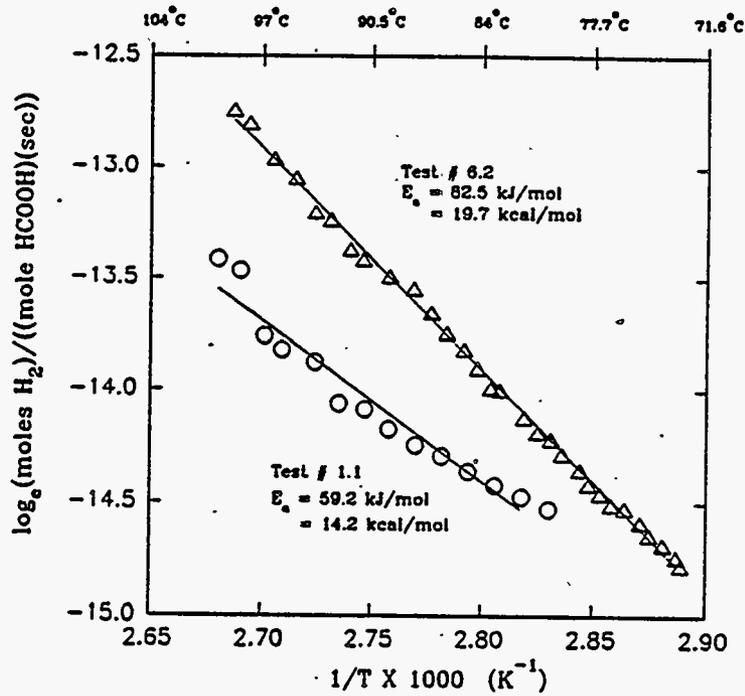


Figure 5.3.1. Activation Energies for Steady-State H₂ Release for Tests 1.1: Maximum Amount of HCOOH and 6.2: HCOOH and Heat Interrupted

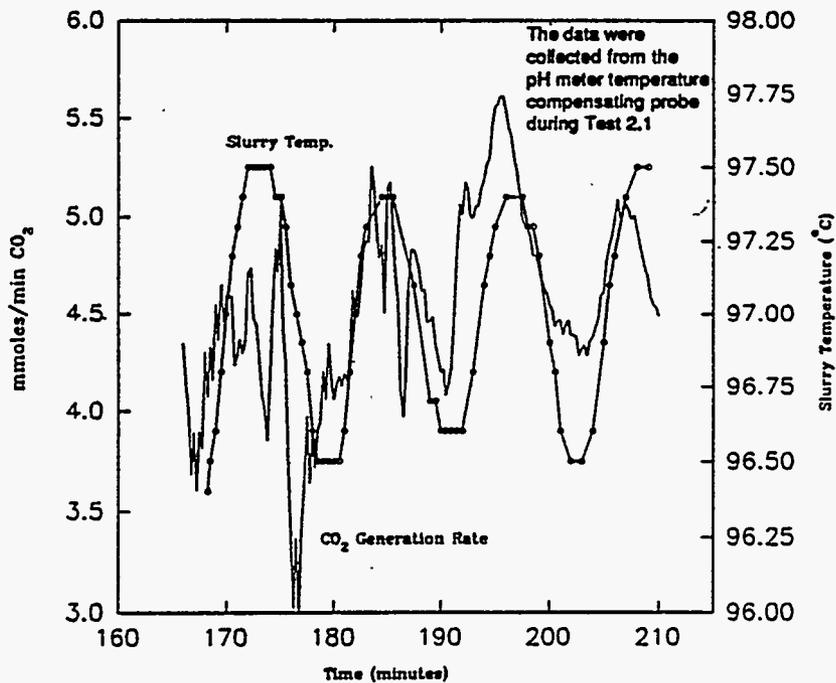


Figure 5.3.2. Dependence of CO₂ Offgas Generation Rate on Temperature Cycling of NCAW Simulant

5.4 Slurry and Condensate Composition

Formate, NO_3^- , and NO_2^- amounts remaining in the slurry and condensate at the end of HCOOH addition, digestion, and recycle waste stream addition (test completion) are given in Table 5.4.1. The values presented in Table 5.4.1 for slurries were derived by calculating the total moles of anion in the slurry from the IC analyses and estimated total slurry volume, and then adding the moles of anion from all slurry samples removed prior to the end of a specific process step. This method of calculation was employed so that a true increase or decrease in amount of an anion could be calculated. For example, the change in the amount of HCOO^- during HCOOH addition for test 1.1 would be calculated by subtracting the amount of HCOO^- in the slurry at the completion of HCOOH addition (and HCOO^- in samples removed during HCOOH addition), 1.65 moles, from the amount of HCOOH added, 2.59 moles.

Ammonium ion data are presented in Table 5.4.1. The potential NH_3 volatilization at pH values >7 negates measuring/calculating true changes in NH_3 production from values in Table 5.4.1. Data is presented for information only. Total HCOO^- , NO_3^- , NO_2^- , and NH_4^+ concentrations found in the condensate are listed in Table 5.4.2.

5.5 Glass Redox

The basecase HCOOH addition for the FY 1991 laboratory-scale feed preparation testing, $\text{HCOOH}/\text{NO}_3^- = 4$, was selected to ensure that a measurable glass redox would be obtained. The basecase amount of HCOOH was added in tests 1.3, 2.1, 2.2, 3.1, and 3.2. Amounts of HCOOH other than basecase were added to address specific test objectives. The process was complicated somewhat by adding recycle waste stream simulant after the digestion step. Adding of recycle waste stream simulant doubled the NO_3^- concentration and increased the organic ($\text{C}_2\text{O}_4^{2-}$ and HCOOH) and Mn concentrations slightly. Taking the total NO_3^- into account from the slurry and recycle simulants, the basecase amount of HCOOH added was 48 mL 87 wt% HCOOH/L at 125 g WO/L slurry. Redox measurements ($\text{Fe}^{+2}/\Sigma\text{Fe}$) were performed on glasses prepared from slurry samples taken before and after recycle waste stream addition to evaluate the effect of recycle waste on glass redox. Table 5.5.1 lists the resultant glass redox values.

5.6 Results of Dried NCAW Simulant Thermal Analyses

Enthalpy and weight changes in four NCAW slurry simulant samples were measured as a function of temperature (40 to 700°C). The samples analyzed were collected from two tests, 1.1 and 1.3, and represented an NCAW slurry simulant (1.3-47.1), a formated NCAW simulant (1.3-32.1), and two formated NCAW slurry simulants to which recycle simulant had been added (1.3-47.1 and 1.1-47.1). Both laboratory-scale forming tests, 1.1 and 1.3, were conducted with nominal amounts of CO_3^{2-} , NO_3^- , and NO_2^- in the initial slurry. The amount of HCOOH added to the slurry in test 1.1 was

Table 5.4.1. Quantities of HCOO⁻, NO₂⁻, and NO₃⁻ at the End of HCOOH Addition, Digestion and Recycle Waste Stream Addition Processing Steps Determined by Slurry and Condensate Concentrations for the FY 1991 Laboratory-Scale Feed Preparation Tests

Test	Species	Initial Moles	HCOOH Addition Complete		Digestion Complete		Increase in Species Due to Recycle Addition (moles)	Test Complete	
			Species ^a Remaining in Slurry (moles)	Species ^a in Condensate (moles)	Species ^a Remaining in Slurry (moles)	Species ^a in Condensate (moles)		Species ^a Remaining in Slurry (moles)	Species ^a in Condensate (moles)
1.1	NO ₂ ⁻	6.50E-01	1.00E-03	6.80E-06	<dl	<dl	0.00E+00	<dl	1.24E-04
	NO ₃ ⁻	2.06E-01	1.97E-01	6.79E-04	1.82E-01	9.26E-05	1.90E-01	3.74E-01	1.33E-04
	HCOO ⁻	(2.59)†	1.65E+00	<dl	1.57E+00	7.04E-04	6.00E-02	1.54E+00	6.79E-05
	NH ₄ ⁺ (††)		3.91E-02	5.22E-06	6.42E-02	6.38E-04		1.09E-01	1.03E-03
1.2	NO ₂ ⁻	6.50E-01	4.29E-01	3.60E-07	3.57E-01	1.30E-05	0.00E+00	<dl	not measured
	NO ₃ ⁻	2.06E-01	2.11E-01	4.30E-04	2.19E-01	4.09E-03	1.90E-01	4.40E-01	not measured
	HCOO ⁻	(0.91)†	6.91E-01	3.14E-06	6.36E-01	1.78E-05	6.00E-02	6.14E-01	not measured
	NH ₄ ⁺ (††)		5.31E-04	3.23E-05	1.71E-04	2.67E-04		3.52E-04	not measured
1.3	NO ₂ ⁻	6.50E-01	1.15E-01	not measured	<dl	2.54E-04	0.00E+00	<dl	6.30E-06
	NO ₃ ⁻	1.90E-01	2.00E-01	not measured	1.97E-01	2.12E-04	1.80E-01	3.50E-01	2.50E-03
	HCOO ⁻	(1.6)†	1.00E+00	not measured	1.05E+00	<dl	5.00E-02	9.61E-01	9.69E-06
	NH ₄ ⁺ (††)		7.79E-04	not measured	4.42E-03	2.08E-04		4.22E-03	1.45E-03
2.1	NO ₂ ⁻	6.50E-01	7.54E-02	1.90E-05	<dl	2.40E-06	0.00E+00	<dl	not measured
	NO ₃ ⁻	1.81E-01	2.14E-01	2.73E-03	2.23E-01	2.46E-03	1.60E-01	3.70E-01	not measured
	HCOO ⁻	(1.52)†	8.90E-01	<dl	9.18E-01	3.10E-06	4.00E-02	9.61E-01	not measured
	NH ₄ ⁺ (††)		1.85E-03	2.57E-06	1.01E-02	2.06E-03		1.19E-02	not measured
2.2	NO ₂ ⁻	6.50E-01	1.83E-01	1.04E-06	7.92E-02	6.04E-06	0.00E+00	<dl	<dl
	NO ₃ ⁻	2.06E-01	2.21E-01	3.95E-04	2.08E-01	6.25E-04	1.80E-01	4.26E-01	1.35E-03
	HCOO ⁻	(1.51)†	9.89E-01	3.54E-06	1.03E+00	2.33E-05	5.00E-02	1.04E+00	<dl
	NH ₄ ⁺ (††)		5.73E-04	2.04E-06	2.50E-04	4.64E-04		2.21E-03	3.50E-04
3.1	NO ₂ ⁻	2.00E-01	<dl	<dl	<dl	<dl	0.00E+00	<dl	<dl
	NO ₃ ⁻	2.09E-01	1.97E-01	4.60E-06	1.87E-01	2.92E-05	1.80E-01	2.90E-01	2.42E-05
	HCOO ⁻	(1.56)†	1.12E+00	3.77E-05	1.05E+00	3.89E-04	5.00E-02	1.09E+00	5.28E-05
	NH ₄ ⁺ (††)		1.56E-02	3.29E-05	2.72E-02	1.16E-03		5.32E-02	3.16E-04
3.2	NO ₂ ⁻	4.00E-01	<dl	<dl	<dl	<dl	0.00E+00	<dl	<dl
	NO ₃ ⁻	2.01E-01	2.00E-01	2.50E-04	1.84E-01	1.84E-04	1.80E-01	4.32E-01	3.50E-05
	HCOO ⁻	(1.51)†	1.09E+00	<dl	8.86E-01	7.58E-05	5.00E-02	1.15E+00	6.69E-06
	NH ₄ ⁺ (††)		2.12E-02	3.01E-06	1.23E-02	2.80E-03		2.25E-02	3.17E-03
4.1	NO ₂ ⁻	6.50E-01	8.39E-02	9.82E-04	<dl	8.99E-04	0.00E+00	<dl	2.21E-03
	NO ₃ ⁻	1.99E-01	2.15E-01	2.60E-04	1.99E-01	2.90E-04	1.80E-01	3.88E-01	1.39E-05
	HCOO ⁻	(1.53)†	7.61E-01	3.70E-06	9.95E-01	6.10E-06	5.00E-02	1.03E+00	4.86E-06
	NH ₄ ⁺ (††)		4.52E-04	3.08E-06	9.42E-04	7.59E-03		1.26E-03	2.11E-04
5.2	NO ₂ ⁻	6.50E-01	<dl	<dl	<dl	<dl	NA	NA	NA
	NO ₃ ⁻	1.93E-01	4.59E-01	1.75E-03	4.70E-01	7.29E-03	NA	NA	NA
	HCOO ⁻	(2.2)†	1.71E+00	1.38E-03	1.61E+00	4.36E-02	NA	NA	NA
	NH ₄ ⁺ (††)		8.63E-05	1.16E-07	1.03E-04	<dl	NA	NA	NA
6.1	NO ₂ ⁻	6.50E-01	<dl	<dl	NA	NA	NA	NA	NA
	NO ₃ ⁻	2.10E-01	1.82E-01	9.43E-04	NA	NA	NA	NA	NA
	HCOO ⁻	(2.03)†	1.25E+00	<dl	NA	NA	NA	NA	NA
	NH ₄ ⁺ (††)		9.46E-03	8.31E-06	NA	NA	NA	NA	NA
6.2	NO ₂ ⁻	6.89E-01	<dl	<dl	NA	NA	NA	NA	NA
	NO ₃ ⁻	1.96E-01	1.93E-01	1.48E-03	NA	NA	NA	NA	NA
	HCOO ⁻	(2.05)†	1.37E+00	9.30E-06	NA	NA	NA	NA	NA
	NH ₄ ⁺ (††)		8.01E-03	2.33E-05	NA	NA	NA	NA	NA
7.1	NO ₂ ⁻	2.00E-01	<dl	<dl	<dl	<dl	0.00E+00	<dl	<dl
	NO ₃ ⁻	6.47E-01	6.00E-01	6.30E-05	5.41E-01	1.60E-04	1.70E-01	7.10E-01	5.87E-04
	HCOO ⁻	(1.68)†	1.19E+00	<dl	1.02E+00	3.72E-03	5.00E-02	9.76E-01	4.65E-03
	NH ₄ ⁺ (††)		3.50E-02	1.58E-05	7.25E-02	3.32E-02		9.96E-02	9.36E-02

† Moles of HCOOH Added.

dl = detection limit

NA = not applicable

^aValues represent the total moles in the slurry plus moles in all slurry samples removed prior to the end of the process phase (i.e. formic acid addition, digestion,...).

For example, the amount of HCOO⁻ consumed in the slurry for Test 1.1 during HCOOH addition was (2.59-1.65) or 0.94 moles of HCOO⁻.

^bThe values in the 'Species in Condensate' represent the total moles present in the condensate that was removed during the process phase (i.e. HCOOH addition, digestion,...). For example, for Test 1.1 the NO₃⁻ moles found in the condensate collected during digestion was 9.26E-5 moles.

††Ammonium ion values may not indicate true production or loss. As the slurry and condensate pH increases above pH 7 ammonia forms from NH₄⁺. Ammonia is volatile and may be lost through the offgas system. Observed decreases in NH₄⁺ values may be the result of volatilization.

Table 5.4.2. Average, Maximum and Minimum Amounts of HCOO⁻, NO₂⁻, NO₃⁻ and NH₄⁺ Measured in Condensate for the FY 1991 Laboratory-Scale Feed Preparation Tests

Test	Total Amount of Ions in Condensate (moles)				Amount of Condensate Collected During Test (ml)	Initial Slurry Volume (ml)#
	NO ₂ ⁻	NO ₃ ⁻	NH ₄ ⁺	HCOO ⁻		
1.1	7.05E-06	1.10E-03	1.68E-03	7.77E-04	409	1590
1.2	1.34E-05	4.52E-03	2.99E-04	2.10E-05	294	1560
1.3	2.61E-04	3.16E-03	1.65E-03	9.69E-08	517	1520
2.1	2.14E-05	5.19E-03	2.07E-03	3.14E-06	151	1580
2.2	1.01E-05	2.37E-03	8.16E-04	2.69E-05	364	1540
3.1	0.00E+00	5.80E-05	1.51E-03	4.79E-04	508	1550
3.2	0.00E+00	4.70E-04	5.77E-03	8.25E-05	536	1540
4.1	4.09E-03	5.64E-04	7.80E-03	1.46E-05	420	1590
5.2	0.00E+00	9.04E-03	1.16E-07	4.49E-02	322	1520
6.1	0.00E+00	9.43E-04	8.31E-06	0.00E+00	5	1550
6.2	0.00E+00	1.48E-03	2.33E-05	9.33E-06	5	1520
7.1	0.00E+00	8.09E-04	9.69E-02	8.36E-03	417	1590
average**	3.67E-04	2.48E-03	9.88E-03	4.56E-03		
max**	4.09E-03	9.04E-03	9.69E-02	4.49E-02		
min**	0.00E+00	5.80E-05	1.16E-07	0.00E+00		

*Amounts were calculated from ion chromatography (NO₂⁻, NO₃⁻, and HCOO⁻) and selective ion electrode (NH₄⁺) analyses of the condensate. The weight of species/L was multiplied by the volume of condensate sample and then converted to moles. The quantities for all condensate samples produced in the test were added to produce the total moles of species for each test. The total volume of condensate collected during each test is shown in "Amount of Condensate Collected During Test." Note: Nitrite, NO₃⁻, HCOO⁻ and NH₄⁺ were also present in the slurry.

**Average, maximum, and minimum values of condensate species produced over the twelve FY 1991 test range.

#The initial slurry volume is shown in case the conversion to moles of species in the condensate per volume of slurry is desired.

approximately 1.6 times greater than in test 1.3. Both DSC and TGA data are summarized in Table 5.6.1. The data are grouped into four regions in which major energy and/or weight changes were observed. The temperature at which an energy change was initiated, and associated energy change (Joule/g slurry), normalized to wet slurry (125 g WO/L) and dried slurry are given. The temperature range and associated weight change relative to a wet slurry (125 g WO/L) are summarized in the TGA data. The thermograms are provided in Appendix G.

Table 5.5.1. Glass Redox ($\text{Fe}^{+2}/\Sigma\text{Fe}$) Before and After Recycle Addition and Selected Test Variables for Glasses Prepared from FY 1991 Melter Feed Simulant

Test	Glass Redox ($\text{Fe}^{+2}/\Sigma\text{Fe}$) ^a		Selected Test Variables		
	Before Recycle	After Recycle	Amount of HCOOH Added (mL 86.7 wt%/L)	Amount of NO ₂ - and NO ₃ - In the Initial Slurry Composition	
				NO ₂ - (mol)	NO ₃ - (mol)
1.1	0.06	0.02	74	0.65	0.20
1.2	0.03	0.05	27	0.65	0.20
1.3	0.02	0.06	49	0.65	0.19
2.1	0.05	0.06	49	0.65	0.20
2.2	0.02	0.02	49	0.65	0.20
3.1	0.02	0.02	49	0.20	0.20
3.2	0.08	0.04	48	0.40	0.20
4.1	0.04	0.03	49	0.65	0.20
5.2	0.01	NA	68	0.65	0.18
7.1	0.01	0.04	63	0.20	0.61

^aBased on preliminary studies at PNL (current study) and WSRC (Ramsey 1991), a large uncertainty (>70%) in the $\text{Fe}^{+2}/\Sigma\text{Fe}$ measurement exists for $\text{Fe}^{+2}/\Sigma\text{Fe} < 0.1$. Reported values are not considered to be significantly different. Total iron in the glass, ΣFe , as measured by ICP-ES was 5.3 wt% in glass. Redox measurements were not collected for tests 6.1 and 6.2

Table 5.6.1. Thermal Stability of NCAW Simulant, Formated NCAW Simulant and Formated NCAW Simulant Plus Recycle Simulant Measured from 40 to 700°C by DSC and TGA

**Region I
Endotherm (40-130 C)**

Sample (a)	DSC Data			
	Peak Initiation Temperature, C	Energy Change, Joule/g slurry		
		Slurry (125 gWO/L)	Dried Slurry	
		Method A (b,c)	Method B (d)	
1.1-47.1				
1.3 -7.1	46	13.5	96.17	103.4
1.3-32.1	possible peak	not measured	not measured	not measured
1.3-47.1	46	16.4	78.0	71.7

TGA Data	
Selected Temperature Range, C	Weight Loss wt% slurry, (125 gWO/L)
43-139	78.3
43-115	78.5
43-138	77.7
43-124	76.6

**Region II
Exotherm (125-250 C)**

Sample (a)	DSC Data			
	Peak Initiation Temperature, C	Energy Change, Joule/g slurry		
		Slurry (125 gWO/L)	Dried Slurry	
		Method A (b,c)	Method B (d)	
1.1-47.1	156	-69.4	-354	-305.1
1.3 -7.1	not observed	not observed	not observed	not observed
1.3-32.1	136	-44.2	-223	-207.2
1.3-47.1	124	-59.4	-283	-260.1

TGA Data	
Selected Temperature Range, C	Weight Loss, wt% slurry (125 gWO/L)
183-295	2.8
149-239	1.8
151-304	2.7

**Region III
Endotherm (230-310 C)
(no weight changes were detected in this region)**

Sample (a)	DSC Data			
	Peak Initiation Temperature, C	Energy Change, Joule/g slurry		
		Slurry (125 gWO/L)	Dried Slurry	
		Method A (b,c)	Method B (d)	
1.1-47.1	274	6.0	30.5	26.3
1.3 -7.1	137	37.1	265	284.9
1.3-32.1	217 to 224	13.7	69	64.1
1.3-47.1	237	10.1	48.2	44.3

No weight change observed.

Table 5.6.1. (contd)

Region IV
Endotherm (>300 C)
(no energy changes detected in this region)

Sample (a)
1.1-47.1
1.3-7.1
1.3-32.1
1.3-47.1

No energy change observed.

TGA Data	
Selected Temperature Range, C	Weight Loss, wt% slurry (125 gWOL)
537-679	1.3
516-641	2.8
516-680	1.6
517-686	1.9

Organic Carbon (as formate), Nitrate, and Nitrite Composition of Samples

Sample (a)	Measured Nitrate, Nitrite and Organic Carbon (as formate),					
	mg/g dried slurry (d)			g/L SRAT slurry (125 gWOL)		
	Organic Carbon	Nitrate	Nitrite	Organic Carbon	Nitrate	Nitrite
1.1-47.1	65.1	81.7	<dl	12.3	15.5	<dl
1.3-7.1	no formate	48.3	122.6	no formate	7.9	19.9
1.3-32.1	40.4	74.9	<dl	8.4	15.6	<dl
1.3-47.1	35.6	66.9	<dl	7.7	14.5	<dl

DSC: Differential Scanning Calorimetry

TGA: Thermogravimetric Analysis

Peak Initiation: Temperature at which change in energy is first detected.

- (a) 1.1-47.1: Test 1.1 conditions, formated NCAW simulant plus recycle.
- 1.3-7.1: Test 1.3 conditions, initial NCAW slurry simulant with nominal nitrite, nitrate and carbonate
- 1.3-32.1: Test 1.3 conditions, formated NCAW simulant (nominal formic acid addition)
- 1.3-47.1: Test 1.3, formate NCAW simulant plus recycle
- (b) Sample type used for thermal analysis
- (c) Method A, DSC sample preparation: a representative sample of slurry dried at 60°C for 24 hours to remove majority of water. The initial drying was required to reduce the risk of foaming/spattering and consequential equipment damage.
- (d) Method B, energy change or composition normalized to a sample dried in an oven at 105°C for 24 hours (refer to physical property data, wt.% solids)

6.0 Discussion

The discussion is directed toward the three primary objectives of the FY 1991 laboratory-scale feed preparation testing: offgas generation, reductant guidelines, and thermal stability of dried NCAW simulant. The offgas and slurry chemistry data presented in Section 5.0 have been evaluated to develop correlations and potential reaction mechanisms that apply to the generating of potentially hazardous gases and developing reductant guidelines to control glass redox. The format of this discussion is as follows:

1. evaluation of offgas generation data
2. assessment of alternative redox indicators and application of an SRTC formula to HWVP using cation solubility measurements
3. bases for HCOOH addition to control glass redox
4. summary of HCOOH offgas and glass redox control
5. evaluation of thermal analyses of NCAW simulant.

Discussion of simulant characterization is presented in Appendix A.

The reported findings are based on a limited number of tests and test variables. The operational and compositional envelope to which the key points apply is defined below.

Slurry simulant composition:	NCAW FY 1991, refer to Table 4.1.1
Recycle simulant composition:	refer to Table 4.1.4
Amount of HCOOH:	27 to 74 mL 86.7 wt% HCOOH/L slurry
HCOOH addition rate:	0.5 to 2 mL/min
HCOOH addition location:	Below slurry surface
NO ₂ concentration:	0.13 to 0.45 moles NO ₂ /L slurry
NO ₃ concentration:	0.13 to 0.40 moles NO ₃ /L slurry
CO ₃ ⁻² concentration:	0.13 moles CO ₃ ⁻² /L slurry
Formating temperature:	95°C
Digestion/concentration temperature:	100°C (rapid boiling not observed)
Test duration:	~ 10 hours
Sweep gas:	Ar/4% O ₂ (air for test set 5)
Initial slurry volume:	1.5 L
Reaction vessel volume:	2 L

Note: All concentrations are based on slurry @ 125 g WO/L.

6.1 Evaluation of Offgas Generation Data

Four offgas components are addressed directly, H_2 , N_2O , NO_x , and NH_3 . The generation of CO_2 is included in material balance calculations discussed in Section 6.3. Carbon monoxide and N_2 were not detected during the laboratory-scale tests.

6.1.1 Hydrogen Generation

It has been speculated that H_2 is derived via noble metal catalysis of $HCOOH$ decomposition.^(a) The plant vessel and ventilation systems must be designed to avoid a potential buildup of H_2 above the LFL. The LFL for H_2 in air is 4% and somewhat lower in the presence of N_2O .

An objective of the FY 1991 laboratory-scale feed preparation study was to measure peak H_2 generation rates that would be considered for evaluation of plant H_2 mitigation options. The following discussion provides a description of the H_2 generation profile and associated peak generation rates, proposes a correlation for predicting when significant H_2 release might occur, suggests possible implications of NH_3 generation relative to H_2 release, and compares the PHTD data with some SRTC data.

The H_2 generation profile for FY 1991 tests with NCAW simulant containing noble metals was characterized by an initial peak rate of <0.05 mmoles H_2 /min-L at 125 g WO/L. The second peak rate, if present, ranged from 0.21 to 0.75 mmoles H_2 /min-L at 125 g WO/L, which is significantly higher than the first peak. The second peak was initiated near the end of $HCOOH$ addition. Hydrogen generation in non-noble metal simulant tests was <0.05 mmoles H_2 /min-L at 125 g WO/L throughout the duration of the test.

Under the conditions tested, a correlation was derived that provided a means of predicting the amount of $HCOOH$ required to initiate significant H_2 release as a function of the initial NO_2 concentration. The correlation is shown in Figure 6.1.1.^(b) A region encompassing the data points rather than a line is shown to indicate some expected uncertainty in the correlation. Figure 6.1.1 indicates that less $HCOOH$ is required to generate significant H_2 release as the NO_2 concentration of the slurry decreases.

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- (a) Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company, HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (b) Within the variable range tested, the "induction time" (defined as the time from beginning of $HCOOH$ addition to initiation of the second H_2 release) increases with an increase in the initial amount of NO_2 present. The induction time appears also to decrease with an increase in $HCOOH$ addition rate. The difference in induction time for significant H_2 release between test 3.1 (0.57 mL/min) and test 7.1 (0.48 mL/min) is illustrated in Figure E6.a.

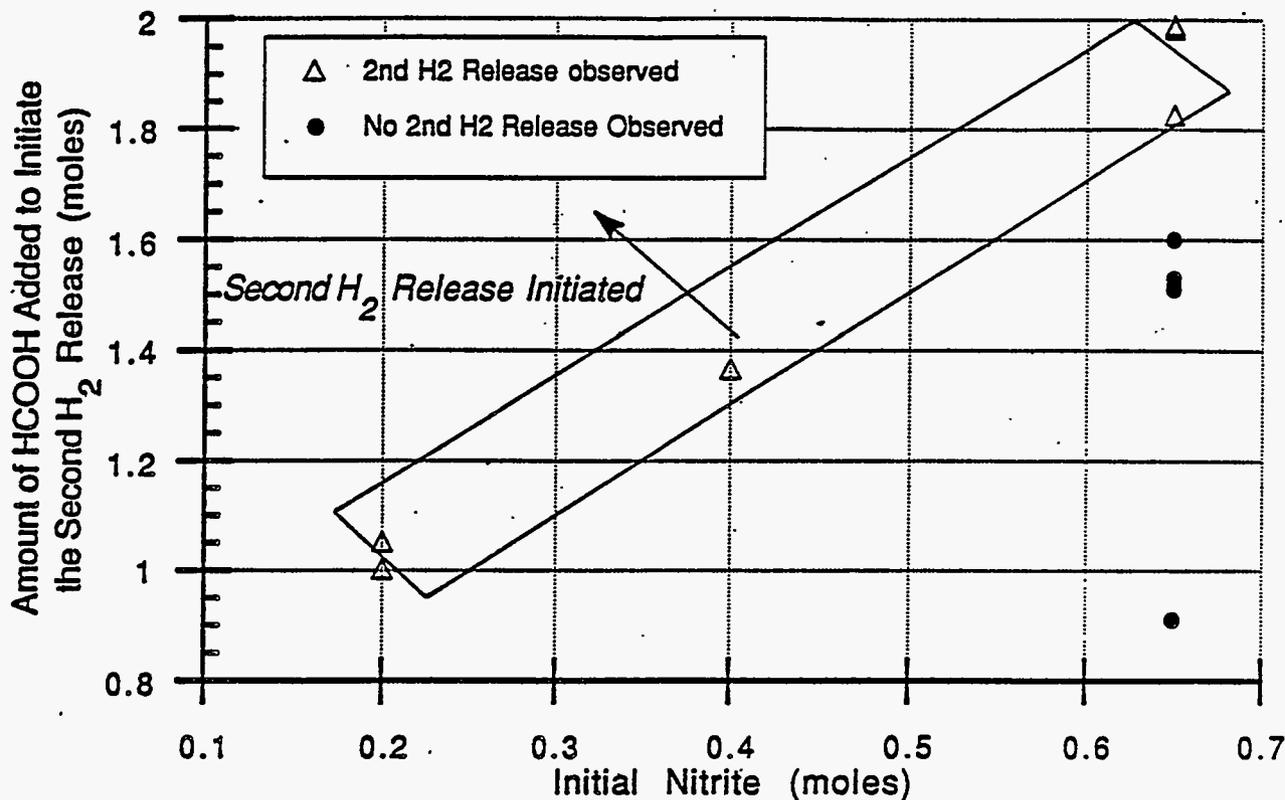


Figure 6.1.1. Estimated Boundary Region for Initiation of Significant H₂ Release as a Function of HCOOH and NO₂ Content in NCAW Simulant

Redox correlations^(a) indicate that the quantity of HCOOH required for glass redox control will increase in proportion to the NO₃ content of the slurries. The redox information and the results from the FY 1991 laboratory-scale tests suggest that the highest H₂ generation case may be a slurry containing noble metals with low NO₂ and high NO₃ concentrations because the slurry would have the largest HCOOH requirement but the lowest NO₂ concentration.

Under the conditions tested, the H₂ generation rate profile and peak height for the second H₂ release appear to be quite sensitive to the point in the process at which HCOOH addition is interrupted. A 20-fold increase (compare tests 1.3 and 6.1; see Figures D3 and D11, respectively) in peak H₂ generation rates was observed over a time interval of less than 10 min. Compared with test 1.1 (Figure D1) in which 7-9 mL/L more HCOOH was added, the H₂ generation rate was 1.3 to 2 times greater for test set 6. This observation is presently unexplained. Other factors to which H₂ generation

(a) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.

is extremely sensitive such as minor differences in noble metal concentration and temperature, may also have contributed to the observed differences in peak H₂ generation rate. Selected tests should be repeated to verify the observed phenomena if these results are found to be important to plant design or operations.

Hydrogen may be consumed in the production of NH₃ (discussed below). Based on the amount of NH₄⁺ measured during laboratory-scale testing, a large fraction of the H₂ liberated from HCOOH decomposition reacts to form NH₃ rather than offgassing as H₂ or reducing metallic waste elements. Based on the total NH₄⁺ measured in test 7.1, 0.197 moles (refer to Table 6.1.3) and the proposed mechanism for NH₃ generation, $2\text{NO} + 5\text{H}_2 \rightarrow 2\text{NH}_3 + 2\text{H}_2\text{O}$, approximately 0.493 moles of H₂ in addition to the H₂ measured, 0.0449 moles, (refer to Table 5.3.2) were generated (0.536 moles H₂ total per 1.5 L NCAW). This amount of H₂ corresponds to approximately 30% of the HCOOH added, decomposing to form H₂ and indirectly NH₃. Note that some of the NH₃ may have escaped from the alkaline condensate into the offgas. The actual amount of NH₃ produced during testing may be higher than reported.

A comparison of peak H₂ generation rates as a function of the amount of HCOOH added for PHTD and SRTC laboratory-scale tests is shown in Figure 6.1.2. The most significant difference in H₂ generation rate between the Laboratories is in the lower HCOOH addition range. The difference may be attributed to a relationship between the initial NO₂ concentration and the amount of HCOOH required to generate the second H₂ release. The amount of NO₂ in all the PHTD tests conducted in the lower HCOOH addition range (tests 3.1, 7.1, and 3.2) was below the FY 1991 reference HWVP NCAW slurry composition. The NO₂ concentration of the SRL simulants was not available at the time of this evaluation.^(a) During some of the SRTC tests, relatively long processing times (15 to 20 h) were experienced before the second H₂ peak was observed. The long processing time prior to the appearance of the second H₂ peak may be due to high initial NO₂ concentrations in the simulants and/or the addition of enough HCOO⁻ in the precipitate hydrolysis process (PHA) stream to reach a required threshold value for significant H₂ release.

Preliminary results from the recent large-scale studies in the Integrated Defense Waste Processing Facility (DWPF) Melter System (IDMS) with HWVP NCAW slurry simulant have lent support to the H₂ generation profile, generation rate, and requirements for the second H₂ release observed during the PHTD laboratory-scale test results.^(b) Studies have been conducted at the SRTC

(a) Nitrite concentrations are given by Ritter (1992) as 2.14 to 9.31 wt% on a dry-slurry basis.

(b) Hutson, N. D. 1992. "Integrated DWPF Melter System (IDMS) Campaign Report." *Hanford Waste Vitrification Plant (HWVP) Process Demonstration*. WSRC-TR-0404, Rev. 0, UC-721.

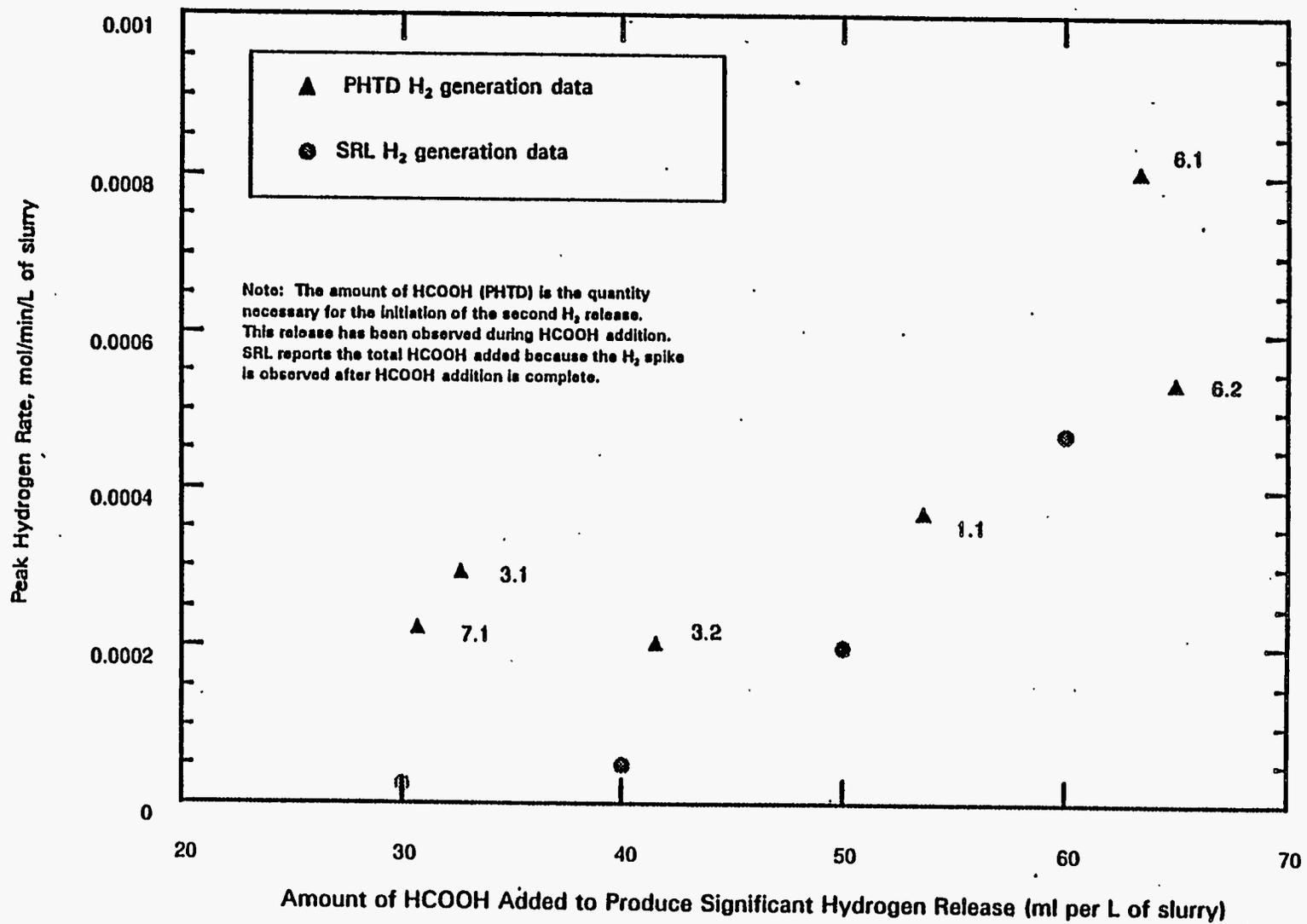


Figure 6.1.2. Comparison of Peak H₂ Generation Rates with Quantity of HCOOH for SRTC and PHTD Simulants

(Ritter et al. 1992) and at the University of Georgia^(a) to characterize the effect of noble metals on H₂ generation in DWPF slurry simulants. These tests indicate that Rh is the most catalytically active metal in the simulants.

Effects of HCOOH addition rate on H₂ generation were not determined because the amount of formic acid added in tests 1.3, 2.1, and 2.2 was not sufficient to generate the second hydrogen peak.

Because the laboratory-scale tests covered a narrow range of possible conditions, other conditions might increase the H₂ generation rate above that observed, including different processing temperatures, catalyst concentrations, and bounding minimum NO₂/maximum NO₃ simulants for the HWVP. Dependence of H₂ generation on variables such as organic complexing agents and pH is not known.

6.1.2 N₂O and NO_x Generation

Nitrous oxide (N₂O) is an oxidant which may impact the LFL for potentially explosive gases released during processing, including H₂ and some organics. Nitric oxide and NO₂ which comprise NO_x are regulated^(b) gases. Determination of NO and NO₂ generation rates are required to design the vessel ventilation and abatement systems properly. Collection of dilute HNO₃ formed from condensation of NO₂ in the condensate streams will need to be considered with respect to pH and NO₃ concentrations in recycle waste streams. Nitric oxide and NH₃ in the vessel ventilation system present a potential for build up of NH₄NO₃, an explosive under certain situations. Organics in the offgas stream may increase the risk of an NH₄NO₃ detonation. Oxides of nitrogen and NH₃ have been detected in the offgas during testing at PNL and SRTC. Analyses of the FY 1991 laboratory-scale feed preparation tests are included below.

Releases of N₂O and NO_x were initiated while adding HCOOH to the NCAW simulant. The release sometimes continued into early stages of digestion. The ratio of the two gas amounts varied significantly, between N₂O/NO_x = ~7 for noble metal-containing slurry simulants and N₂O/NO_x = ~0.07 for a non-noble metal slurry simulant. In general, for a slurry simulant containing noble metals, the release was initiated around a slurry pH of 7.5 (@ 95°C). This corresponds to approximately 20 to 30 min after starting to add HCOOH under specific test conditions. In the non-noble metal slurry simulant, the release was initiated at a much lower pH, between 4 and 5 (@ 95°C). In test 5.2, the release of N₂O and NO_x occurred approximately 50 min after starting to add HCOOH. It appears that releases of both gases are initiated at about the same time, but further evaluation of the data would be necessary to confirm the exact initial detection times.

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- (a) Refer to technical reports prepared by R. B. King, A. D. King, N. K. Bhattacharyya, T.-H Lim and G. Vemparaia. The report series is entitled "Elucidation of Noble Metal/Formic Acid Chemistry During DWPF Feed Preparation."
 - (b) Regulation agencies include the Environmental Protection Agency, Washington State Department of Ecology and Occupational Safety and Health Administration.

For a typical run with a noble metal slurry simulant, the N_2O generation rate initially increased rapidly, flattened, and then decreased suddenly (see Appendix D). Increase in generation rate of NO_x was much less rapid and decreased suddenly with N_2O . The decrease in generation of N_2O and NO_x coincided with the estimated time for NO_2^- depletion in the slurry and the initiation of the second H_2 release. Figure 6.1.3 illustrates this phenomena with a graph of H_2 generation rate and slurry NO_2^- concentration for test 3.2.

The simultaneous depletion of NO_2^- with the initiation of H_2 release suggests that NO_2^- may inhibit H_2 release. Depletion of NO_2^- may result in additional H_2 release, the amount and generation rate being dependent upon conditions such as the concentration of $HCOOH/HCOO^-$, slurry pH, temperature, and noble metals concentration. It should be noted that the laboratory-scale tests reported herein were conducted over a ~ 10 h period at elevated temperatures. Ritter (1992) has observed H_2 generation 15 to 20 h into test runs using the DWPF process flowsheet. The DWPF process flowsheet includes the addition of a PHA stream after $HCOOH$ addition and digestion. Additional formate in the PHA stream

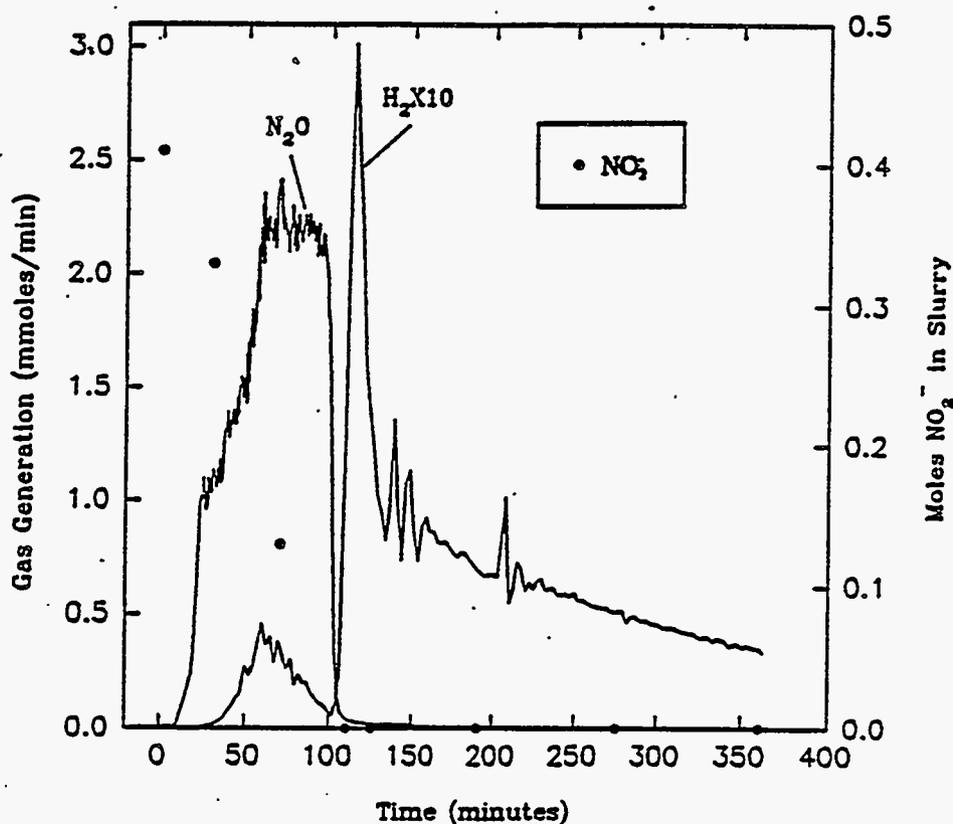


Figure 6.1.3. Hydrogen and N_2O Generation Rates and NO_2^- Concentration in NCAW Simulant (Test 3.2) as a Function of Process Time Showing the Initiation of the Second H_2 Release and the Decrease of N_2O Production with NO_2^- Depletion

may be sufficient to initiate H₂ release in the extended processing phases (e.g., 15-20 h after HCOOH addition). A second H₂ release was not observed within the 2-h period after adding the recycle waste stream simulant during the FY 1991 testing suggesting that the amount of HCOOH in the recycle waste stream was not sufficient to initiate additional significant releases. Testing the HWVP process cycle for longer durations would be required to examine the potential for H₂ release later in the process steps.

Carbon dioxide generation preceded or was coincident with N₂O and NO_x release. (Generation of CO₂ results from H₂CO₃ decomposition and as a product of reactions in which HCOOH is a reductant.) For the non-noble metal slurry simulant (refer to Figures D10 and E5a to d), two stages of CO₂ were observed. The first may correspond to H₂CO₃ decomposition, followed by the release of CO₂ coincident with NO_x and N₂O generation as a product of NO₂ reduction. Integration of the second peak may provide some insight in to the amount of NO_x produced via HCOOH reduction of NO₂ versus NO_x produced by disproportionation of HNO₂. For the noble metal slurry simulant tests, the CO₂ produced from HCOOH reduction versus HNO₂ disproportionation is not visually differentiated.

The relative amounts of N₂O and NO_x produced vary depending on test conditions. Table 6.1.1 compares the N₂O and NO_x ratios for NCAW and DWPF slurry simulants after treatment with HCOOH. Equipment configuration, HCOOH addition rate, slurry composition, and pH are a few of the variables thought to contribute to the observed differences. Further data is required to fully characterize conditions controlling generation of N₂O and NO_x. Identification of process conditions and their relationship to HWVP slurry chemistry is required to predict offgas compositions and generation rates from the wide range of HWVP slurry compositions. Reactions that produce N₂O and NO_x via HCOOH consumption may also affect glass redox because of the reduced amount of reductant available to react in the melter.

Table 6.1.1. Comparison of N₂O/NO_x Ratios for NCAW and DWPF Slurry Simulants After Treatment with HCOOH

<u>Origin</u>	<u>Scale</u>	<u>Type of Feed</u>	<u>N₂O/NO_x</u>
PHTD	laboratory	NCAW with noble metals	7
PHTD	laboratory	NCAW w/o noble metals	0.07
SRL ^(a)	large	NCAW with noble metals	~1
SRL ^(b)	large	DWPF with noble metals	<<1

(a) Hutson, N. D. 1992. "Integrated DWPF Melter System (IDMS) Campaign Report. *Hanford Waste Vitrification Plant (HWVP) Process Demonstration.*" WSRC-TR-0403, Rev. 0, UC-721.

(b) Ritter, J. A., et al. 1990. "Integrated DWPF Melter System (IDMS) Campaign Report Coupled Feed Operation." WSRC-TR-90-131.

The N_2O/NO_x ratios for PHTD FY 1991 laboratory-scale tests with an NCAW slurry simulant are listed in Table 6.1.2. The earlier reported value of $N_2O/NO_x = 7$ is based on tests 1.1, 1.3, 2.2, 3.2; and 4.1. The discussion below uses the amounts and ratio of N_2O/NO_x from these five tests as a reference point. The reference N_2O/NO_x value is the highest and most reproducible value observed for gas measurements. Other higher reported ratios were derived with gas data close to the analytical detection limit and are therefore less reliable.

The lower overall $N_2O + NO_x$ emissions observed in test 1.2 can be attributed to the low amount of HCOOH added compared with tests using the same amount of NO_2 (1.1, 1.3, 2.1, 2.2, 4.1, 5.2, 6.1, and 6.2). Approximately 2/3 the amount of N_2O and NO_x were produced during test 1.2. Nitrite remained in the slurry even after an additional ~6 h of processing at 100°C. The persistence of NO_2 is attributed to insufficient HCOOH addition. A somewhat higher N_2O/NO_x value for test 1.2 was observed, which suggests that release of N_2O over NO_x may be more favorable in the alkaline pH regime experienced throughout this run.

The overall amount of $N_2O + NO_x$ emissions was exceptionally low in tests 3.1 and 7.1. This is attributed to the lower initial amount of NO_2 . Within estimated experimental error, the ratio of N_2O/NO_x for tests 3.1 and 7.1 is the same as the reference tests (1.1, 1.3, 2.2, 3.2, and 4.1). A larger uncertainty exists with the N_2O/NO_x ratios for tests 3.1 and 7.1 because the measured gas concentrations were near detection limits.

The lower N_2O/NO_x ratio in test 2.1 may be attributed to a higher rate of HCOOH addition. High HCOOH addition rates may lead to more concentrated zones of acid, favoring NO_x production via HNO_2 disproportionation. Higher NO_x production was also observed when HCOOH was added for short periods (< 1 min) above the slurry surface, a configuration that could also result in localized high acid conditions. Lower total N_2O and NO_x amounts for test 2.2 may be due to an observed loss of reaction vessel gas tightness during the test.

Tests 5.1 and 5.2 did not contain noble metals. The ratio of N_2O/NO_x was < 1. The production of N_2O may be in some way assisted by the presence of noble metals; however, it is not certain whether the N_2O/NO_x ratio depends on the noble metal concentration. The highest N_2O/NO_x ratios have been observed in the presence of a calculated 25% excess of Rh (above FY 1991 NCAW reference value). The slurry pH reached during forming of the non-noble metal slurry simulant was several pH units lower (more acidic) than in tests conducted with slurry simulants containing noble metals. The acid environment may be one contributor to a favored NO_x over N_2O production.

Tests 6.1 and 6.2 were conducted in a manner similar to test 1.1 (in NO_3 and NO_2 concentrations) with the exception of a slightly reduced HCOOH addition rate and interruption of the second H_2 release through early termination of HCOOH addition. The interruption occurred after the N_2O and NO_x releases were completed. The somewhat lower N_2O/NO_x value for tests 6.1 and 6.2 is currently unexplained.

Table 6.1.2. Comparison of NCAW Slurry Target Amount of NO₂, Measured N₂O and NO_x Offgas and Related Molar Ratios, and HCOOH Addition (amount and rate) for FY 1991 Laboratory-Scale Feed Preparation Tests

Test Number	Target Amount of NO ₂ - In Slurry, moles	Measured Amount of Gas, moles		Stoichiometry Ratios**		HCOOH Addition	
		N ₂ O	NO _x	N ₂ O/NO _x	N ₂ O/NO ₂ -	Amount, mL/L	Rate, mL/min
1.1	0.65	0.236	0.03	7.8	0.4	74	0.6
1.2	0.65	0.153	0.014	10.9	0.2	27	0.6
1.3	0.65	0.243	0.035	6.9	0.4	49	0.57
2.1	0.65	0.162	0.118	1.4	0.2	49	2, 1, 0.52*
2.2	0.65	0.219	0.032	6.8	0.3	48	0.99
3.1	0.2	0.077	0.007	11.5	0.4	49	0.64
3.2	0.4	0.148	0.019	7.7	0.4	46	0.57
4.1	0.65	0.243	0.032	7.5	0.4	45	0.56
5.2	0.65	0.021	0.265	0.1	0.0	68	0.51
6.1	0.65	0.241	0.052	4.6	0.4	65	0.49
6.2	0.65	0.223	0.046	4.8	0.3	67	0.49
7.1	0.2	0.08	0.004	18.4	0.4	55	0.48

Test data used collectively as a reference case in text are shaded. These test conditions resulted in the highest N₂O/NO_x ratios of acceptable analytical certainty.

*Due to excessive foaming the formic acid addition rate was slowed from 2 mL/min to 1 mL/min and finally to 0.52 mL/min. It was necessary to reduce the formic acid addition rate to reduce the foam and prevent further fouling of the condenser system.
 **Ratios given for stoichiometry were calculated from N₂O, NO₂-, and NO_x data with more significant figures. Direct calculation from N₂O, NO₂-, and NO_x data may not result in the exact values given in "stoichiometry."

The fraction of NO₂ reduced to N₂O during the addition of HCOOH to noble metal-containing simulants ranged from 57 to 100%. The lowest fraction was observed for the minimal amount of HCOOH addition (test 1.2, 27 mL 87 wt% HCOOH/L @ 125 g WO/L slurry). Nitrite remained in the slurry at the completion of test 1.2. The highest fractions of NO₂ converted to N₂O were observed with the higher HCOOH additions (tests 1.1 and 7.1) and in tests with low NO₂ (tests 3.1, 3.2, and 7.1). These five tests resulted in complete NO₂ depletion. Tests with nominal NO₂ and relatively mid-range HCOOH addition (tests 1.3 and 4.1, 48 mL 87 wt% HCOOH/L @ 125 g WO/L slurry) resulted in relatively mid-range fractions of NO₂ conversion to N₂O (78 to 86%) released during HCOOH addition. Increasing the HCOOH addition rate decreased the fraction of NO₂ reduction to N₂O (during HCOOH addition) to 66%. The above observations suggest that the release of N₂O may be related to the initial amount of NO₂, the amount of HCOOH added, and the HCOOH addition rate. Other variables such as pH and the concentration of noble metals may also affect the N₂O production.

For the NCAW slurry simulants containing noble metals, the stoichiometry based on estimated HCOOH consumption, NO₂ depletion time, and measured N₂O production compares well with the reaction

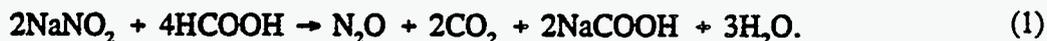


Figure 6.1.4 illustrates the nearly 1:1 correlation of measured NO₂ and HCOOH consumed. To produce Figure 6.1.4, the assumption was made that the consumption of HCOOH was entirely due to the reduction (consumption) of NO₂ to N₂O rather than NO. The amount of HCOOH consumed was based on measured values of HCOO⁻ remaining in the slurry versus the amount of HCOOH added. The reduction of MnO₂ also consumed HCOOH, but was considered negligible because the MnO₂ concentration in the slurry was ~0.03 moles^(a) compared with 0.65 moles of NO₂ in 1 L of FY 1991 NCAW reference simulant.

Using a plot of NO₂ concentration versus time from the beginning of HCOOH addition, the time for total NO₂ consumption was estimated by extrapolation of three data points for slurry NO₂ concentration to zero NO₂ in the slurry. The amount of HCOO⁻ in the slurry at that time was estimated by interpolation between measured HCOO⁻ slurry concentrations. The amount of HCOOH consumed was estimated by subtracting the measured amount of HCOO⁻ in the slurry from the total amount of HCOOH added at that time.

Nitric oxide may be produced by disproportionation of HNO₂,



(a) For every mole of MnO₂, one mole of HCOOH is consumed. If all of the slurry MnO₂ was reduced by HCOOH only 0.03 moles of HCOOH would be consumed.

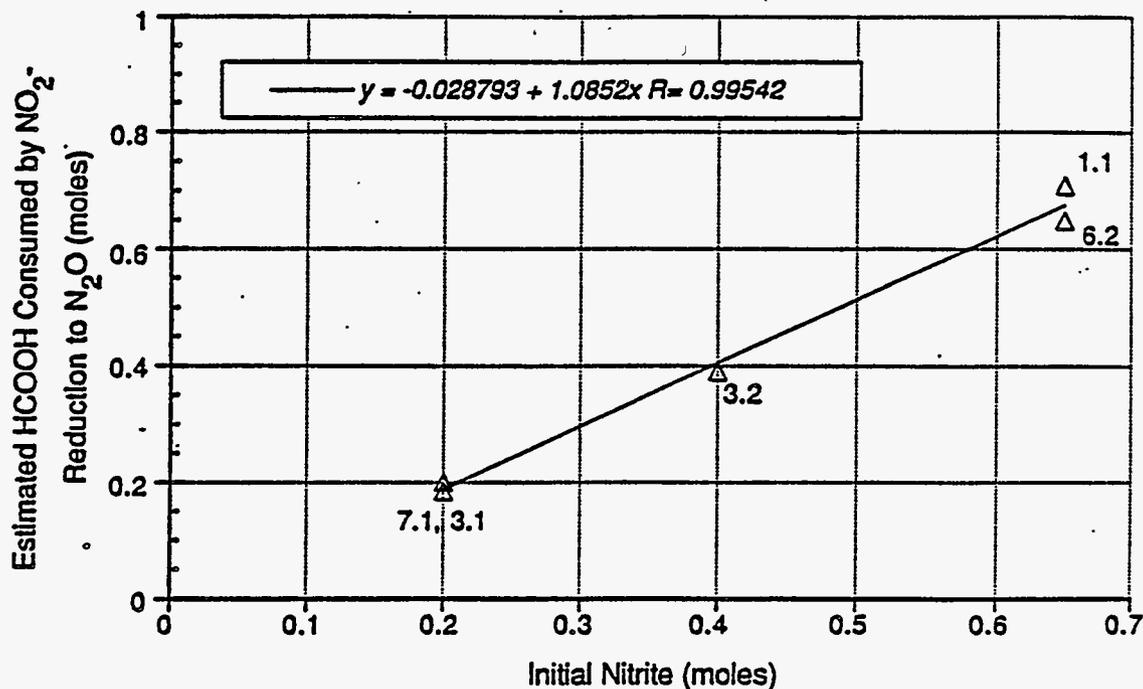
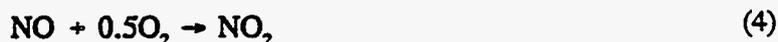


Figure 6.1.4. Estimated Amount of HCOOH Consumed by Reaction with NO₂⁻ (reduction to N₂O) for Selected NCAW Slurry Tests

or reduction of NO₂⁻ by HCOOH,



Nitric oxide may be consumed and NO₂ produced by the exothermic reaction,



Although small amounts of NO₂ may have been produced during forming of simulants containing noble metals, the characteristic yellow-brown color of NO₂ gas was only observed during tests without noble metals (test 5.2). A measured decrease in the oxygen concentration was also measured during test 5.2 which might be expected as given by equation 4.

Because the observed amount of NO_x released during forming of simulants containing noble metals was so low relative to N₂O (~ a factor of 10), the origin and speciation of the NO_x did not significantly impact the stoichiometry observed between NO₂⁻ and HCOOH. As a first approximation, it

was assumed that all of the measured NO_x represented NO and that the NO was produced via disproportionation of NO_2 (refer to equation 2) rather than reduction of nitrite by HCOOH (refer to equation 3). HCOOH consumption was therefore attributed only to reduction of NO_2 to N_2O (refer to equation 3). Reactions with other oxidized species such as MnO_2 were not accounted for in this preliminary estimate.

Measurement of NO release was conducted only on an intermittent basis. In general, the NO/NO_x ratio for tests with slurry containing noble metals ranged from 0.71 to 0.88. During a test with a non-noble metal simulant, the NO/NO_x ratio was measurably lower, ranging from 0.25 to 0.64. This agrees well with the visually observed NO_2 (brown) gas during tests with non-noble metal simulants and the absence of brown gas during tests with noble metal-containing simulants.

Figure 6.1.5 illustrates the increase in N_2O and NO_x in NCAW slurry with NO_2 consumed. The $\text{N}_2\text{O}/\text{NO}_x$ is 0.36, close to the predicted 0.5 (per equation 1).

Stoichiometry and mass balance of slurry components and product gases were not evaluated for the non-noble metal slurry simulant test (test 5.2) because efforts in this study concentrated on the noble metal slurry simulant offgas generation, in particular, H_2 . Test 5.2 does provide a significantly

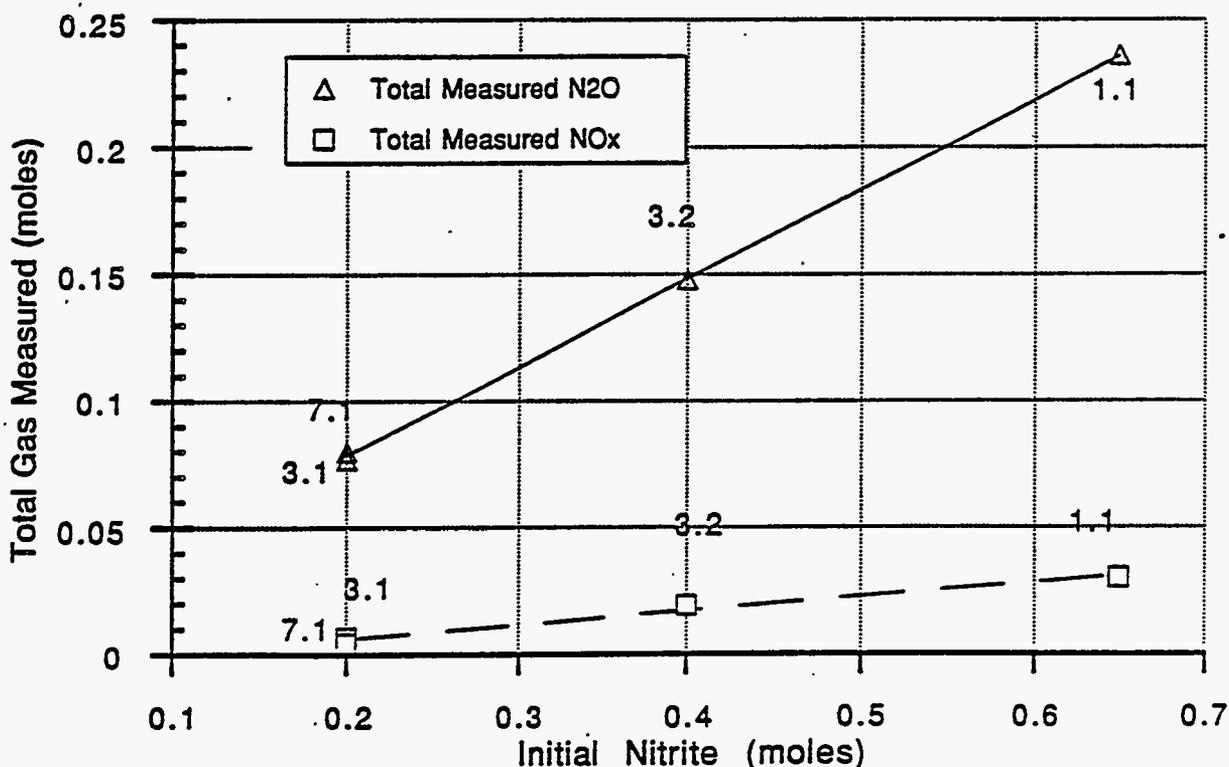


Figure 6.1.5. Total Amount of N_2O and NO_x , Generated by the NCAW Slurry as a Function of Initial NO_2

important reference point with respect to noble metal behavior by providing the zero noble metal concentration case for H₂ generation. The offgas data from test 5.2 may also be applicable to safety reviews for large-scale tests and to evaluation of offgas design issues related to HWVP slurries that do not contain noble metals, assuming other components relevant to offgas generation such as CO₃⁻² and NO₂ are within the test variable range.

6.1.3 Ammonia Generation

Ammonia generation is a safety concern because in the presence of NO₂ and water vapor in the offgas, a potential exists for buildup of NH₄NO₃ in the ventilation system. Under some conditions, particularly in the presence of organics, NH₄NO₃ can be explosive (Sykes et al. 1963). Ammonia has been previously reported as a product of HCOOH addition to NCAW simulant.^(a) Deposits of NH₄NO₃ have been recently observed during the operation of IDMS.^(b) Amounts of NH₄⁺ measured, changes during processing, distribution between slurry and condensate phases, and correlations with other test variables are discussed below.

Ammonium ion concentrations were measured for both slurry and condensate samples collected during the FY 1991 laboratory-scale feed preparation testing. Ammonia that remained gaseous or was revolatilized from the condensate was not measured. Table 6.1.3 summarizes the NH₄⁺ data for slurry and condensate samples. Total moles of NH₄⁺ measured in the slurry (including moles of NH₄⁺ in slurry samples removed) as a function of time is shown for each test in Appendix H. Changes in amount of NH₄⁺ on the order of 0.0001 moles are considered to be at the analytical detection limit. The detection limit for NH₃ using the selective ion electrode instrument is 0.1 ppm. The following is a guide to assist in correlating the principle test variables with the appropriate figures:

Figure	Tests Variable	Test Set
H1	HCOOH amount	1.1, 1.2, 1.3
H2	HCOOH addition rate	1.3, 2.1, 2.2
H3	Nitrite concentration	1.3, 3.1, 3.2
H4	Reflux during digestion	1.3, 4.1
H5	Noble metal concentration	1.1, 5.2
H6	Quenching of second H ₂ peak	1.1, 6.1, 6.2
H7	Low NO ₂ /high NO ₃ concentration	3.1, 7.1

- (a) Wiemers, K. C. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.
- (b) Chang, B., P Shriner and B. Nguyen. 1992. *Ammonium Nitrate Mitigation in the CPC*. WSRC-TR-02-379.

Table 6.1.3. Amount of NH_4^+ in Slurry and Condensate Samples Collected During FY 1991 Laboratory-Scale Feed Preparation Tests

Test	Total Amount of NH_4^+ Produced During Testing (moles)			Percent of NH_4^+ in Condensate
	Slurry	Condensate	Total	
1.1	1.09E-01	1.68E-03	1.11E-01	1.5
1.2	3.36E-04	2.99E-04	6.35E-04	47.1
1.3	4.42E-03	1.65E-03	6.07E-03	27.2
2.1	1.19E-02	2.07E-03	1.40E-02	14.8
2.2	2.83E-03	8.16E-04	3.65E-03	22.4
3.1	5.33E-02	1.53E-03	5.48E-02	2.8
3.2	2.25E-02	5.77E-03	2.83E-02	20.4
4.1	1.26E-03	7.80E-03	9.06E-03	86.1
5.2	1.03E-04	1.16E-07	1.03E-04	0.1
6.1	9.47E-03	8.31E-06	9.48E-03	0.1
6.2	8.01E-03	2.33E-05	8.03E-03	0.3
7.1	9.97E-02	9.69E-02	1.97E-01	49.3

The greatest fraction of NH_4^+ measured (0.4 to 0.6) was observed after recycle waste stream addition and during subsequent concentration. The second greatest fraction of NH_4^+ (0.2 to 0.35) was measured during HCOOH addition and the least amount during digestion (0.2-0.24%). In test 4.1, in which the digestion period was increased from 4 to 8 h, 93% of the NH_4^+ was generated during digestion. This suggests that the generation of NH_4^+ may be time dependent.

Changes in the amount of NH_4^+ measured in the condensate over the processing period were observed. The difference in values from sample to sample was generally within analytical and calculated uncertainties (1×10^{-4} to 1×10^{-6} moles). The relative change in the amount of NH_4^+ measured in the condensate was less than 3% of the total NH_4^+ produced.

Relative distribution of NH_4^+ between slurry and condensate is shown in Figure 6.1.6. The relative distribution of NH_4^+ between slurry and condensate is believed to be strongly dependent on the slurry pH, process duration, and perhaps, the total amount of NH_3 produced. Release of NH_3 from the slurry is promoted by alkaline pH, extended processing periods, and higher NH_3 production. The highest fractions of NH_4^+ measured in the condensate were found in test 4.1 (extended digestion period), test 1.2 (low HCOOH addition resulting in relatively high pH (>7) through most of processing period), and test 7.1 (largest amount of NH_3 produced per liter of NCAW simulant and relatively high final pH (>7)). Because the condensate was alkaline (pH ~ 9) during significant NH_3 generation

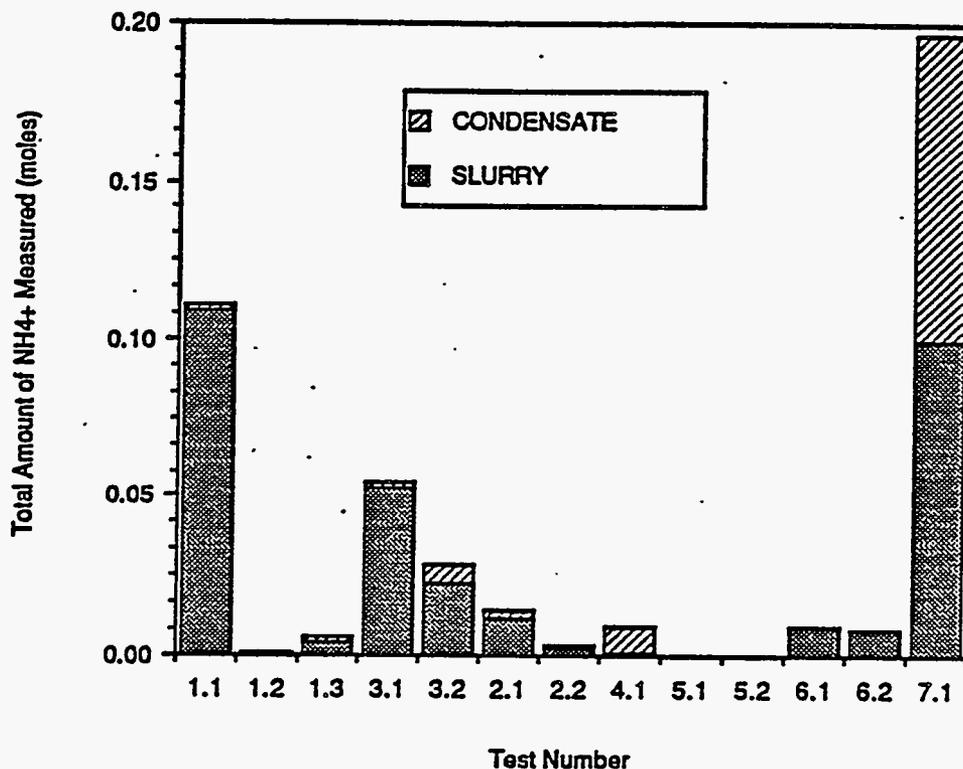


Figure 6.1.6. Distribution of Total NH_4^+ in Slurry and Condensate Collected During Processing of NCAW Simulant for FY 1991 Feed Preparation Tests

periods, an unknown amount of NH_3 may have been swept away by the carrier gas. Ammonia was not measured in the offgases for reasons discussed in the equipment description section.

The maximum NH_3 generation was observed in test 7.1. Simulant for this test contained a low NO_2 /high NO_3 concentration. The amount of HCOOH added was sufficient to initiate the second H_2 release. Unlike most other tests, approximately one-half of the NH_4^+ was found in the condensate. The amount of NH_4^+ in the condensate was much (1 to 5 orders) higher than any other test condensate. A profile of NH_4^+ production for test 7.1 is shown in Figure 6.1.7. As in other tests, the majority of NH_4^+ in the condensate was detected in the condensate collected after the recycle waste stream addition and during the subsequent concentration step.

A positive correlation of NH_3 production with measured H_2 production and NO_3 present in the slurry was observed. Conditions that favored H_2 production, such as NO_2 depletion and the presence of noble metals, resulted in higher concentrations of NH_4^+ . The amount of NH_3 produced in tests without a second H_2 release (tests 1.2 and 5.2) was relatively low.

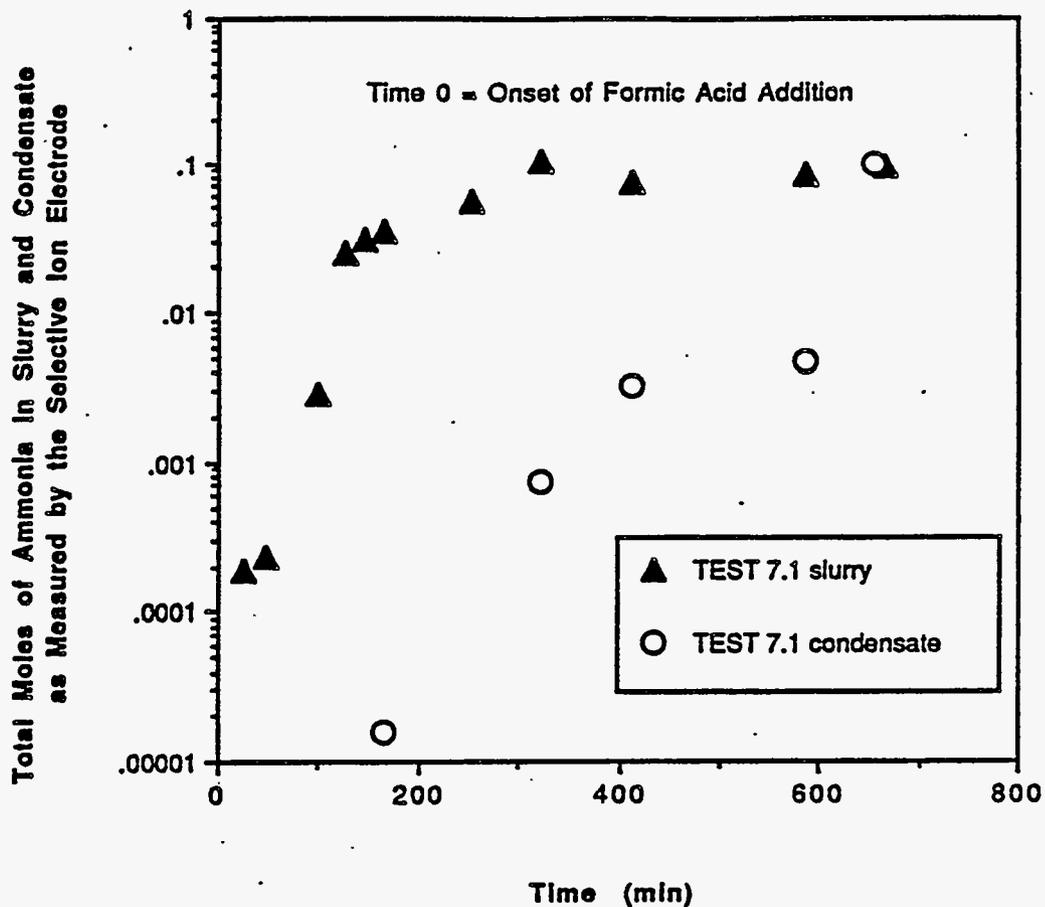


Figure 6.1.7. Distribution of NH_4^+ in Slurry and Condensate Collected During Processing of NCAW Simulant for FY 1991 Tests 7.1. Ammonium ion is reported as NH_3 , as measured by selective ion electrode.

Estimated initiation times for significant NH_3 production,^(a) initiation time for second H_2 release, and estimated time for complete depletion of NO_2 are given in Table 6.1.4. The times are

- (a) The criterion for estimating the initiation of ammonia generation was concentration of ammonium ion in slurry $> 2 \times 10^{-2}$ to 3×10^{-2} g NH_4^+ /L. This concentration range was chosen because in tests where the second H_2 release did not occur, the concentration of ammonium ion did not increase above this range. This time range shown in Table 6.1.4 for ammonia induction as provided by a limited number of samples taken at various times during processing. It was not possible to estimate the actual time of ammonia evolution unless the time corresponded to the withdrawal of a slurry sample. The width of the ammonia induction time range is entirely dependent on the sample removal time and not on any process variables. Hence there is no significance to the larger induction range exemplified by test 1.1.

Table 6.1.4. Comparison of Times for NO₂ Depletion, Initiation of the Second H₂ Release, and Measurable NH₄⁺ Production for FY 1991 Laboratory-Scale Feed Preparation Tests (1.1, 3.1, 3.2, 6.1, 6.2, 7.1)

Test No.	Second H ₂ Release Initiation Time* (min)	NO ₂ ** Depletion Time (min)	NH ₃ *** Induction Time Range (min)
1.1	127	141	80-183
3.1	74.6	66.1	47-87
3.2	102	100.9	71-108
6.1	178	NA	172-201
6.2	186	178.6	167-214
7.1	94	80.7	47-98

*The second H₂ release refers to the significant H₂ release observed after NO_x and N₂O generation decrease. For example, refer to profiles for H₂, Appendix E.1a and E.6a.

**The NO₂- depletion time was estimated by plotting the concentration of NO₂- measured in slurry samples as a function of process time. The depletion time (nitrite concentration = 0) was estimated by extrapolation, assuming a constant depletion rate. An estimated error of 15% is associated with this approach.

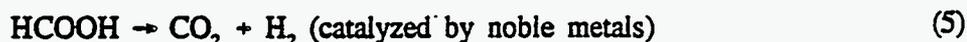
***A larger uncertainty exists in estimating the NH₃ induction time. The range given is based on samples which contained less than 0.02-0.03 g NH₄⁺/L of slurry for the low end and greater than 0.02-0.03g NH₄⁺/L of slurry for the high end. Larger ranges are in part attributed to sample collection times.

comparable, suggesting that H₂ generation and NO₂ depletion may affect NH₃ production. The apparent relationship between NO₂ depletion and NH₃ generation may be related to hydrogen generation. It is possible that NO₂ and NO compete for the HCOO⁻/HCOOH. The NO₂ reduction is favored under the conditions tested. A test with a nitrite-free simulant may help to provide a better understanding of this relationship. Pre-1991 simulants did not contain NO₂; however, offgas analyses are limited to a single scoping study using "grab" gas samples and no quantitative NH₄⁺ analyses.^{(a)(b)} Preliminary data from tests at IDMS with HWVP NCAW simulant have lent support to the correlation between H₂ and NH₃ generation; increased amounts of NH₄⁺ were measured in the presence of the second H₂ release.^(c)

Tests 3.1 and 7.1 were both conducted with a low NO₂ simulant. The simulant in test 7.1 contained triple the initial NO₂ concentration. Approximately 3.6 times more measured NH₄⁺ was observed during test 7.1 compared to test 3.1. Approximately 0.12 mole (about a 7% increase) more HCOOH was added to the simulant in test 7.1 than to the slurry from test 3.1. The increase in the amount of HCOOH may have resulted in somewhat higher H₂ production; ~25% more H₂ was measured in test 7.1 than in test 3.1. Higher hydrogen production may contribute to higher NH₃ production.

As described above, significant NH₃ production was observed after recycle addition. Recycle addition doubled the NO₂ concentration. As with test 7.1, increased NO₂ concentrations appear to be associated with increased NH₃ production. The rate of HCOOH addition did not appear to have a significant effect on NH₃ production. In Figure H2, the measured NH₃ in the slurry for tests 2.1 and 2.2 in which the HCOOH addition rate was increased to 2 and 4 times the basecase are of the same order of magnitude as the test 1.3 basecase addition rate.

Figure 6.1.8 shows the correlation between H₂ and the ratio of measured NH₄⁺ and initial slurry NO₂. This correlation is not yet fully understood; however, the data suggest that H₂, NO₂, and NH₃ are related in some manner. The following mechanism for NH₃ production is proposed:



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- (a) Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company, HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (b) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (c) Hutson, N. D. 1992. "Integrated DWPf Melter System (IDMS) Campaign Report." *Hanford Waste Vitrification Plant (HWVP) Process Demonstration*. WSRC-TR-0403, Rev. 0, UC-721.

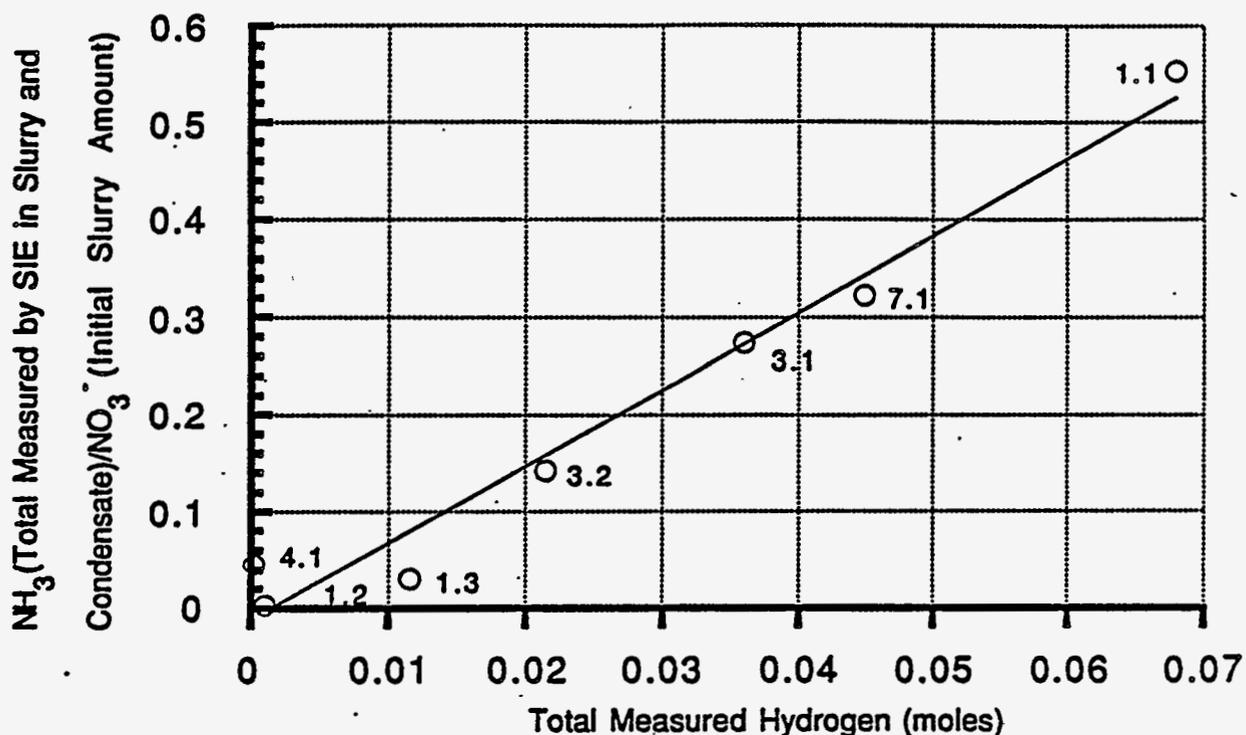
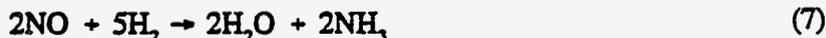


Figure 6.1.8. Correlation Between H₂ Present in the Offgas and NH₄⁺/NO₃⁻ Present in the NCAW Slurry Simulant and Collected Condensate for FY 1991 Tests 1.1, 1.2, 1.3, 3.1, 3.2, 4.1 and 7.1. Ammonium ion is reported as NH₃.



A material balance (not shown) designed to test the theoretical reactions that may produce NH₃ proved inconclusive. Changes in NO₃⁻ and HCOO⁻ that would occur in the simulant to produce the measured amounts of NH₄⁺ were within analytical uncertainties. Analytical uncertainties in ion chromatography (IC) analysis and in offgas measurements are estimated to total at least 20 to 30%. The percent error on the nitrogen mass balance varied from 2 to 18%.

During recycle waste stream addition, a second relatively minor CO₂ release was observed, and measured H₂ and NO were much less than observed during HCOOH addition. It is proposed that this CO₂ is derived primarily from HCOOH decomposition or oxidation, not from CO₃²⁻. Carbonate initially in the simulant is believed to be released as the simulant becomes acidic during HCOOH addition. The H₂ produced via HCOOH decomposition (equation 5) and the NO produced by reduction of NO₃⁻ by HCOOH (equation 6) may be consumed in producing NH₃, and thus are not measured in the

offgas. However, CO_2 observed during recycle waste stream addition (refer to Table 5.3.2) is generally less than would be predicted based on the stoichiometry of reactions (refer to total amount of NH_4^+ measured, Table 6.1.3) given in equations 5 to 7. It may be that in the alkaline simulant, some of the CO_2 is absorbed as CO_3^{2-} . Carbonate and NH_3 formation may account, in part, for the observed increase in pH after HCOOH addition in noble metal-containing simulants. However, small increases in pH for noble metal-containing simulants were also observed in the absence of measurable H_2/NH_3 production (test 1.2). Clearly, the complete set of reactions remains to be identified.

6.2 Assessment of Alternative Redox Indicators and Application of an SRTC Formula for Minimum Formic Acid Addition to HWVP Using Cation Solubility

This section of the report addresses two issues: 1) assessing whether the SRTC formula applies to HWVP feeds and 2) evaluating alternatives for using the glass redox measurement ($\text{Fe}^{+2}/\Sigma\text{Fe}$) as a gauge for reductant requirements. The approach to addressing these two issues was to measure the solubility of metal cations during the feed preparation process steps. The solubility measurements were compared directly with the SRTC guidelines for $\text{Ni}(\text{OH})_2$ dissolution (producing soluble Ni^{+2}) and MnO_2 reduction (producing soluble Mn^{+2}). The measured changes in solubility of three metal cations, Mo, Mn, and Fe, were evaluated as these changes were believed to relate to the extent of reduction during feed preparation.

The following discussion summarizes general solubility trends that directly apply to assessing the SRTC formula and evaluating alternative redox indicators. The trends relate the extent of metal cation dissolution with changes in the simulant pH during the laboratory feed preparation steps. Potential alternative redox indicators are discussed using solubility data for estimating the extent of reduction during feed preparation. Using Pourbaix diagrams for predicting solubility and redox products as a function of pH and solution electromotive potential is introduced in this section. Lastly, the HWVP NCAW solubility data is compared with the SRTC guidelines for minimum HCOOH addition. This section includes an assessment of the potential limitations of the SRTC guidelines for HWVP feed processing.

6.2.1 Summary of Observed Cation Solubility Trends During Titration of NCAW Simulant with Formic Acid

Metal cation solubility was calculated using the measured amount of metal ion in supernate and slurry samples. The slurry samples collected during laboratory-scale feed preparation testing were stored at 10°C and analyzed at 22°C . Sample preparation of the supernate consisted of slurry filtration, filtrate acidification and/or dilution, and immediate analysis of the filtrate by ICP-ES. No precipitation of solids in the supernate was observed before the analysis. Slurry samples were acidified with HCl/HNO_3 and diluted and acidified with HNO_3 again. Little or no solids remained after the final acidification of slurry samples.

Figure 6.2.1 shows the change in metal cation solubility and pH as a function of process time for tests 7.1 and 3.1. The solubility and corresponding pH observed in these tests are representative of most of the FY 1991 test cases.^(a) Cations whose solubility increased consistently with increase in acidity were Al, Ca, Cd, Cr,^(b) Cu,^(b) Fe, Mg, Mn, Na, Ni, Sr, and Zn.^(c) Iron and Mn are believed to have been reduced to a more soluble species, Fe⁺² and Mn⁺², respectively. The measurable increase in solubility of Al, Ca, Cd, Cr, Cu, Mg, Na, Ni, Sr, and Zn metal cations is attributed to dissolution of respective hydroxides/hydrous oxides and carbonates. Molybdenum solubility decreased with increase in acidity, which may be attributed to reactions such as reduction to MoO₂ or precipitation of molybdates. Silver, Pb and Ti were not observed in the filtrates. Silicon, Ba, and Zr were observed in only a few filtrates with no apparent correlation with pH.

With the exception of Mn, Ni and Na, all of the elements with measurable solubility during HWVP feed preparation steps are not included in the SRTC formula for minimum HCOOH addition amount (discussed below). Should the extent of neutralization reactions be important criteria for the amount of reductant added to HWVP feeds, neutralization reactions in addition to those accounted for by SRTC for DWPF feeds would be required as part of the HWVP reductant addition formula.

6.2.2 Potential Alternatives Considered for Monitoring Glass Redox

A simple and more sensitive analytical technique that provides a basis for reductant addition based on correlation of initial slurry component concentration with the glass oxidation state is preferable to the current measurement of Fe⁺²/ΣFe in glass. Decreases in metal cation solubility that might be attributed to a decrease in the metal ion valence during feed preparation were evaluated to identify potential slurry candidates for redox indicators. As discussed previously by Wiemers,^(d) understanding the feed preparation chemistry such that product oxidants and reductants may be predicted is only part of the total redox equilibria pertinent to control of the HWVP melter performance. A second integral part of the system is a fundamental understanding of the melter cold cap chemistry.

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- (a) A detailed discussion of the changes in metal cation solubility will be considered for a subsequent report. The data provided here were limited to those addressing specific task objectives, comparing results with the SRTC formula and evaluating alternative redox indicators.
 - (b) Chromium and Cu are not shown in Figure 6.2.1. Chromium and Cu were soluble only in non-noble metal tests where pH of the sample (@ 22°C) was below 5.
 - (c) The metal cations investigated were Al, Ag, Ba, Ca, Cd, Cu, Cr, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sr, Ti, Zn, and Zr.
 - (d) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.

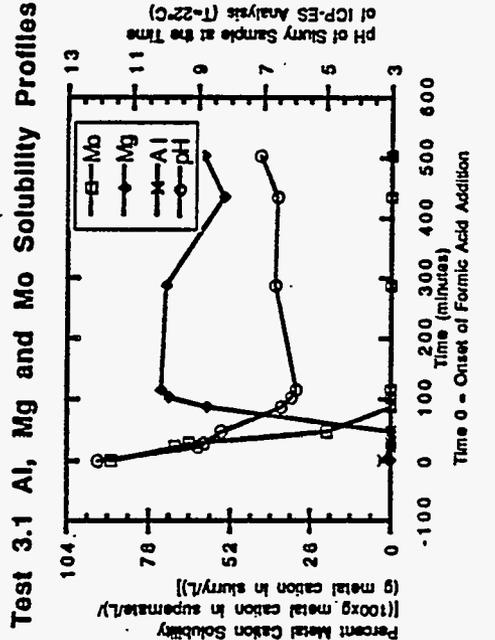
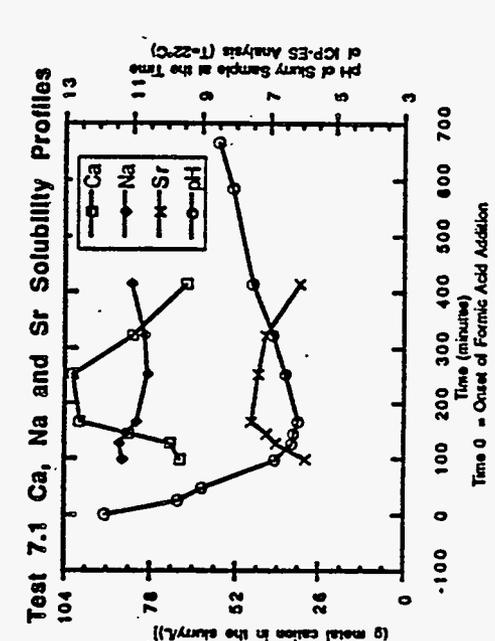
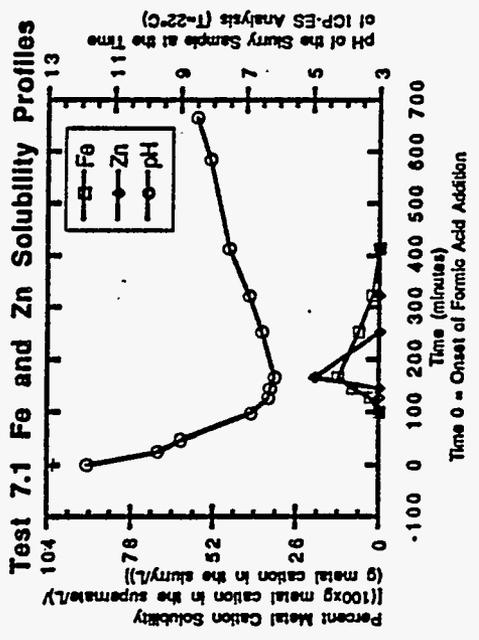
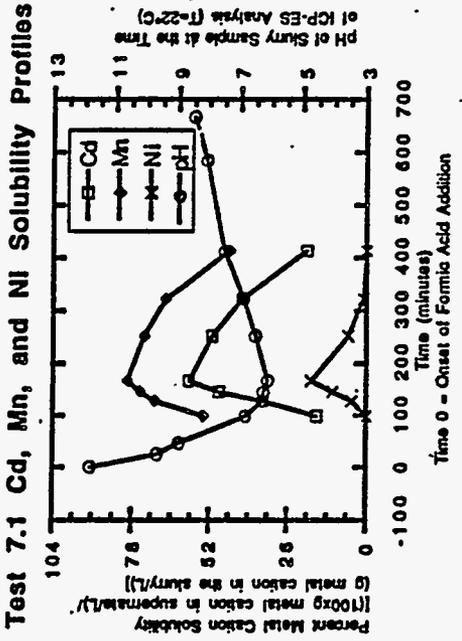


Figure 6.2.1. Representative Solubility Profiles for Selected Elements in Hanford Waste Vitrification Plant (HWVP) Neutralized Current Acid Waste (NCAW) Feed Simulant During Testing

The following criteria were used to select slurry component candidates as potential redox indicators:

1. cation has at least two stable oxidation states (i.e., Mn forms Mn(IV) and Mn(II))
2. cation is present in the simulant in its higher oxidation state that forms an insoluble compound (i.e., Fe(III) forms insoluble Fe(OH)₃)
3. cation is reduced by interaction with HCOOH to a lower oxidation state
4. the lower oxidation state cation is soluble and detectable in the supernate by the ICP technique at the end of processing.

Based on these criteria and the observed solubility behavior, three candidates were considered, Mo, Mn, and Fe. Pourbaix diagrams were used to assist in analyzing solubility and redox behavior. Because the use of Pourbaix diagrams for this application has not previously been presented, a brief discussion of Pourbaix diagrams is provided. For additional information, the reader is referred to Pourbaix (1974).

Pourbaix diagrams for Mo, Mn, and Fe are shown in Figures 6.2.2 to 6.2.4. The dotted line labeled (a) represents the equilibrium conditions of the reduction of water to gaseous H₂. The dotted line labeled (b) represents the equilibrium conditions of the oxidation of water to gaseous O₂. Between the two lines (a) and (b), water is thermodynamically stable. Above line (b), water is oxidized and O₂ liberated. Below line (a), water is reduced and H₂ is liberated. When H₂ is generated during the feed preparation steps, the system equilibrium conditions are approximated on the Pourbaix diagram using the pH and line (a). It must be noted that during feed preparation steps, the temperature is 95 to 102°C, not 25°C as represented on the Pourbaix diagrams. Measuring the supernate and slurry samples by ICP-ES was, however, completed at 22 to 25°C. In the following discussion, reference to a more reduced simulant implies that the system is located closer to line (a) than line (b).

The chemistry of Mo, Mn, and Fe related to solubility and redox reactions during feed preparation is discussed below. This discussion addresses the predicted reactions, the observed metal cation solubility behavior, and potential limitations for applying the selected indicator.

Molybdenum was added to the slurry in an oxidized state, Mo(VI). The Pourbaix diagram for Mo indicates that Mo(VI) is stable and would remain soluble until pH < 3.5 if the solution potential does not become more negative [i.e., if the solution becomes reduced as would be indicated by the production of H₂—reduction to an insoluble species would then be predicted (refer to Figure 6.2.2)]. Precipitation of the Mo may result from two mechanisms:

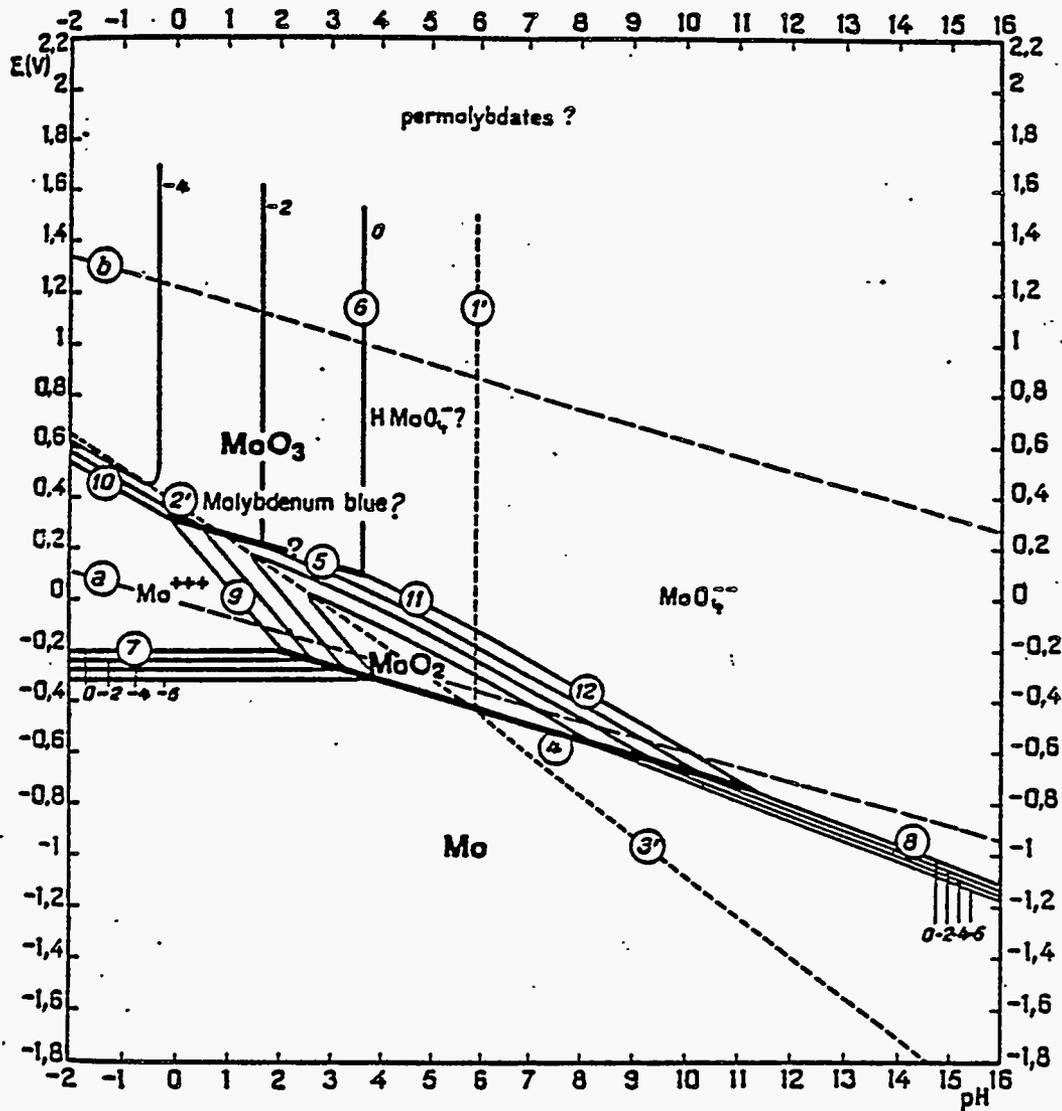


Figure 6.2.2. Potential-pH Equilibrium Diagram for the System Molybdenum-Water at 25°C

1. reduction of Mo(VI) to Mo(IV), which forms the insoluble MoO_2
2. formation of insoluble molybdates with cations solubilized during HCOOH titration.

As shown in Figure 6.2.2, during the laboratory forming tests with NCAW simulant, Mo was no longer detectable in supernates with $\text{pH} < 7.6$ (solubility decreased with increase in acidity). A decrease in Mo solubility with increase in acidity was also observed during the pilot scale ceramic melter run 23 (Goles 1990). However, based on solubility data alone, it is not certain which phase, the MoO_2 (reduced species) or insoluble molybdates (original oxidized state), was formed. Using Mo as a redox indicator would require discrimination between these two phases.

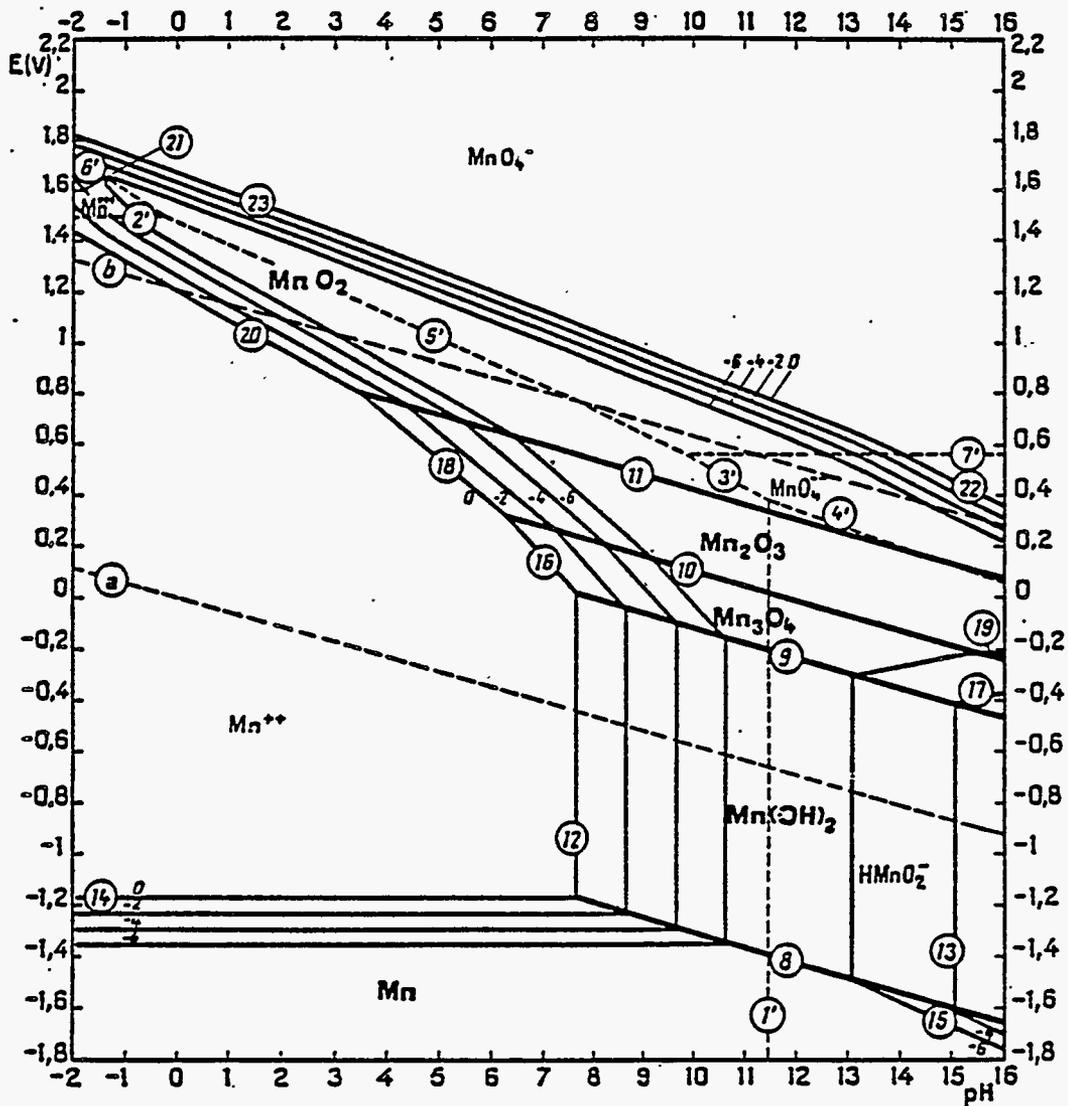


Figure 6.2.3. Potential-pH Equilibrium Diagram for the System Manganese-Water at 25°C

The NCAW simulant was prepared using insoluble, hydrated manganese dioxide, $\text{MnO}_2 \cdot x \text{H}_2\text{O}$. In an acid slurry, detection of the soluble, reduced Mn species, Mn^{+2} , might provide a basis for developing reductant demands (refer to Figure 6.2.3). However, only the non-noble metal simulants remained sufficiently acid to ensure Mn^{+2} solubility. Feed with an alkaline pH would require discrimination between two insoluble phases, $\text{Mn}(\text{OH})_2$ (reduced species) and $\text{MnO}_2 \cdot x \text{H}_2\text{O}$ (original, oxidized state).

orders of magnitude less (test 5.2). The apparent dependence of measurable Fe reduction on H₂ production suggests that the reduction of Fe in the slurry may not be a sensitive enough indicator for determining minimum reductant requirements for all HWVP feeds. Two other limitations to the measurement of Fe⁺² are

1. The Fe⁺² forms an insoluble hydroxide in the alkaline regime (pH > ~6.5) that might be experienced by HWVP feeds after feed preparation steps. Similar to both Mo and Mn, potential precipitation of the lower oxidation state would necessitate development methods to distinguish between species ferric and ferrous species in the slurry.
2. The relative ease at which Fe⁺² is oxidized to Fe⁺³ in the presence of air would add some complications to the analytical method.

Further assessment of the applicability of Mo, Mn, and Fe as alternative redox indicators requires additional analytical development and correlation with melter performance. Another potential redox indicator, the slurry formate and nitrate concentration is discussed in Section 6.3.

6.2.3 Assessment of the Applicability of the SRTC Minimum Formic Acid Addition Formula to the HWVP

The SRTC has developed an empirical formula which provides guidelines for the minimum amount of HCOOH required for processing of DWPF feeds.^(a) The SRTC formula is based on neutralization, decomposition, and redox reactions believed to be representative of the DWPF feed chemistry. The reactions were derived from compositional analyses of formated, non-noble metal DWPF simulants. Melter feeds prepared from these simulants and processed in large-scale melters resulted in glass with an acceptable Fe⁺²/ΣFe value.

Under no conditions in PNL testing did the extent of Ni(OH)₂ dissolution and MnO₂ reduction compare simultaneously with the SRTC formula while processing an HWVP NCAW non-noble metal simulant. For a non-noble metal simulant, the SRTC target nickel solubility of 30% was observed at a pH of 4 (22°C). The solubility of manganese (i.e., the reduced species, Mn⁺²) at pH 4 (22°C) was ~80% compared to the SRTC guidelines of 50%. The SRTC target Mn reduction of 50% was observed at a pH of ~6 (22°C). The solubility of nickel at pH 6 (22°C) was <10%. No detectable Ni⁺² and only a small amount of soluble Mn⁺² were present in the supernate of formated HWVP NCAW noble metal-containing simulants to which a nominal amount of HCOOH was added (30 mL 87 wt% HCOOH/L).

Based on the comparison of solubility data alone from FY 1991 laboratory-scale feed preparation tests, it appears that application of the SRTC 50% Mn and 30% Ni guidelines to the HWVP NCAW is not representative of the HWVP feed preparation chemistry.

The amount and type of reductants and oxidants added to the melter are believed to be a primary factor in controlling melter processing rate. The current empirical formula developed by PNL for glass

(a) Hsu, C. W. 1990. Formic Acid Requirement in the DWPF Chemical Processing Cell. WSRC internal memo to J. R. Knight, 5 July 1990. WSRC-RP-90-0554.

redox control assumes that reductant addition during feed preparation should be based on the amount of oxidant present in the melter feed (Ramsey 1991).^(a) Based on the format of the SRTC formula, the neutralization capacity of the slurry could notably impact the amount of reductant added to the waste stream. When the SRTC formula is applied to the HWVP NCAW simulant, the prescribed neutralization reactions would contribute to over 75% of the HCOOH requirement for HWVP NCAW slurry. The neutralization reactions do not directly affect the HCOO⁻ (reductant) or NO₃⁻ (oxidant) concentration seen in the melter, as the formate ion is not consumed in the neutralization reactions.^(b) In addition, the SRTC formula prescribes the amount of HCOOH to be added to the DWPF alkaline sludges. It does not take credit for any reductants/oxidants or acid/base components that are subsequently added to the formated sludge by the PHA waste stream. The PHA waste stream is not part of the HWVP process flowsheet. Major differences in the DWPF and HWVP waste streams might significantly impact downstream processing from both a rheology and redox perspective.

Neutralization reactions may need to be considered with respect to slurry rheology. Slurry rheology is known from an engineering perspective to affect agitation and pumping requirements. Melter feed rheology may also impact the melter process rate. Based on solubility studies using HWVP NCAW simulants, additional neutralization reactions should be added to the SRTC formula on the assumption that a decrease in slurry pH is used as a means for rheology adjustment. Depending on pH criteria, the additional HCOOH requirements would include neutralization of Al, Cd, Ca, Cr, Cu, Mg, Sr, and Zn. This is not a comprehensive list of potential reactants as not all elements were measured due to the use of a simulant, and cost and analytical limitations. The FY 1991 solubility studies suggest that for a majority of the cations measured, the solubility behavior as a function of pH is fairly predictable. A standard technique involving data presented in a Pourbaix diagram format may provide the plant with a generic method for determining equivalent acid addition requirements, should such an adjustment be necessary.

This assessment leads to the conclusion that a single source chemical such as HCOOH for adjustment of both rheology and glass redox may not be feasible for HWVP because, depending on the feed composition (for example, high carbonate and low oxidant), the criteria for rheology may not match with the criteria for reductant addition. It is recommended that a fundamental understanding of the chemistry controlling rheology and melter cold cap reactions be acquired to support development of HWVP flowsheet options.

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- (a) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (b) Indirectly, the slurry pH may alter the redox reaction products during feed preparation steps which, if large amounts of HCOOH or perhaps NO₃⁻ are involved, could possibly impact the glass redox. Under the conditions tested, changes in the melter feed reductant (HCOO⁻) to oxidant (NO₃⁻) mole ratio were small and did not significantly impact the measured glass redox, Fe⁺²/ΣFe, value.

6.3 Bases for HCOOH Addition to Control Glass Redox

The oxidation state of the melt is an important parameter impacting efficiency of the vitrification process. Glass redox acceptance criteria have generally been based on measuring the $Fe^{+2}/\Sigma Fe$ in the glass. The acceptable working range for HWVP is $0.005 \leq Fe^{+2}/\Sigma Fe \leq 0.23$.^(a) Process guidelines are required for chemical additions necessary to maintain glass in the acceptable range. A reductant, HCOOH (or sugar), may be added to the SRAT slurry to provide a glass redox in the acceptable range. Addition of HCOOH also serves to reduce the slurry viscosity.^(b)

The PHTD approach to deriving guidelines for reductant addition is to develop an understanding of feed preparation, melter cold cap, and melt reactions which allows for a correlation to be developed between reductants and oxidants in the HWVP slurry feed and the glass redox value, $Fe^{+2}/\Sigma Fe$.^(c) Figure 6.3.1 shows schematically the PHTD integrated system considerations proposed for developing reductant addition guidelines.

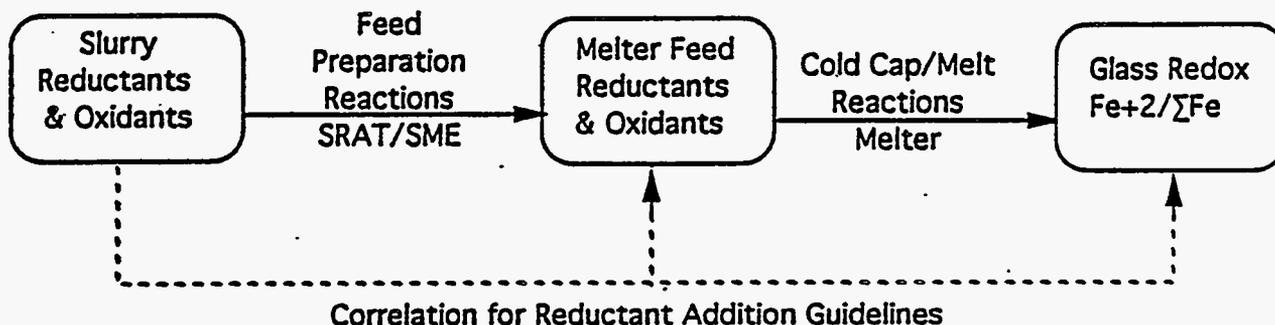


Figure 6.3.1. PHTD Integrated System Considerations in Developing Reductant Addition Guidelines

- (a) *Hanford Waste Vitrification Plant Technical Data Package*, WHC-SD-HWV-DP-001, section 13, Item 310, October 1990, Rev. 5H.
- (b) Formic acid is also added to control feed rheology. For the present study, the amount of HCOOH added was selected for glass redox requirements and investigation of the H₂ issue. The rheology issue may need to be revisited.
- (c) Melter operation factors, such as residence time in the cold cap, air in-leakage, and melter plenum temperature, should also be included. These variables are not presently addressed directly in the FY 1991 laboratory-scale feed preparation studies.

Based on previous bench-scale studies, Wiemers^(a) found that a measurable amount of Fe⁺² in the glass was obtained if the threshold condition HCOOH/NO₃⁻ = 3 (a mole ratio based on the initial NO₃⁻ concentration and the amount of HCOOH added) was satisfied. The data from Wiemers^(a) is reprinted in Figure 6.3.2 for reference. The initial NO₃⁻ loading in the earlier study ranged from 0.115 to 0.42 M (FY 1992 nominal NO₃⁻ concentration, including recycle, was ~0.26 M). The earlier tested slurries did not contain two oxidants that are now major components of the NCAW simulant, NO₂ and MnO₂.

In the FY 1991 studies, chemical reactions during slurry processing steps (HCOOH addition, digestion, recycle addition, and concentration) were characterized to quantify the impact of selected slurry components on melter feed reductant/oxidant loadings. This approach provided an opportunity

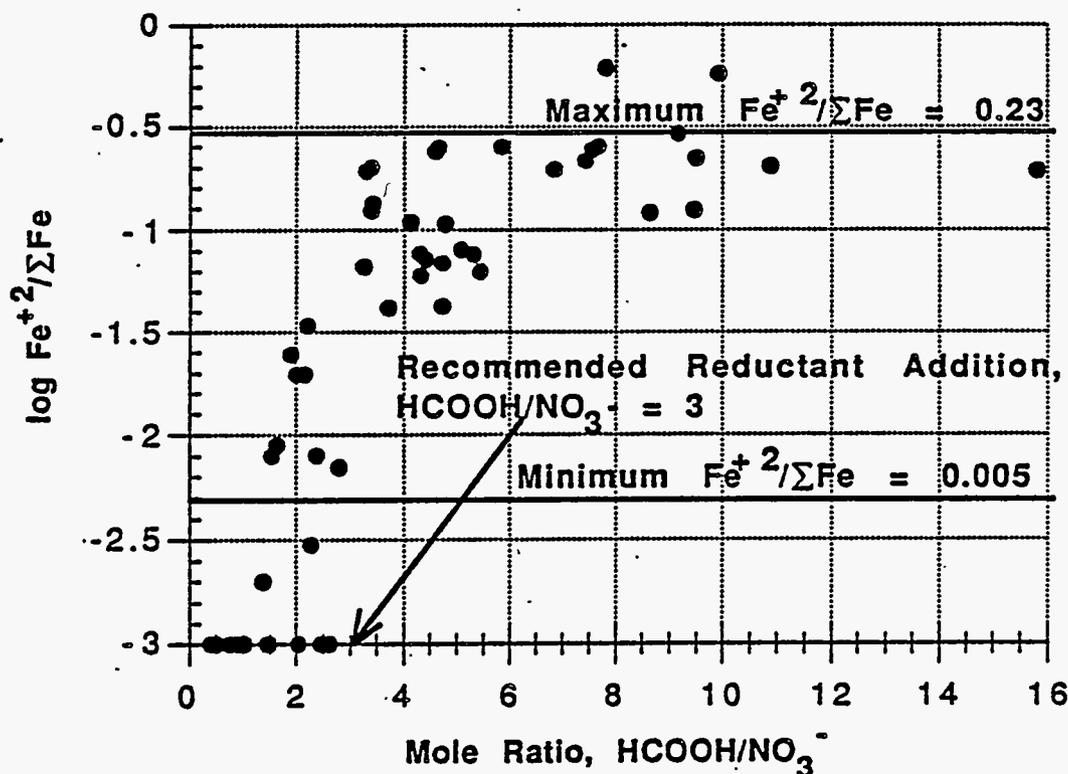


Figure 6.3.2. Correlation of HCOOH/NO₃⁻ with Fe⁺²/ΣFe for NCAW Waste Glasses Showing HCOOH/NO₃⁻ Threshold Value of 3^(a)

(a) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.

to optimize reductant addition and more confidently adapt the guidelines to other slurry compositions. The correlation is limited to a semi-empirical relationship because the cold cap chemistry is not thoroughly understood.

The results of the FY 1991 glass redox evaluation are provided below. In addition, comparisons of the PHTD guidelines with other approaches to reductant addition for glass redox control are provided.

A glass redox within the acceptable range was measured for all glass specimens prepared from FY 1991 laboratory-scale feed preparation tests. The $Fe^{+2}/\Sigma Fe$ values ranged from 0.01 to 0.1. The HCOOH addition ranged from 27 to 74 mL 87 wt% HCOOH/L @ 125 g WO/L slurry that is equivalent to a HCOOH/NO₃ range of 4.6 to 12 before recycle and 2.2 to 6.7 after recycle.^(a) The glass redox data are summarized in Table 6.3.1. Based on the data in Table 6.3.1, it appears that the HCOOH requirements might be decreased to HCOOH/NO₃ = 2. However, before a lower limit can be recommended, additional data are needed for verification.^(b)

Within the analytical uncertainties of the glass redox measurement in the range tested, no significant trends were identified between the test variables, addition of recycle, and the glass redox. This may in part be accounted for by an apparent dampening effect on HCOO⁻ concentration during slurry processing reactions and a buffering phenomena in the melter cold cap. Reactions contributing to the former are discussed in subsequent text. Cold cap reactions were not studied directly in this investigation.

Unexpectedly, increasing the HCOOH/NO₃ to 12^(c) provided an acceptable glass redox ($Fe^{+2}/\Sigma Fe = 0.056$). Previous tests with NCAW simulant at HCOOH/NO₃ of 10 resulted in an unacceptable, reduced glass with a $Fe^{+2}/\Sigma Fe$ of 0.57 ($Fe^{+2}/Fe^{+3} = 1.34$).^(d) The earlier slurry simulants did not contain NO₂, which may consume some reductant, thereby reducing the net HCOOH/NO₃ seen by the melter.

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- (a) Additional tests may be required to establish/verify a minimum HCOOH requirement. During the FY 1991 testing, emphasis was placed on the H₂ generation, which at the nominal NO₂ loadings required at least the reference amount of HCOOH (4 moles HCOOH/mole NO₂). Only a limited number of tests used a HCOOH/NO₃ less than 4.
 - (b) The reference feed composition for HWVP gives a boundary concentration of NO₂ + NO₃ = 36 g/L slurry. In the FY 1991 testing, the maximum slurry simulant NO₃ concentration before recycle waste addition was 25 g NO₃/L @ 125 g WO/L slurry. Adding the recycle waste stream approximately doubled the amount of NO₃ in the slurry.
 - (c) A HCOOH/NO₃ = 12 for test 1.1 (before recycle addition) was equivalent to adding 74 mL 87 wt% HCOOH/L @ 125 g WO/L slurry.
 - (d) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.

Table 6.3.1. Comparison of HCOO⁻, NO₃⁻ and HCOO⁻/NO₃⁻ Before and After Recycle Waste Stream Addition with Glass Redox (Fe⁺²/ΣFe)

Test Number	NCAW Slurry Simulant Composition						Glass Redox (Fe ⁺² /ΣFe) ^{***}	
	HCOO ^{-*}		NO ₃ ^{-**}		Molar Ratio, HCOO ⁻ / NO ₃ ⁻		Before Recycle	After Recycle
	Before Recycle, moles	After Recycle, moles	Before Recycle, moles	After Recycle, moles	Before Recycle	After Recycle		
1.1	2.59	2.65	0.21	0.40	12.57	6.69	0.06	0.02
1.2	0.91	0.97	0.18	0.37	4.97	2.60	0.03	0.05
1.3	1.60	1.65	0.19	0.38	8.42	4.34	0.02	0.06
2.1	1.52	1.56	0.18	0.34	8.40	4.57	0.05	0.06
2.2	1.51	1.56	0.21	0.39	7.33	4.04	0.02	0.02
3.1	1.56	1.61	0.21	0.37	7.46	4.36	0.02	0.02
3.2	1.51	1.56	0.20	0.36	7.51	4.32	0.08	0.04
4.1	1.53	1.58	0.20	0.38	7.69	4.17	0.04	0.03
5.2	2.20	NA	0.19	NA	11.40	NA	0.01	NA
7.1	1.68	1.73	0.65	0.82	2.60	2.12	0.01	0.04

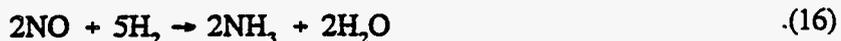
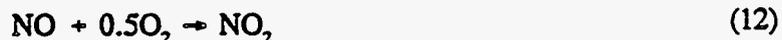
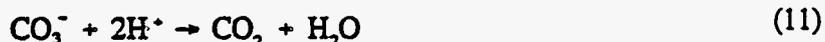
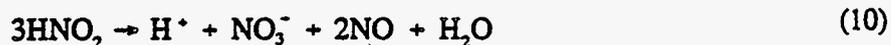
*The "before recycle" HCOO⁻ values are based on the amount of HCOOH added to the slurry. "After recycle" HCOO⁻ values are based on the amount of HCOOH added to the recycle plus the HCOO⁻ values from the before recycle column.

**The "before recycle" NO₃⁻ values are based on slurry IC analyses for NO₃⁻. The "after recycle" NO₃⁻ is based on the target concentration for recycle waste stream NO₃⁻, multiplied by the volume of recycle waste stream simulant added to the slurry, plus the NO₃⁻ value from the "before recycle" column.

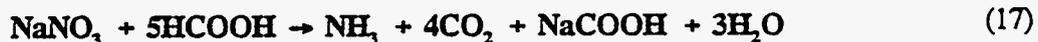
***Based on preliminary studies at PNL (current study) and WSRC (Ramsey 1991), a large uncertainty (>70%) in the Fe⁺²/ΣFe measurement exists for Fe⁺²/ΣFe < 0.1. Reported values are not considered to be significantly different. Redox measurements were not collected for tests 6.1 and 6.2.

A mass balance for the slurry processing reactions was performed in terms of HCOOH/HCOO⁻ and nitrogen compounds to provide a basis for predicting the amount of reductant and oxidant in the melter feed. The relative amount of oxidants and reductants in the melter feed is believed to be a primary part of glass redox control (Ramsey 1991).^(a) The mass balance was limited to tests in which the second H₂ release was observed.

The following reactions were assumed as a basis for the mass balance calculations:



net for reactions 15 and 16:



(a) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.

The reactions printed in bold consume reductant, HCOOH. Minor contributions to HCOOH consumption (< 10%) by reduction of slurry simulant cations such as Mn were not included in this first mass balance attempt. The primary source of NO was considered to be disproportionation of HNO₂ (equation 10).

The fraction of HCOOH consumed by each feed preparation reaction is illustrated in Figure 6.3.3. The fraction for HCOOH consumption was calculated as follows:

Reaction	Calculation for HCOOH Consumption	Equation
reduction of NO ₂	2.0 x moles of N ₂ O measured	8
decomposition	1 x moles of H ₂ measured	13
NH ₃ generation	4.0 x moles NH ₄ ⁺ measured	17

The reported amount of unreacted HCOO⁻ is a measured value.

The amount of HCOO⁻ remaining in the processed simulant was observed to be a function of both the amount of NO₂ and NO₃:

$$\frac{\text{moles melter feed HCOO}^-}{\text{moles HCOOH added} - A[\text{moles NO}_2] - B[\text{moles NO}_3]} = \quad (18)$$

For slurry simulants containing noble metals, the mass balance indicates that about 1 mole of HCOOH was consumed per mole of NO₂ (A = 1) (refer to equation 8).^(a) In the presence of excess^(b) HCOOH and/or NO₃, HCOOH was predicted to be consumed by the production of NH₃. The latter reaction consumes 4 moles of HCOOH per mole of NH₃ produced (refer to equation 17) and in some cases, noticeably decreases the HCOO⁻/NO₃ ratio in the melter feed. For example, NH₃ production reduced the melter feed HCOO⁻ by 22% in test 1.1 and 45% in test 7.1 (refer to Figure 6.3.3). Under the conditions tested, the amount of NH₃ produced was linear with NO₃ concentration and measured H₂ (refer to Section 6.1). Additional data analysis is required to provide the coefficient, B.

One consequence of the NH₃ reaction is to diminish the measurable correlation of NO₂ with glass redox. For example, approximately the same amount of HCOOH was added to tests 1.3, 3.1, and 3.2. Based on the initial NO₂ loadings which varied by a factor of 3.25, one might predict a similar

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- (a) The N₂O/NO_x ratio is not constant and is believed to be dependent on test conditions. Therefore, the coefficient, A, may become A₃(T₁) + A₂[X₂] +, where X₁, X₂, ... are operating or compositional variables.
- (b) "Excess" in this context refers to the amount of HCOOH added greater than that required to deplete the NO₂.

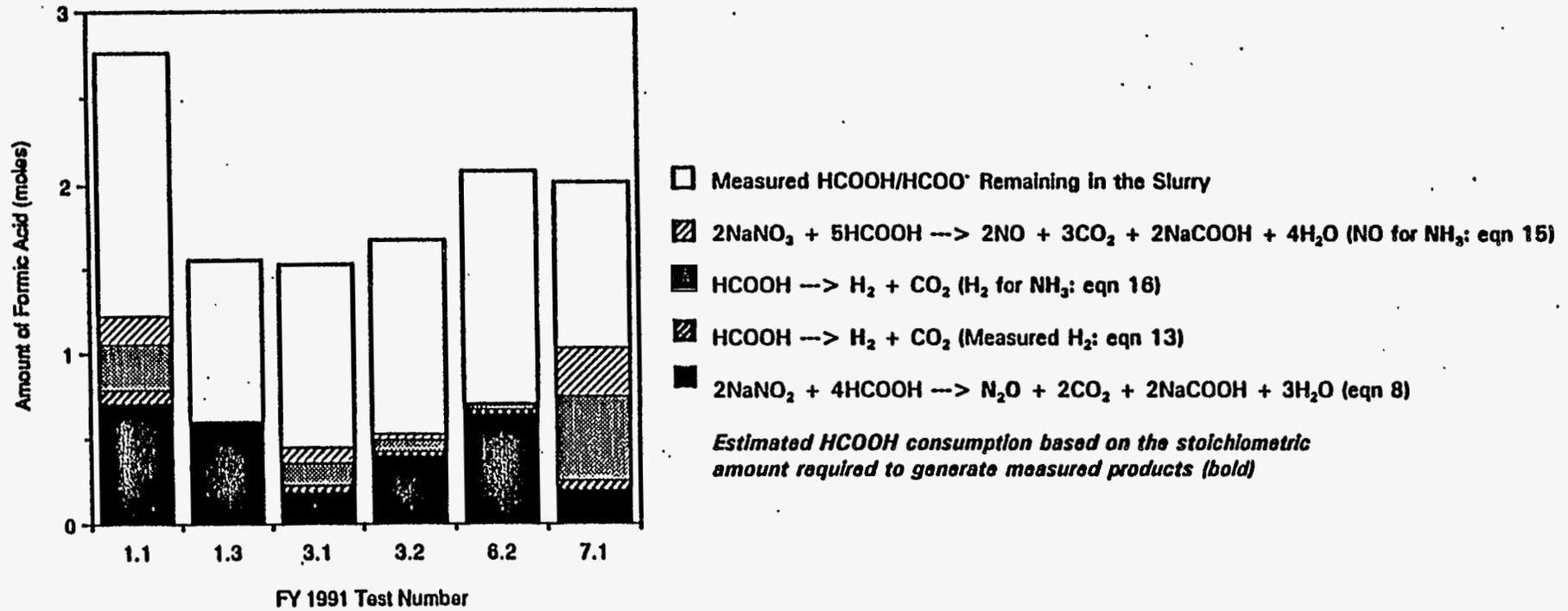


Figure 6.3.3. Amount of HCOOH Consumed in Individual SRAT Reactions Defined by FY 1991 NCAW Simulant Laboratory-Scale Tests

difference in the final HCOO^- concentration, i.e., ~ 3 times more HCOOH would be consumed by reducing NO_2^- while processing the maximum NO_2^- simulant. However, because of subsequent HCOOH consumption by production of NH_3 , particularly in lower NO_2^- simulants, the amount of HCOO^- remaining in the melter feed was nearly the same for each of the tests (refer to Figure 6.3.3). Approximately 60% of the HCOOH added (1 mole of HCOO^- out of the 1.65 moles of HCOOH added in each test) remained in the simulant after processing. The nearly constant HCOOH to NO_2^- ratio observed in the melter feed and consistent glass redox values may be partly attributed to the net equilibrating effect of NH_3 producing reactions on the HCOOH consumption. Figure 6.3.4 illustrates the linear consumption of HCOOH with HCOOH added during forming of a HWVP NCAW feed simulant.

The $\sim 60\%$ retention ($\sim 40\%$ consumption) of HCOOH added appeared to be fairly constant for all the tests with slurry simulants containing noble metals (refer to Figure 6.3.3). Calculated values for percent HCOOH consumed for selected FY 1991 tests are presented in Table 6.3.2. Values of HCOOH in Table 6.3.2 are based on the measured HCOO^- remaining in the simulant (after HCOOH addition, digestion and recycle waste stream addition) and on the amount of HCOOH added. While the

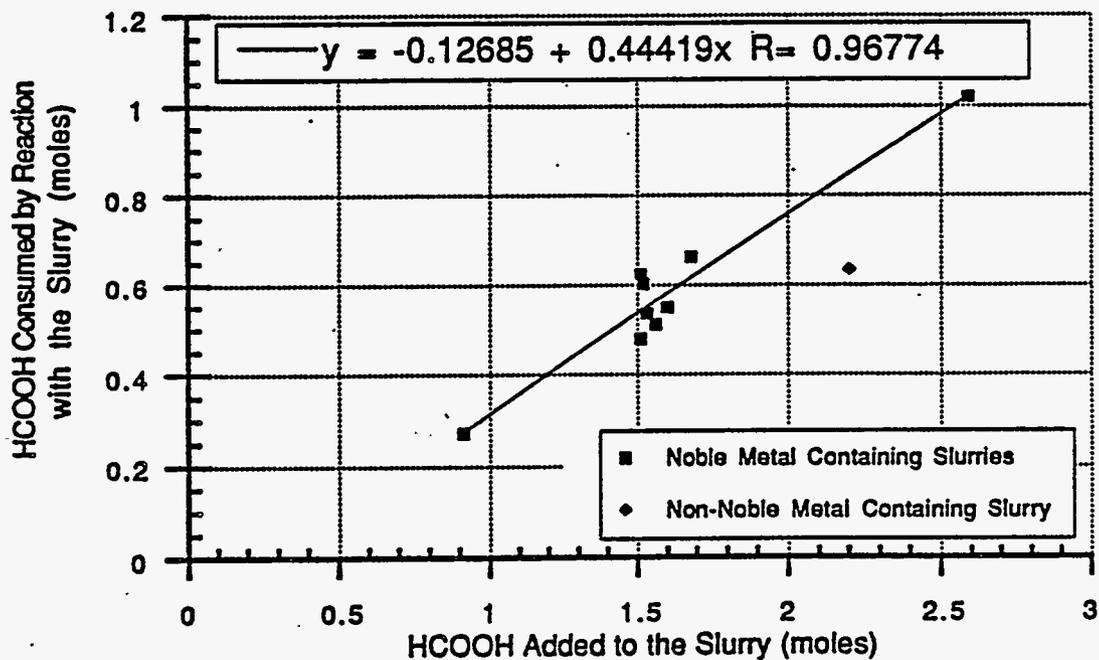


Figure 6.3.4. Quantity of HCOOH Consumed During the Formating of HWVP NCAW Noble Metal and Non-Noble Metal (Test 5) Slurry Simulants as a Function of HCOOH Added to the Slurry

Table 6.3.2. Percent HCOOH Consumed After HCOOH Addition, After Digestion and Total for the Duration of the Test for FY 1991 Laboratory-Scale Feed Preparation Tests

Test Number	%HCOOH Consumed During Specified Process Period		
	HCOOH Addition	HCOOH Addition plus Digestion	For Duration of Test
1.1	36	39	42
1.2	24	30	44
1.3	38	34	42
2.1	41	40	38
2.2	35	32	33
3.1	28	33	32
3.2*	28	41	26
4.1	50	35	35
5.2	22	27	N/A
6.1	35	N/A	N/A
6.2	31	N/A	N/A
7.1	29	44	44

*Total HCOOH consumed appears low.
Potential error in HCOO- measurement.

measurement of percent HCOOH consumption provides a simple empirical approach to estimating the reductant/oxidant in the melter feed (which may then be correlated with the glass redox), the reasons for the consistently observed 40% consumption are not fully understood. Additional data and/or analyses are required to explain this observation.

Based on the PNL studies to date and WHC criteria for glass redox, the recommendations for HCOOH addition remain $\text{HCOOH}/(\text{total } \text{NO}_3) = 3$, which is equivalent to ~30 mL 90 wt% HCOOH/L slurry at the current nominal NO_3 loading (8 g NO_3 /L SRAT slurry and 40 g NO_3 /L recycle waste stream @ 125 g WO/L).^(a) At higher NO_3 loadings, sugar may be considered as a supplementary reductant. Recommended guidelines for reductant addition have not been tested for maximum NO_2 loadings or slurries with organics. Nitrite is considered relevant to the reductant addition guidelines because it may consume reductant during feed preparation. Organics (other than HCOOH) may provide sources of additional reductant in the melter cold cap. Verification via correlation of glass redox from actual waste samples and from large-scale melter tests is also required.

(a) Addition of the recycle waste stream to the SRAT feed doubled the amount of NO_3 .

Guidelines for reductant addition described above have been compared with correlations for glass redox in nuclear waste glass for two other vitrification facilities, the DWPF and West Valley Demonstration Project (WVDP). Results of the preliminary study of glass redox correlations indicate that the approach to providing guidelines in terms of reductants and oxidants is widely accepted and that the proposed guidelines for HWVP NCAW slurry, $\text{HCOOH}/\text{NO}_3 = 3$, provide melter feed compositions (oxidants/reductants) compatible with other glass redox correlations. The correlations summarized below are followed by a comparative analysis with the recent PHTD data:

- Hsu (1990)^(a) envelope for a maximum HCOO^- limit related to NO_3 in melter feed empirical formulation for minimum HCOOH requirement
- Ramsey (1991) For melter feed: if molar HCOO^- minus molar $\text{NO}_3 < 0.9$, then glass redox, $\text{Fe}^{+2}/\Sigma\text{Fe} < 0.1$
- Jain et al. (1992) empirical model based on reducing [carbon from sugar ($\text{C}_{11}\text{H}_{22}\text{O}_{11}$)] species, oxidizing (NO_3) species, and water content of melter feed.

The envelope for a ratio of HCOOH to NO_3 developed by Hsu^(b) for DWPF melter feed simulant is shown in Figure 6.3.5.^(b) Note that the axes are in terms of melter feed composition and that the data points are from analysis of glass prepared during large-scale melter tests. Points below the envelope boundary line represent melter feed simulants that contained the appropriate reductant to NO_3 balance for obtaining an acceptable glass redox. Using the measured amount of HCOO^- and NO_3 in the PHTD FY 1991 laboratory test simulants (refer to Table 6.3.3) and the approximate Fe content given in Table A1, comparative values for HWVP simulants were within the proposed envelope, with the exception of two points representing test 1.1 before and after recycle waste addition. The amount of Fe^{+2} measured in these samples is lower than expected based on the large amount of HCOOH added.

The empirical formulation for minimum HCOOH addition to DWPF simulants is discussed in Section 6.2. In general, this formulation did not directly apply to HWVP NCAW simulants.

The effects of HCOO^- , NO_3 , and phenol on the oxidation state of glasses being considered for vitrification at DWPF were evaluated by Ramsey (1991). The model for glass redox versus melter

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- (a) Hsu, C. W. 1990. Formic Acid Requirement in the DWPF Chemical Processing Cell. WSRC internal memo to J. R. Knight, 5 July 1990. WSRC-RP-90-0554.
- (b) Hsu noted that a preliminary "operating envelope" was developed to define constraints on the HCOO^- and NO_3 levels in the melter feed to ensure acceptable redox control of the melter feed. The envelope is based on data from a limited number of process demonstrations and does not reflect an adequately precise method for predicting the glass redox.

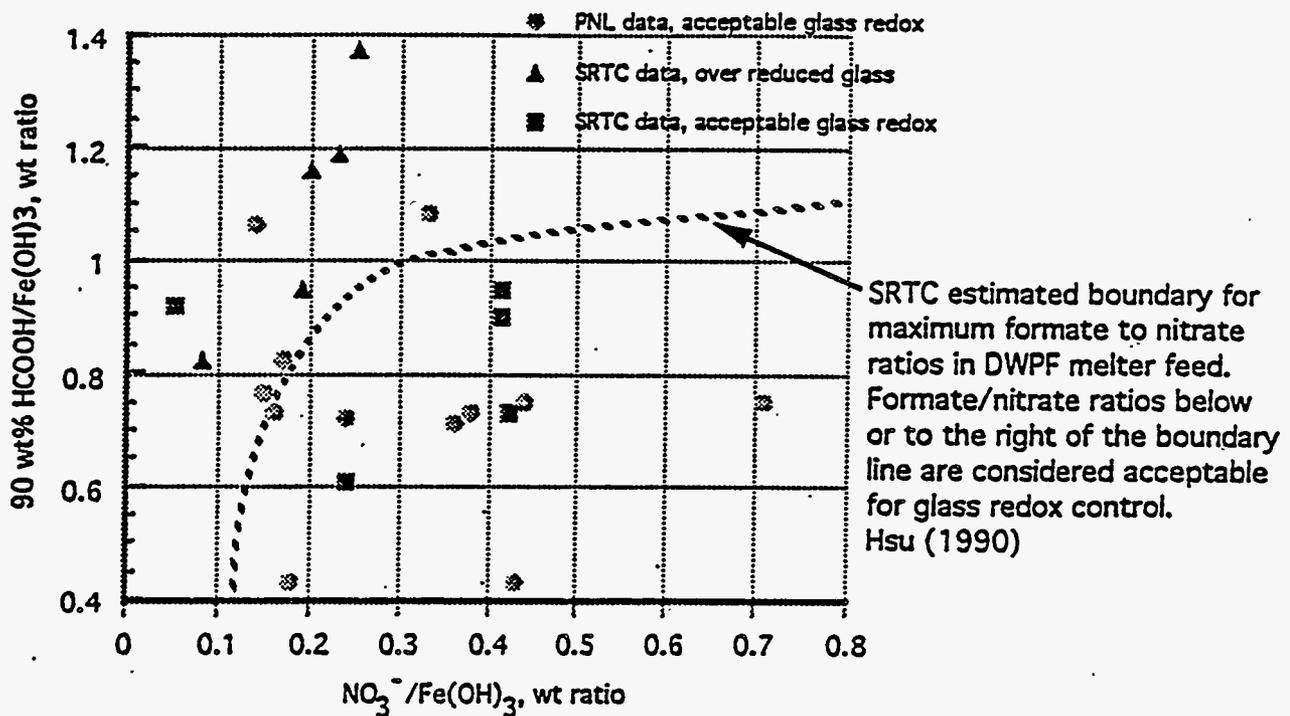


Figure 6.3.5. Comparison of FY 1991 PHTD Laboratory-Scale Glass Redox Data with the SRTC Maximum HCOOH Envelope^(a)

feed composition developed by Ramsey (1991) indicated that the glass redox may be predicted by determining the HCOO⁻ and NO₃⁻ content of the melter feed. The general trends demonstrated a correlation between the molar HCOO⁻ minus NO₃⁻ value and the glass redox:

$$\text{Fe}^{+2}/\sum\text{Fe} < 0.1 \pm 0.05 \text{ for } \text{HCOO}^- \text{ minus } \text{NO}_3^- \text{ (mole basis)} < 0.9. \quad (19)$$

As shown in Table 6.3.3, the redox data collected during the PHTD FY 1991 laboratory-scale studies agree well with the Ramsey model. Test 1.1, (before recycle addition) is the only exception. This discrepancy was also noted in previous discussions concerning the SRTC envelope for HCOO⁻ and NO₃⁻ loading and the HWVP reductant addition formula, HCOOH/NO₃.

(a) Hsu, C. W. 1990. Formic Acid Requirement in the DWPF Chemical Processing Cell. WSRC internal memo to J. R. Knight, 5 July 1990. WSRC-RP-90-0554.

Table 6.3.3. Amounts of HCOO⁻ and NO₃⁻ in Melter Feed; HCOO⁻ minus NO₃⁻ in Melter Feed; and Glass Redox (Fe⁺²/ΣFe) Before and After Recycle Waste Stream Addition for FY 1991 Laboratory-Scale Feed Preparation Tests

Test	Slurry Composition				Ramsey Value		Glass Redox (Fe ⁺² /ΣFe)**	
	HCOO ⁻ (moles/L)*		Nitrate (moles/L)*		HCOO ⁻ minus NO ₃ ⁻ , moles/L.		Before Recycle	After Recycle
	Before Recycle	After Recycle	Before Recycle	After Recycle	Before Recycle	After Recycle		
1.1	1.57	1.54	0.18	0.37	1.39	1.17	0.06	0.02
1.2	0.64	0.61	0.22	0.44	0.42	0.17	0.03	0.05
1.3	1.05	0.96	0.20	0.35	0.85	0.61	0.02	0.06
2.1	0.92	0.96	0.22	0.37	0.70	0.59	0.05	0.06
2.2	1.03	1.04	0.21	0.43	0.82	0.61	0.02	0.02
3.1	1.05	1.09	0.19	0.28	0.86	0.81	0.02	0.02
3.2	0.89	1.15	0.16	0.43	0.72	0.72	0.08	0.04
4.1	1.00	1.03	0.20	0.39	0.80	0.64	0.04	0.03
5.2	1.61	NA	0.47	NA	1.14	NA	0.01	NA
7.1	1.02	0.98	0.54	0.71	0.48	0.27	0.01	0.04

* The concentration values reported in this table were calculated by dividing the measured amount of HCOO⁻ or NO₃⁻ (moles) in the slurry (refer to Table 5.4.1) by the estimated volume of the slurry, 1L, at the time of sampling. The volume estimate is believed to introduce an error of ~+/- 10 to 15% in the "Ramsey" value.

**Based on preliminary studies at PNL (current study) and WSRC (Ramsey 1991), a large uncertainty (>70%) in the Fe⁺²/ΣFe measurement exists for Fe⁺²/ΣFe < 0.1. Reported values are not considered to be significantly different. Redox measurements were not collected for tests 6.1 and 6.2.

A modeling effort was conducted by West Valley Nuclear Service (WVNS) (Jain 1992) to correlate slurry feed characteristics (reducing and oxidizing species in the feed) and observed redox response for the WVDP. Bowan^(a) developed a model previously based on the feed characteristic termed Index of Feed Oxidation (IFO):

$$\text{IFO} = (1 - \phi) \text{NO}_3^- / \text{TC} \quad (20)$$

where TC is the total carbon (ppm) in the feed
 ϕ is the solids fraction in the feed (by weight)
 NO_3^- is the total nitrate (ppm) in the feed.

A correlation relating WVDP melter feed components and the glass redox is given as

$$\log (\text{Fe}^{+2} / \text{Fe}^{+3}) = -0.8406 (\text{IFO}) + 1.19. \quad (21)$$

The PHTD FY 1991 laboratory test data are compared with the Bowan model in Figure 6.3.6. The correlation does not seem to apply to HWVP slurries at this time. Differences in slurry composition, reductant (sugar versus HCOO^-), and the redox range may account for the observed discrepancies.

6.4 Summary of Process Data

Section 6.4 summarizes specific process data related to HWVP vessel ventilation system design, emission control, and attainment issues. Previous sections of this report are referenced for detail regarding the application of the data. Peak gas generation rates are given in Table 5.3.1. The total amounts of offgas measured are listed in Table 5.3.2. Note gas release correction factor is discussed in Section 5.3.

(a) Bowan, B. W. 1990. "A Redox Forecasting Correlation Developed Using a New One-Tenth Area Scale Melter for Vitrifying Simulated High-Level Radioactive Wastes." M. S. Thesis, Alfred University, Alfred, New York.

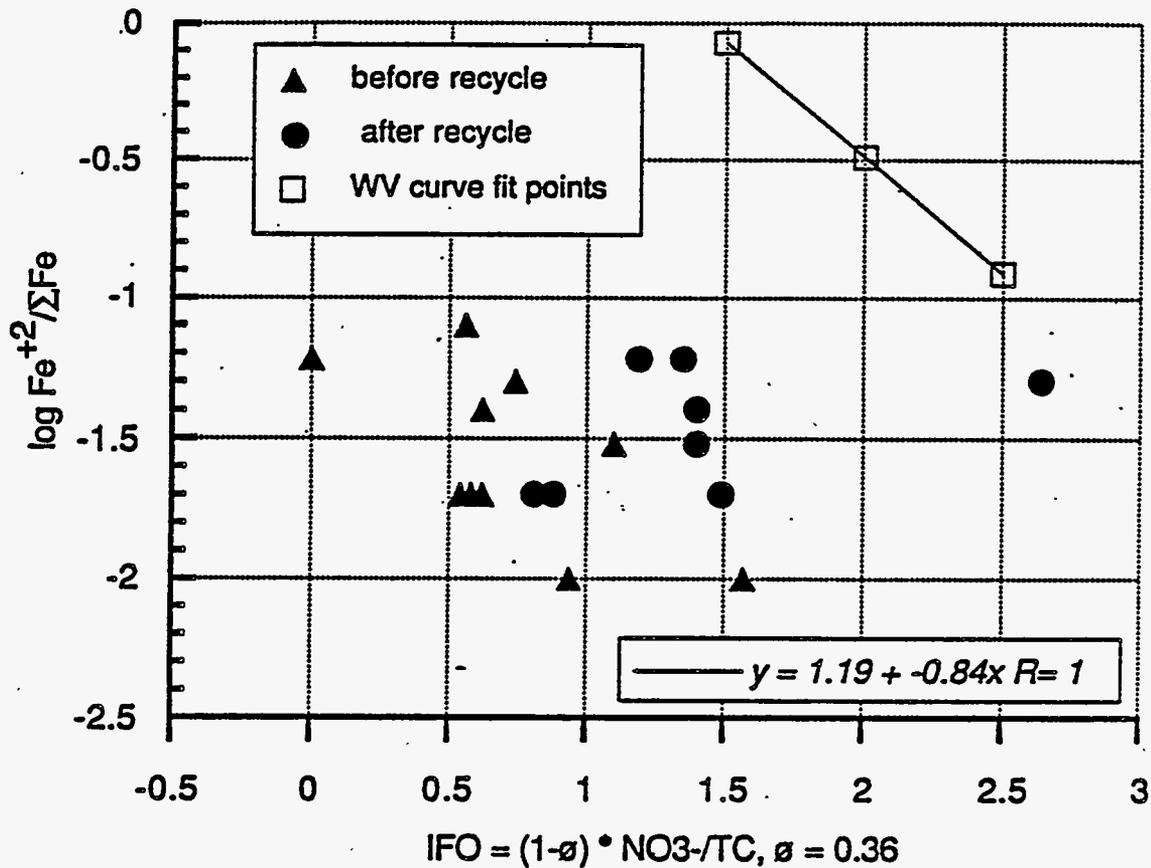


Figure 6.3.6. Comparison of FY 1991 PHTD Laboratory-Scale Glass Redox Data with the WVDP Model (Jain 1992)

6.4.1 Offgas Generation

Correlations have been developed for maximum offgas generation rate and total gas generation by species during treatment of an NCAW simulant with HCOOH. The gases detected were H₂, N₂O, NO, NO₂, CO₂, and NH₃. No CO or N₂ was observed (below detection limits). The NO_x was measured continuously with intermittent measurements of NO. Ammonia as NH₄⁺ was measured in the condensate and slurry, but not in the gas phase.

Offgas generation rate is sensitive to a number of process parameters (HCOOH addition rate, amount of HCOOH added, temperature), slurry composition (concentration of noble metals, NO₂, NO₃, and CO₃²⁻), and pH. The correlations presented apply specifically to conditions and simulants tested. The uncertainty associated with application of offgas generation rate data outside of the test envelope should be considered.

Offgas generation depends on the slurry pH. As HCOOH is added to the slurry, the pH decreases. The rate of decrease depends on the presence of bases (primarily, OH^- and CO_3^{2-}) and rate of addition. Offgas generation is initiated between a pH of 8 to 9. In the pH range of 7.5 to 7, the gas generation rate increases significantly. For the simulants tested, about 0.3 moles of HCOOH/L_{slurry} is required to reach a pH of 7. Foaming was observed only during the maximum gas release period of the slurry preparation steps (pH 7.5 to 7). An anti-foaming agent was not used during the tests.

Gas generation rates of CO_2 and N_2O increased simultaneously and sharply with process time. Carbon dioxide and N_2O were the principle contributors to offgas generation during HCOOH addition for the NCAW simulant tested with noble metals. The ratio of N_2O to NO_x generation rates varied significantly. The difference is not yet understood, although it is thought to be related to the pH, mixing efficiency, and HCOOH addition rate. Maximum NO_x generation rates were observed in the absence of noble metals and at high HCOOH addition rates. In the presence of noble metals and at an equivalent of 2 gpm HCOOH addition rate, the NO_x generation rate was a factor of 10 less than the N_2O and CO_2 generation rates. Hydrogen generation rates were a factor of 10 lower on a molar basis than the principle gases. Based on the summation of NH_4^+ measured in the slurry and condensate, the maximum NH_3 generation rate was estimated to be ~ 0.5 mole/min, ~ 10 times less than the CO_2 generation rate.

The cumulative maximum offgas generation rate (sum of all gases measured) and maximum offgas generation rate for CO_2 are proportional to the HCOOH addition rate over the range tested (2 to 8 gpm full-scale equivalent) as shown in Figure 6.4.1. The correlation of N_2O and NO_x with HCOOH addition rate is slightly more scattered, suggesting that interactions with other variables may be significant. Generation rates of N_2O and NO_x are given to provide a comparison of the relative rates. Hydrogen and NH_3 generation rates are not shown because major releases of these gases require a threshold amount of HCOOH, independent of addition rate. Hydrogen and NH_3 are not major contributors to the maximum total offgas generation rate.

These data suggest that the HCOOH addition rate can be used to control the maximum offgas generation rate. Decrease in temperature will also decrease the generation rate and may be used as a control variable (refer to Appendix F). Significant changes in the amount of CO_3^{2-} are predicted to impact the maximum generation rate.

The relative amounts of gas generated are shown for major species in Figure 6.4.2. The total amount of gas generated is proportional to the amount of HCOOH added. Carbon dioxide is the primary contributor (average 68.5% for nominal NO_2 concentration) to the net amount of gas evolved. Nitrous oxide is the second major contributor (in the presence of the noble metals). The amount of N_2O produced depends on the amount of HCOOH added and the amount of NO_2 present (refer to Figure 6.1.5). Stoichiometrically, 0.5 moles of N_2O are produced and 1 mole of HCOOH consumed for every mole of NO_2 consumed (refer to Section 6.3). The fraction of N_2O and NO_x measured varies significantly (refer to Table 6.1.1), which is not currently well understood. With the exception of

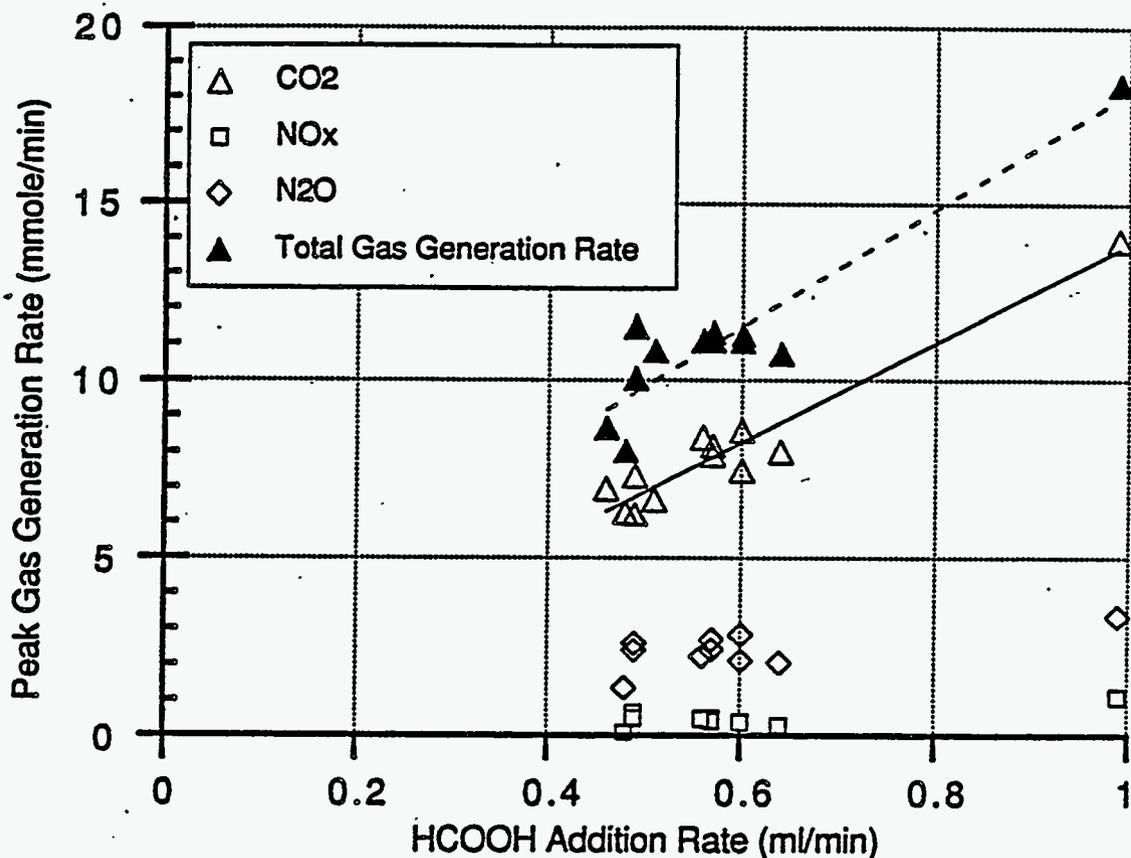


Figure 6.4.1. Correlation of Peak Offgas Generation Rate (CO₂, NO_x, N₂O, total gas) with HCOOH Addition Rate. Lines are placed by linear regression.

test 7.1, the N₂O and NO_x comprised from 20 to 30% of the total gas produced. In test 7.1 (high nitrate/low nitrite), which had high NH₃ production, the N₂O and NO_x comprised < 10% of the total amount of gas measured.

Hydrogen and NH₃ are minor contributors to the total gas produced. The amount of H₂ measured was < 1% of the total amount of gases measured. The largest amount of H₂ was observed only in the presence of noble metals and after a threshold value related to the amount of HCOOH added and the initial NO₂ was reached (refer to Figure 6.1.1). Once the threshold was reached, the amount of H₂ produced appears to be proportional to the amount of HCOOH added.

The amount of NH₃ generated is proportional to the amount of H₂ produced and the amount of NO₂ present in the slurry (refer to Figure 6.1.8). At the nominal NO₂ loading (0.13 M), the amount of NH₃ measured was < 10% of the total moles of gas produced. At higher NO₂ concentrations (0.4 M), the NH₃ made up 22% of the total offgas measured (on a molar basis).

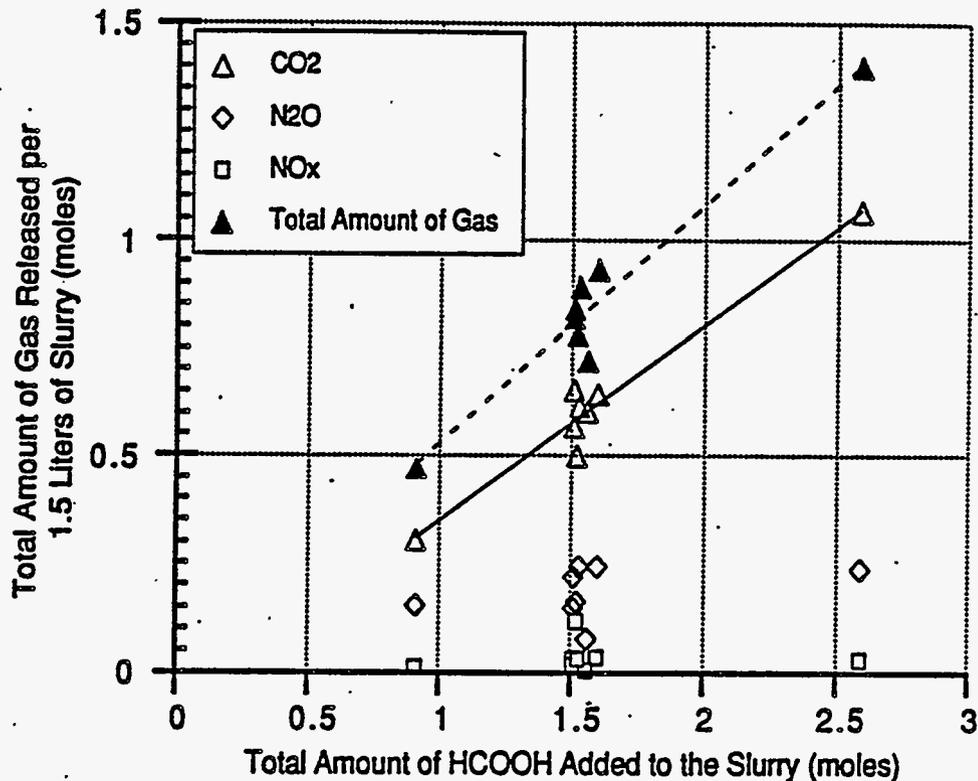


Figure 6.4.2. Correlation of Offgas Generation (CO₂, NO_x, N₂O, total gas) with Amount of HCOOH Added to NCAW Slurry Simulant. Lines are placed by linear regression.

The ratio of NO/NO_x for conditions tested with noble metals present was 0.71 to 0.88, with the balance of the NO_x being NO₂. The origin of the NO₂ is not certain. It may be from forming reactions or via oxidation of NO by O₂ in the gas stream. Laboratory tests will be conducted in FY 1992 to estimate the NO and NO₂ generated directly by SRAT slurry reactions.

Conditions required to initiate a major H₂ release during processing of pretreated NCAW are fairly well defined. However, because the range of conditions tested is rather limited, the data are not sufficient to determine the maximum H₂ generation rate for all realistic and worst case generation conditions that may be encountered in HWVP processing. Major H₂ releases are observed in the presence of noble metals and when sufficient HCOOH has been added to deplete the NO₂. The dependence of H₂ peak initiation on temperature and pH has not been investigated. In the FY 1991 studies, simulant was treated with HCOOH at 95°C. The major H₂ releases were observed only at a pH < 5.5. In the studies at SRL with DWPF simulants, a significant delay in H₂ initiation was sometimes observed. This may be caused by differences in composition and process conditions.

The maximum H₂ generation rates are provided in Table 5.3.1. Conditions that could affect the rate of H₂ generation include slurry temperature, noble metal and base (eg., OH⁻ and CO₃²⁻) concentration, concentration/species of organics present, and the amount of HCOOH added. Effects of these parameters on H₂ generation rates have not been adequately investigated for all HWVP slurries.

The absence of noble metals significantly changes slurry gas generation characteristics during feed preparation steps; a major reduction occurs in the generation of H₂, NH₃, and N₂O. The amount of NO₂ increases substantially. Similar to tests with noble metal-containing simulant, the major fraction of evolved gas was CO₂.

6.4.2 Glass Redox Control

Control of glass oxidation state to avoid melt foaming or crystalline solids formation requires integration of both slurry preparation and vitrification chemistry. Potential reaction scenarios are discussed in this report and have been identified previously Wiemers,^{(a)(b)} and Bickford (1985a; 1985b). Empirical approaches have been established at each waste vitrification site in the United States to control melt redox. Each correlation appears to work well for the slurries from which the correlation was developed. Sections 6.2 and 6.3 of this report address application of these correlations to HWVP NCAW simulant.

For HWVP, the measurement of Fe⁺²/ΣFe in the waste glass is used as an indicator for suitable redox control. The glass redox criteria is $0.005 \leq \text{Fe}^{+2}/\Sigma\text{Fe} \leq 0.23$.^(c) The lower limit (more oxidized state) is based on an analytical detection limit for Fe⁺² and the observation that foaming has not occurred when Fe⁺² was detected in the glass. The upper limit (lower reduced state) is a conservative value to avoid crystalline solids formation in the melt.

Operation of the melter under more oxidizing conditions has been recently considered by SRL; more oxidized glass requiring less reductant (HCOOH) is desirable to reduce the potential for H₂ generation and NH₃ production in the SRAT. Alternative rheology adjustments, such as adding HNO₃ or dilution, may be required if the amount of HCOOH added is lowered.

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- (a) Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company, HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (b) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-90-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (c) *Hanford Waste Vitrification Plant Technical Data Package*, WHC-SD-HWV-DP-001, section 13, Item 310, October 1990, Rev. 5H.

Based on the studies conducted to date with NCAW simulants, the recommended reductant (HCOOH) addition for obtaining an acceptable glass redox is a molar ratio of 3 HCOOH/NO₃⁻. The amount of NO₃⁻ in the waste and recycle streams added to the waste during HWVP processing is included in the calculation for reductant requirements. This is an empirical relationship and is provided to ensure that the glass redox criteria is met. The FY 1991 laboratory-scale feed preparation studies suggest that the HCOOH/NO₃⁻ requirement may be lowered to 2 (refer to Table 6.3.1); however, it is not certain whether this would apply to bounding oxidizing (e.g., high NO₂ and NO₃) conditions.

Rather than the proposed empirical approach, it would be preferable to predict the glass redox based on reactions of the slurry/melter feed components both in the SRAT/SME processing and in the melter cold cap. This provides more certainty in adjusting process requirements based on slurry composition, an important issue for HWVP because of the potential for a highly variable slurry composition. Under test conditions employed during FY 1991 testing, HCOOH was consumed primarily through NO₂ reduction to nitrous oxide, decomposition to H₂, and production of NH₃ (refer to Section 6.3). The fraction of HCOOH consumed by individual reactions is dependent on test conditions and slurry composition (refer to Figure 6.3.3). The net result, i.e., cumulative effect of these reactions, is that approximately the same percentage of HCOOH is consumed (refer to Figure 6.3.4). The amount of HCOO⁻ remaining after processing in the SRAT and SME is sufficient to balance the NO₃⁻ in the melter cold cap, providing an acceptable glass redox. The specific reactions of the melter cold cap that provided this relationship have not been investigated.

The disparity in the empirical formula for glass redox control (ratio of HCOOH to NO₃⁻) lies in the fact that the reactions that consume the reductant (HCOOH/HCOO⁻) in the SRAT/SME are not entirely accounted for. It appears that over the range of compositions tested, this consumption does not measurably impact the empirical glass redox correlation. Measurement of glass redox in theoretical cases, such as simulant processed/vitrified in the absence of HCOO⁻, NO₃⁻, and/or NO₂ might provide a better understanding of the redox phenomena and provide a basis for lowering the glass redox limit.

6.5 Evaluation of NCAW Simulant Thermal Analyses

Two endotherms and an exotherm were observed in the thermograms between 50 and 550°C (thermograms are provided in Appendix G). The two endotherms were observed between 50 and 130°C, and 230 and 310°C. The enthalpy of these two endotherms was approximately 80 and 60 J/g dried slurry, respectively. The exotherm was observed between 124 and 250°C with an enthalpy change of -207 to 305 Joule/g dried slurry. The low initiation temperature (124°C) observed in this test suggests that a potential for initiating exothermic reactions may exist under conditions described in the PSAR (Herborn and Smith 1990). Further testing will be required to confirm this finding. The exotherm was observed in all thermograms except for sample 1.3-7.1 (initial slurry simulant). This suggests that HCOO⁻, which is not present in sample 1.3-7.1, may contribute to the observed exotherm. The weight loss associated with the exotherm is greater for samples 1.1-47.1 and 1.3-4.7, perhaps because these samples included the recycle stream which approximately doubled the NO₃⁻ loading

(compare with sample 1.3-32.1). For a relative comparison, reported major enthalpy changes for a West Valley slurry simulant (SF-10) ranged from -229 to -854 J/g.^(a) The exotherm for the West Valley simulant was observed in the temperature range of 240 and 600°C, and is attributed to the combustion of sugar.

The first (low temperature) endotherm was not observed in the thermogram of 1.1-47.1 (formed slurry simulant plus recycle waste stream simulant). The uniqueness of these samples with respect to this endotherm is not understood at this time.

The endotherms observed in Region III (230 to 310°C) may be attributed to the fusion of nitrate and nitrite salts. No weight change was observed in Region III as would be expected for a physical change in the material. A small weight loss (1.3 to 2.8%) was observed in Region IV (>500°C). No measurable weight change in the higher temperature range was observed. The lack of measurable energy change in Region IV may be due to the cancelling effect of simultaneous exothermic and endothermic reactions.

No events were observed in the Henkin tests.

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

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Appendix A

Comparison of Analytical Methods for NCAW Slurry Simulant Characterization

Appendix A

Comparison of Analytical Methods for NCAW Slurry Simulant Characterization

A.1 Objectives

Simulant compositional analyses of neutralized current acid waste (NCAW) are challenging due to the complex nature of the simulant matrix that consists of over 40 elements. Previous analytical results showed large deviations between target composition and analytical values depending on the particular element, specific technique, or sampling procedure.^(a) Interferences due to sampling techniques and analytical methods must be determined and the data corrected if possible to have confidence in analytical results. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), and X-ray Fluorescence (XRF) techniques were evaluated for accuracy and precision in determining the known constituents of the NCAW simulant. This study of analytical methods was intended to show the current capabilities of ICP-MS, ICP-ES, and XRF (using existing quality assurance [QA] Level II procedures) in the analysis of NCAW simulant. Project funding and scope were limited. Although other analytical methods, such as ion chromatography, are available, only the three methods listed above were considered for evaluation.

A.2 Compositional Analyses

Target values are presented for measured stock NCAW slurry simulant composition in Table A.1. The target values are the best estimation of NCAW simulant composition based on the weighed amounts of chemicals added to prepare the simulant. Further analytical development/study is necessary before full confidence in data can be established and/or values can be determined for each element in the simulant. Note that the noble metal target values are approximately 25% higher than in the FY 1991 NCAW reference composition shown in Table 4.1.1. Due to a calculation error, the noble metals were added at the concentrations shown in Table A.1.

(a) Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company, HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.

Table A.1. NCAW Stock Feed Simulant Target Composition for FY 1991 Laboratory-Scale Studies

Element	Slurry Molarity (Assuming 125.0 g oxides/L slurry) gmoles element /L	Component	Composition (Assuming 125.0 g oxides/L slurry) g oxide/L
Ag	1.32E-03	Ag2O	1.53E-01
Al	2.27E-01	Al2O3	1.16E+01
B	2.10E-04	B2O3	7.31E-03
Ba	1.46E-03	BaO	2.24E-01
Ca	1.80E-02	CaO	1.01E+00
Cd	3.00E-02	CdO	3.85E+00
Ce	4.77E-03	CeO2	8.21E-01
Cr	4.39E-03	Cr2O3	3.34E-01
Cs	5.43E-03	Cs2O	7.65E-01
Cu	3.93E-03	CuO	3.13E-01
F	6.52E-03	F	1.24E-01
Fe	4.51E-01	Fe2O3	3.60E+01
K	5.32E-03	K2O	2.51E-01
La	5.12E-03	La2O3	8.34E-01
Li	6.05E-06	Li2O	9.04E-05
Mg	1.15E-02	MgO	4.64E-01
Mn	3.15E-02	MnO2	2.74E+00
Mo	4.95E-03	MoO3	7.13E-01
Na	0.58 to 0.88	Na2O	18.0 to 27.3
Nb	1.10E-04	Nb2O3	1.29E-02
Nd	2.64E-02	Nd2O3	4.44E+00
Ni	3.93E-02	NiO	2.94E+00
P	1.56E-02	P2O5	1.11E+00
Pb	3.74E-03	PbO2	8.95E-01
Pd	1.45E-03	PdO	1.77E-01
Pr	1.18E-03	Pr2O3	1.95E-01
Rb	6.70E-04	Rb2O3	7.33E-02
Rh	1.28E-03	Rh2O3	1.62E-01
Ru	4.79E-03	Ru2O3	6.02E-01
SO3	1.04E-02	SO3	8.33E-01
Sb	5.11E-05	Sb2O3	7.45E-03
Se	1.82E-04	SeO2	2.02E-02
Si	8.56E-02	SiO2	5.14E+00
Sm	5.44E-04	Sm2O3	9.48E-02
Sn	9.99E-05	SnO	1.35E-02
Sr	1.46E-03	SrO	1.51E-01
Ta	1.92E-05	Ta2O5	4.24E-03
Te	7.94E-04	TeO2	1.27E-01
Ti	1.04E-02	TiO2	8.31E-01
Y	9.04E-04	Y2O3	1.02E-01
Zn	5.24E-03	ZnO	4.26E-01
Zr	1.56E-01	ZrO2	1.92E+01

Anions/TOC	gmoles element/L
NO3-	0.13 to 0.40
NO2-	0.13 to 0.45
CL-	1.06E-02
SO4--	1.04E-02
PO4--	1.56E-02
CO3--	1.25E-01
F-	6.52E-03
TOC	1.39E-02

Note: Values given are based on the amount of source chemical added to prepare the slurry.

In testing, Na actually varied from 0.58 M to 0.88 M, based on the amount of anion adjustment (addition of NaNO₂, NaNO₃, and Na₂CO₃). Nitrite concentration was a test variable that varied from 0.13 M to 0.45 M. Table 4.1.3 lists sodium nitrite/carbonate/nitrate addition for each test. Sodium carbonate was added at the target value for carbonate for each test. Nitrate was increased by 0.27 M for test 7.1 to investigate the effect of high nitrate on forming and offgas reactions.

A.2.1 Method/Approach

The composition of NCAW slurry simulant was measured by ICP-MS, ICP-ES, and XRF. Methods' comparison provided an indication of the current method's applicability to NCAW simulants, the relative error associated with sampling, and the uncertainty associated with each NCAW component concentration value. The resultant information may be applied to optimize future analyses selection, to refine slurry simulant preparation steps, and to clarify limitations based on compositional data. A study of characterization methods should provide information on the actual analytical errors for the NCAW simulant matrix using existing QA Level II procedures. Historically, the acceptable range of error for preparing major components of NCAW simulant slurry is plus or minus 10% from target concentrations.^{(a)(b)}

Nine FY 1991 stock NCAW slurry simulant samples were analyzed (three per method) for 5 major elements (Al, Fe, Mn, Ni, Zr) and 31 minor elements. Each sample was analyzed in triplicate. The major elements were analyzed by all three methods. The minor elements were evaluated by one or two methods depending on the applicability of each method and cost considerations. Table A.2 lists which elements were analyzed by which method. Values were not determined for Sb, I, K, Cl, P, S, and F due to instrument detection limits, difficulties and inaccuracies in sample preparation, or cost limitations of the three methods (see Table A.2 footnotes for details).

The following analytical procedures were applicable to the compositional analyses:

- Procedures and Quality Control for Energy Dispersive X-ray Fluorescence Spectroscopy Using the Backscatter Fundamental Parameter (BFP) Approach with the KeveX 0180A System, R.W. Sanders. 1990. PNL-7-40.48, Rev. 1.

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- (a) Wiemers, K. D., C. A. Anderson, and M. E. Peterson. 1987. *Evaluation of Process Offgases Released During the Forming of an HWVP Feed Simulant*. Letter Report to Westinghouse Hanford Company, HWVP-86-V110203G, Prepared by Pacific Northwest Laboratory, Richland, Washington.
 - (b) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Letter Report to Westinghouse Hanford Company, HWVP-0-1.2.2.03.03A, Prepared by Pacific Northwest Laboratory, Richland, Washington.

Table A.2. Comparison of Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Inductively Coupled Plasma Emission Spectroscopy (ICP-ES), and X-ray Fluorescence (XRF) for Neutralized Acid Current Acid (NCAW) Simulant Composition Analysis

Element	Target Values* Simulant mole element/L	ICP-ES Simulant mole element/L	ICP-ES Percent Deviation from target	Footnotes	ICP-MS Simulant mole element/L	ICP-MS Percent Deviation from target	Footnotes	XRF Simulant mole element/L	XRF Percent Deviation from target	Footnotes	Element
Ag	1.32E-03	1.61E-03	21.7	*1				1.35E-03	2.5		Ag
Al	2.27E-01	2.22E-01	-2.4		1.65E-01	-27.2	*6	2.51E-01	10.4	*11	Al
B	2.10E-04	8.48E-03	3938.0	*2							B
Ba	1.46E-03	1.50E-03	3.1					8.88E-04	-39.2	*12, *13	Ba
Ca	1.80E-02	9.48E-03	-47.3	*3				1.43E-02	-20.7	*3	Ca
Cd	3.00E-02	3.01E-02	0.3					2.69E-02	-10.2	*13	Cd
Ce	4.77E-03				1.19E-03	-75.0	*7	3.53E-03	-26.0	*13, *14	Ce
Cr	4.39E-03	4.49E-03	2.2								Cr
Cs	5.43E-03			*3	6.04E-04	-89.9	*3	6.45E-04	-88.1	*3	Cs
Cu	3.93E-03	3.83E-03	-2.6					2.79E-03	-29.1	*12	Cu
F	6.52E-03										F
Fe	4.51E-01	4.40E-01	-2.3		3.90E-01	-13.5	*6	4.36E-01	-3.4		Fe
I	4.53E-08										I
K	5.32E-03									*21	K
La	5.12E-03				8.83E-04	-82.8	*7	3.03E-03	-40.9	*13, *15	La
Li	6.05E-06										Li
Mg	1.15E-02	1.08E-02	-5.8								Mg
Mn	3.15E-02	3.21E-02	1.9		2.95E-02	-6.4		2.84E-02	-9.7		Mn
Mo	4.95E-03	4.52E-03	-8.8					5.46E-03	10.3	*11	Mo
Na	1.97E-01	2.17E-01	10.2	*4							Na
Nb	1.08E-04				1.37E-04	26.6	*8	1.04E-04	-4.1		Nb
Nd	2.64E-02				6.55E-03	-75.2	*7				Nd
Ni	3.93E-02	4.26E-02	8.4		3.32E-02	-15.5	*6	3.78E-02	-3.9		Ni
P	1.56E-02			*21						*21	P
Pb	3.74E-03	3.80E-03	1.5					3.62E-03	-3.2	*20	Pb
Pd	1.45E-03				1.11E-03	-23.4	*9	3.65E-03	-2.4	*20	Pd
Pr	1.18E-03				3.19E-04	-73.0	*7	1.18E-03	-18.1	*16	Pr
Rb	6.70E-04			*3	7.72E-05	-88.5	*3	6.58E-05	-90.2	*3, *20	Rb
Rh	1.28E-03				7.31E-04	-43.0	*9	7.22E-05	-89.2	*3, *20	Rh
Ru	4.79E-03				4.08E-03	-14.7	*9	1.06E-03	-17.7	*16	Ru
S	1.04E-02							4.87E-03	1.6	*16	S
Sb	5.11E-05			*21						*21	Sb

Table A.2. (contd)

Element	Target Values* Simulant mole element/L	ICP-ES Simulant mole element/L	ICP-ES Percent Deviation from target	Footnotes	ICP-MS Simulant mole element/L	ICP-MS Percent Deviation from target	Footnotes	XRF Simulant mole element/L	XRF Percent Deviation from target	Footnotes	Element
Se	1.82E-04			*21				1.66E-04	-8.9		Se
Si	8.56E-02	1.31E-02	-84.7	*5				1.22E-01	42.6	*17	Si
Sm	5.54E-04				1.59E-04	-71.4	*7				Sm
Sn	9.99E-05			*21				3.54E-05	-64.8	*18	Sn
Sr	1.46E-03	5.48E-04	-62.5	*3				5.61E-04	-61.8	*3	Sr
Ta	1.92E-05				2.30E-05	19.6	*10				Ta
Te	7.94E-04				1.54E-03	94.0	*8	6.85E-04	-13.0	*11	Te
Ti	1.04E-02	6.33E-03	-39.1	*5, *9				7.34E-03	-29.4	*19	Ti
Y	9.04E-04				2.33E-04	-74.2	*8	8.75E-04	-3.2		Y
Zn	5.24E-03	5.05E-03	-3.7					4.68E-03	-10.8	*11	Zn
Zr	1.56E-01	1.52E-01	-2.8	*5	1.37E-01	-12.4	*6	1.60E-01	2.7		Zr

Footnotes

* NCAW simulant composition differs slightly from the reference feed composition presented by WHC FY1991 revision due to sub/del (ie. for radioactive and hazardous elements) See Redox/Rheology Scoping Studies Test Plan, HWVP-91-1.2.203.02A, pp 22. Simulant composition (mole EA) is based on 125 g WOA. Na target value is ~77% lower than simulant target value. Na₂CO₃ and NaNO₂ were not added to slurry. See *4. Pd, Rh, Ru target values are 15%, 25%, and 25% higher respectively than the NCAW Simulant Composition. See *16.

*1 Interference from zirconium will cause silver number to be high. Silver can be corrected in future analyses for Zr interference.

*2 Boron/Na impurities may leach out of the borosilicate glassware used for dissolution of samples and/or be present as impurities in source chemicals.

*3 Ca, Cs, Rb, and Sr were present in the wash during slurry preparation. They will be underrepresented in the slurry.

A further 13% error was introduced to Ca content by overcompensating for impurities in the mixed hydroxide slurry. Not enough Ca nitrate was added to the slurry.

*4 Na target value reported for slurry that does not contain Na₂CO₃ or NaNO₂. These compounds were intentionally left out. They were added prior to each Redox/Rheology test so that concentrations could be modified if desired. Simulant target for Na with Na₂CO₃ and NaNO₂ is 0.882 mole Na/L.

*5 Residue present after dissolution of slurry. Residue consisted of SiO₂, TiO₂ and possibly some ZrO₂.

*6 ICP-MS is designed to measure ppm and ppb amounts. The accuracy of this technique is decreased when large quantities are measured.

Additional sample dilutions and runs may be required to analyze major elements. Analytical development may be required.

*7 Rare earth elements may have formed insoluble fluorides with HF which may have been used to dissolve the slurry for ICP-MS. Reported values are low.

*8 Y₂O₃, Nb₂O₃ and TeO₂ were reported within ±3-14% of target by XRF technique. It is possible that they did not dissolve during sample preparation for ICP-MS.

*9 Analytical development and/or revision of existing procedures necessary to provide more precise or acceptable results.

*10 Approximately 0.085 g of Ta₂O₅ was added to a 20L volume. Further accuracy on such a small quantity may not be possible.

*11 Within the estimated experimental error (±12%) for the XRF technique for slurry analysis.

Table A.2
misc # 26

Table A.2. (contd)

Footnotes (continued)

*12 Ba and Cu are within $\pm 10\%$ as reported by ICP-ES. A good matrix standard was not available for XRF analyses.

The Cu peak in the XRF spectrum was very poorly defined due to overlap from other elements.

*13 The gain was optimized for the noble metals in the XRF analysis possibly resulting in the low values for elements with atomic numbers greater than Ba.

Normal procedure is to allow a variable gain in the region of interest. Elements that would be affected are La, Ce, and Ba.

*14 A good matrix standard was not available for XRF analysis. Exact error on analysis undeterminable. Ce source may have absorbed moisture.

*15 A good matrix standard was not available for XRF analysis. Exact error on analysis undeterminable. La(OH)₃ source may have also gained moisture.

*16 Pd was added in 15% excess due to calculation error. Ru and Rh were added in a 24% excess. The error on XRF analysis is approximately 12%.

This error is composed of 5% error from thin film standard calibration, 5% from actual analysis, and 2% from overlap correction.

*17 A good matrix standard was not available for XRF analysis. Exact error on analysis undeterminable.

Si had a large overlap correction due to its location at the low end of the spectrum (XRF).

*18 Approximately 0.45g of SnCl₂·2H₂O was added to 20L volume. Accuracy within 10% for such a small quantity may not be possible.

*19 A further 5% error may have been introduced by overcompensating for impurities in the mixed hydroxide slurry. Not enough TiO₂ was added to the slurry.

Fe escape peak interfered with the resolution of the Ti peak from the XRF spectrum. Overlap correction difficult.

*20 Pb and Bi have two values reported by XRF due to two different x-ray producing targets. Each x-ray target has a range of elements/energies (eV) associated with it. Some overlap exists between x-ray targets. Quantitative information can be obtained twice for those energies which are the same.

*21 In ICP-ES Sb, Sn, Se, and P were below detection limits due to sample dilution. In XRF Sb, S, Cl, I, P, and K peaks were not resolvable from the spectrum due to overlap or the element was below detection limits.

- Determination of Elements by Inductively Coupled Argon Emission Spectroscopy, J. J. Wagner. 1991. PNL-ALO[®]-211, Rev. 0.
- Inductively Coupled Plasma Mass Spectroscopy, E. J. Wyse. 1991. PNL-ALO-280, Rev. 0.

A.2.2 Sample Preparation

Samples of ICP-ES slurry were prepared by taking a known quantity of NCAW slurry and dissolving the solids using HCl with a small quantity of HNO₃. Acidified mixtures were heated until most or all of the solids were dissolved. A 10X dilution was performed followed by adding 2% HNO₃. The sample was then stirred well and analyzed by ICP-ES. Some solids may have been present in the final sample. Because SiO₂ and TiO₂ are particularly hard to dissolve they would likely comprise the larger percentage of any solid residue. Sample dilution may make analyses of elements present in small concentrations difficult or impossible as detection limits are approached. Sodium and B impurities may be leached from the glassware during sample dissolution, possibly resulting in slightly higher concentrations of Na and B. The ICP-ES analysis was performed on a Jarrel-Ash Model 975 Plasma Atomcomp ICP-ES.

Samples of ICP-MS NCAW slurry were dried overnight in an oven at 90°C to a powder. Then HNO₃, HCl, or HF were used to dissolve the dried powder. The acidified mixture was microwaved in an oven until most or all of the solids were dissolved. Samples were diluted as necessary to bring the major element concentrations within the detection range of ICP-MS and prevent overloading of the detector. However, sample dilution made analyses of elements present in very minor concentrations difficult or impossible because detection limits were approached or exceeded. By using the above sample preparation method, the lanthanides or other elements that might react with HF to form insoluble precipitates or volatile complexes (i.e., YF₃ and SiF₄, respectively) could not be accurately determined. The analysis was performed on a VG ICP/MS PQ1.

Samples of XRF were dried overnight in an oven at 100 to 105°C. The dried powder was pressed into pellets and analyzed. Low atomic number elements are hard to resolve on the XRF spectrum because there are many overlapping peaks in the lower energy part of the spectrum, making resolution difficult or impossible. Elements such as S, P, Cl, and K may experience peak overlap interferences. Matrix effects may also enhance or suppress signals for a variety of elements. Thin film standards were used in the XRF analysis; a more suitable matrix standard would eliminate some of the error in XRF analysis of slurries. Estimated experimental error was ±12% for NCAW slurries. Experimental error consisted of approximately 5% error from thin film standard calibration, 5% from actual analysis, and 2% from overlap correction. However, matrix effects could significantly increase errors to >12%. The XRF analysis was performed on a Kevex XRF0810A instrument.

(a) Analytical laboratory operations.

The results of the NCAW simulant compositional analyses are outlined in Tables A.2, A.3, and A.4. Table A.2 compares analytical results for the three methods to the compositional target values from Table A.1. Deviations from target values are summarized in Table A.3 for ICP-ES, ICP-MS, and XRF. Table A.4 identifies the standard deviation between the nine analyses for each element per each method.

A.2.3 Major Element (Al, Fe, Mn, Ni, and Zr) Concentrations

Included in Table A.2 is a comparison of the results of the three analytical methods to the major element target values from Table A.1. Detailed footnotes in Table A.2 explain where deviation from target values exceeded 10%. The major components were measured by ICP-ES within 1.9 to 8.4% of target values. The major elements in the NCAW simulant were measured by XRF within the range of 2.7% to 10.4% of the target values (Al was the only element over 10%). Aluminum is a low atomic number element with peaks on the low energy end of the spectrum in XRF. Overlap is more pronounced in the low energy region of the spectrum; hence, a larger error and uncertainty exists. Measurements by ICP-MS resulted in larger deviations from target than ICP-ES or XRF for the major elements. The percent deviation from target values ranged from ± 6.4 to 27.2%. Manganese was the only element with less than 10% deviation from target value analyzed by ICP-MS. The ICP-MS method is designed to measure ppm and ppb concentration levels. Increased sample dilution may improve the results for the major elements, but may also cause lower concentration elements to be diluted below detection limits. Repeated sample analyses might be required. After comparing the results of the three analytical methods, additional development would be necessary for ICP-MS to increase the accuracy of quantifying the major elements in the NCAW simulant. The average major element deviation from target was 3.6% for ICP-ES, 15% for ICP-MS, and 6% for XRF.

A.2.4 Minor Element Concentrations

The minor component elements in the NCAW slurry were shown to be within 10% of the target values except where large uncertainties in the analytical data exist. In all cases, deviations could be accounted for by specific sample or simulant preparation technique or by a limitation in the specific analytical method. Element-specific limitations are listed in Table A.2. Percent deviation from target values are summarized in Table A.3. Note that the error from target values represents sampling, sample preparation, and analytical limitation errors. It is difficult to assign a certain percentage of the total error from target values to a particular error. Theoretically, ICP-MS, ICP-ES, and XRF would, in an ideal sample (no sample matrix effects present) with elemental concentrations above detection limits, produce results within $\pm 5\%$.

Table A.3 is provided for review and comparison of analytical results for NCAW simulant minor element composition. Minor components analyzed within the range of $\pm 0.3\%$ to 10.2% from target values by ICP-ES were Ba, Cd, Cr, Cu, Pb, Zn, Mg, Mo, and Na. Not all of the elements were analyzed by ICP-MS as an expense consideration. The range of percent deviation from target values for minor elements analyzed by ICP-MS was ± 12.4 to 94%. Results from XRF analysis

Table A.3. Analytical Error (% Deviation From Target) in Measuring Metal Cation Concentration in Neutralized Current Acid Waste (NCAW) Slurry by X-ray Fluorescence (XRF), Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

Percent Deviation From Target#	ICP-ES	ICP-MS	XRF
<5%	Al, Ba, Cd, Cr, Cu, Fe, Mn, Pb, Zn, Zr		Ag, Fe, Nb, Ni, Pb, Ru, Y, Zr
5-10%	Mg (5.8%), Mo, Ni	Mn	Mn, Se
10-15%	Na(10.2%)	Fe, Ru, Zr	Al(10.43%), Cd(10.2%), Mo(10.27%), Te, Zn(-10.78%)
15-20%		Ni, Ta	Pd, Rh
20-43%	Ag, Tl	Al, Nb, Pd, Rh	Ba, Ca(-20.71%)*, Ce, Cu, La, Si, Tl
>43%	B*, Ca*, Si, Sr*	Ce, Cs*, La, Nd, Pr, Rb*, Sm, Te, Y	Cs*, Rb*, Sn, Sr*

#Target values are given in Table A.1.

*Significant portion of the deviation from target value can be accounted for by simulant preparation procedure or impurities present in starting materials. Analytical techniques may produce results with significantly less deviation from target values for Ca, Cs, Rb, Sr, and B.

Table A.4. Percent Relative Standard Deviation in Measuring Metal Cation Concentrations in Neutralized Current Acid Waste (NCAW) Slurry by X-ray Fluorescence (XRF), Inductively Coupled Plasma Emission Spectroscopy (ICP-ES) and Inductively Coupled Plasma Mass Spectroscopy (ICP-MS)

%RSD*	ICP-ES	ICP-MS	XRF
<5%	Ag, Al, B, Ca, Cd, Cr, Cu, Fe, Mn, Mo, Mg, Na, Ni, Pb, Sr, Ti, Zn, Zr	Al, Fe, Mn, Ni, Pd, Rh, Ru, Te, Zr	Ag, Ca, Cd, Ce, Co, Cu, Fe, La, Mn, Mo, Ni, Pd, Pb, Rb, Rh, Ru, Se, Sr, Te, Ti, Y, Zn, Zr
5-10%	Si#	Ce$\Delta\Delta$, Cs\dagger, La$\Delta\Delta$, Nd$\Delta\Delta$, Pr$\Delta\Delta$, Rb\dagger, Y$\Delta\Delta$ Sm$\Delta\Delta$	Nb**, AlΔ, SiΔ
10-15%			Ba***
>15%	Ba***	Nb**, Ta**	Sn**

*%RSD (relative standard deviation) was determined for the average values for triplicate runs of each sample.

**Nb, Sn, and Ta were present in concentrations of 0.1 mmole element/L or less.

***Ba was added as Ba(OH)₂·8H₂O which was extremely clumpy and difficult to crush adequately. This may have produced an inhomogeneous distribution.

Δ Al and Si are on the low energy end of the XRF spectrum and have large overlap corrections.

$\Delta\Delta$ The rare earth elements and Y formed insoluble fluorides during sample preparation for ICP-MS.

\dagger Ce and Rb were washed out during simulant preparation. Concentrations remaining were 0.1 mmole element/L or less.

#Si did not dissolve completely during sample preparation for ICP-ES. Samples were dissolved with HNO₃ and HCl. Residue analysis showed Si and Ti were present. Precipitates were not homogeneously distributed within the liquid sample that was analyzed by ICP-ES. This resulted in an increase in the uncertainty of the data.

showed percent deviations from $\pm 1.6\%$ to 10.78% for Ag, Nb, Pb, Ru, Y, Se, Cd, Mo, Te, and Zn. The percent deviation from target for any of the three methods for the elements B, Ca, Cs, Rb, and Sr is not valid because the actual target values were not known. Impurity concentrations of B were likely present (from impurities in source chemicals and glassware leaching) resulting in the high percent deviation from target. Calcium, Cs, Rb, and Sr as reported earlier (NCAW simulant preparation section) were washed out during simulant preparation in unknown quantities because simulant preparation was in a developmental stage, and previous procedures were used as a basis. Previous procedures washed out these same four elements. See subsequent sections on ICP-ES, ICP-MS, and XRF for more details about minor component analyses.

A.2.5 Noble Metal Concentrations

Noble metals were evaluated by XRF and ICP-MS. Data from XRF varied from expected values as follows: Ru was within 2% of the target value, but Rh and Pd were 18% below the target values. The ICP-MS test showed Ru 15% low, Rh 43% low and Pd to be 24% low with respect to target values. The large deviation from target values needs to be improved because of the critical role noble metals play in H_2 generation during simulant forming. Fusion of ICP-MS samples may improve results, although dilution of the sample is significantly increased by the fusion method, and Ru volatilization may be a problem. Increased dilution may also result in lower concentration elements being diluted below detection limits. Matrix matching and standard addition methods are expected to improve the accuracy of the XRF method. Proton-induced X-ray Emission is recommended as an independent confirmation of these critical components' concentration.^(a)

A.2.6 Sampling Error: Standard Deviation Between Duplicate Analyses

The slurry's homogeneity is affected by the components' solubility and particle size. The purpose of comparing analytical methods was to determine if the variability in analytical results was due to inhomogeneity in the slurry or in sampling technique. Differentiation between the two can be accomplished by calculating the standard deviation between duplicate runs and by comparing analytical methods. If all analytical methods produced variability for all elements, then sampling error^(b) may be responsible. If a particular element has a high standard deviation when analyzed by two of the three methods (ICP-ES, ICP-MS, and XRF), then it may not be distributed homogeneously in the slurry. It is also possible that elements present in very small quantities (near the detection limits) may

(a) Wiemers, K. D., M. H. Langowski and M. R. Powell. 1991. *Detailed Design Data Package, 1.9a Measure Hydrogen Generation During Formating, 1.10a Nitrate Salt Reaction*. PHTD-91-03.02-K898.

(b) The sampling error is defined as the variation between aliquots taken from a slurry batch. The slurry will settle if not stirred well when a sample is removed. Larger or more dense particles may prefer to be in the bottom third of the slurry. Lighter particulates may be located preferentially in the top third. Where the sample is removed may make a difference in the chemical composition of the sample.

not be homogeneous. This is because the simulant may not disperse uniformly if < 1 g of a component with low solubility is added to 20 L of the simulant. Sample preparation may also affect the standard deviation between duplicate samples if sample dissolution is required for the analysis, especially if a component is difficult to dissolve. However, the percent deviation from a known target is more sensitive to sample preparation difficulties.

Table A.4 identifies the standard deviation for the three analyses for each element per each analytical method. A large portion of the elements had <5% standard deviation. The simulant as a whole was homogeneous, and the sampling technique was good. Repeatability was excellent between duplicates and for all analytical methods except where noted in Table A.4. In all cases, there were explainable contributing factors. Elements with greater than 5% relative standard deviation were Nb, Al, Si, Ba, Sn, Mg, Ce, Cs, La, Nd, Rb, Y, Sm, Pr, and Ta. Niobium, Ta, Sn, Cs, and Rb were all present in concentrations of 0.1 mmole/L or less. Homogeneity on a small scale is difficult to achieve; therefore, the percent relative standard deviation (%RSD) is expected to be slightly higher. Aluminum, Si, Mg, Cs, La, Nd, Ce, Y, Sm, and Pr have a higher %RSD due to characteristic difficulties inherent in sample preparation or analytical technique. See footnotes in Table A.4 for specific reasons. Barium's high %RSD is probably due to its inhomogeneous distribution within the simulant. Barium was added as $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, which was extremely lumpy and difficult to crush; the large particle size caused poor distribution within the simulant. As a consequence of the homogeneity problems encountered with Ba, particle size specifications have been added to the NCAW simulant preparation procedure.

A.2.7 Inductively Coupled Plasma Emission Spectroscopy

Data from ICP-ES provided acceptable accuracy and precision for the major components (Al, Fe, Mn, Ni, and Zr) and also the minor elements Cu, Cd, Cr, Mo, Na, Pb, Mg, and Zn. The Ba value was accurate, but had a high standard deviation. Barium, as stated previously, was probably not homogeneously distributed within the simulant. Detection limitations were observed for Si, Ti, Ag, and B. Silicon and Ti were in the NCAW simulant in fairly insoluble forms. In ICP-ES, slurries are dissolved and injected in liquid form into the plasma; therefore, insoluble precipitates will not be homogeneously distributed within the liquid sample, resulting in low concentrations for these components. Higher than actual Ag concentrations were reported due to Zr interference, which is easily corrected. Future ICP-ES analyses will specify a Ag correction for Zr interference. Boron impurities from the glassware containers used for sample dissolution could increase analytical results slightly. Impurities from stock chemicals are more likely the cause of the higher concentrations of B. Calcium, and Cs were washed out in unknown quantities during simulant preparation; therefore, analytical results cannot be evaluated for accuracy. The percent deviation from target given in Tables A.2 and A.3 for Sr, Ca and Cs (also Rb analyzed by ICP-ES and XRF) represents the difference between measured analytical values and their respective starting quantities. The values for Sr, Ca, Cs and Rb in the two tables are for information only.

A.2.8 Inductively Coupled Plasma Mass Spectroscopy

Analysis of the major elements by ICP-MS showed an average error of 15% from target with the high error being 27% for Al and the low being 6.4% for Mn. The XRF and ICP-ES methods appear to be better suited to measure the higher concentrations of the major elements within $\pm 10\%$. However, increased sample dilution may produce better results for major elements using ICP-MS. The lanthanide elements were underestimated by 70 to 88% because they characteristically form insoluble fluorides during sample preparation or are difficult to dissolve in their present form. Adding boric acid to the slurries during sample preparation to aid dissolution may significantly improve rare earth detection accuracy. The noble metals were reported 14 to 43% below expected target values; improvement in such low accuracy is essential in order to make adjustments to the NCAW slurry. Fine tuning sample preparation procedures to increase applicability to the NCAW slurry may produce better results. Investigation into other analytical techniques for noble metal detection may be necessary. It should be noted that ICP-MS was not used to analyze all the elements possible, primarily a cost consideration. The ICP-MS test may have excellent capabilities for minor elements which were not investigated such as Sb, Se, Pb, P, S, Si, Sn, Sr, Ag, Ti, Zr, B, Ba, Ca, Cd, Cr, Cu, I, Mg, Mo, and Na.

A.2.9 X-ray Fluorescence

The XRF method is acceptable to analyze major elements and many minor components. It is especially good for measuring Ag, Nb, Pb, Ru, Se, and Y (<5% deviation from target). Analyzing by XRF also gave the lowest percent average deviation from target for the noble metals (1 to 18%). The unavailability of a suitable matrix standard, however, produced uncertainty in some measurements (i.e., Al, Ba, Cd, Ce, Cu, La, Pd, Rh, Si, Ta, Te, and Ti). Low atomic number elements (i.e., P, Cl, S etc.) have peaks that are very close together and therefore difficult to resolve. Wavelength Dispersive X-ray Fluorescence (WDXRF) would help to resolve the low atomic number elements. Barium, Ce, and La deviated from target values by 20 to 40%. Development of a more suitable matrix standard and/or the use of WDXRF for some elements may produce better results.

A.2.10 Summary of Compositional Analysis Analytical Methods

Results of the analytical method analyses demonstrate the need for multiple, independent, compositional methods. Evaluating ICP-ES, ICP-MS, and XRF for compositional determination of NCAW simulant showed that none of the three analytical methods could analyze for major elements, minor elements, and noble metals within 10% of the target values. It is apparent that each analytical method has strengths and limitations which must be taken into account to achieve the best results. The major components (Al, Fe, Mn, Ni, and Zr) and several minor components (i.e., Ag, Ba, Cd, Cr, Cu, Mg, Mo, Na, Nb, Pb, Ru, Se, Y and Zn) were analyzed with acceptable results by either ICP-MS, ICP-ES, or XRF or by a combination of the three methods.

Elements with significant analytical limitations for ICP-ES, ICP-MS, and XRF techniques at this time are B, Si, Ti, Rh, Pd, Ce, La, Nd, Pr, Sm, S, P, I, Cl, and F. Other analytical methods may need to be explored. Large errors associated with simulant preparation and/or sample preparation for analyses affected analysis of the rare earths, alkali metals, and alkaline earths (e.g., Cs, Sr, Rb, and Ca). Recommendations for the best method for Ca, Cs, Rb, and Sr analyses could not be made because actual target values were unknown.

Steps that could be or have been changed to allow for improved accuracy and precision are 1) ICP-MS results for the rare earths may be improved by an additional sample preparation step of adding boric acid to dissolve otherwise insoluble fluorides; in addition, increased sample dilution may reduce the percent deviation from target values for the major elements; 2) during simulant preparation, alkali metals and alkaline earths (i.e., Cs, Rb, Sr, Ca, and Mg) were lost in various quantities during the washing steps employed to reduce NO₃⁻; the simulant procedure was revised to minimize loss of these components in the washing steps in the future; 3) development of a good, matching matrix standard for XRF analysis is essential to correct for interferences.

Appendix B

Full-Scale Operation Steps for HWVP Feed Preparation

Appendix B

Full-Scale Operation Steps for HWVP Feed Preparation

Feed preparation steps planned for full-scale operations at the HWVP are outlined below, beginning with pretreated NCAW slurry transfer to the slurry receipt and adjustment tank (SRAT) and ending with frit addition to the slurry mix evaporator (SME). Steps 2 to 5 provide the basis for the laboratory test procedure (PHTD-WTC-006-35, Procedure for the Treatment of Slurries with Formic Acid).

1. Pretreated NCAW slurry is batch fed to the SRAT where it is concentrated to 100 to 150 g WO/L. The boil-off is condensed and routed to the Slurry Mix Evaporator Condensate Tank (SMECT) for subsequent waste treatment.
2. The concentrated NCAW slurry is cooled to 93 to 96°C, and HCOOH is added per process specifications.
3. After adding HCOOH, the NCAW slurry is reheated and maintained at boiling for up to 6 h. This period is referred to as "digestion." The boil-off liquid is routed to the SMECT for subsequent waste treatment.
4. The slurry is cooled and sampled for compositional analyses. Based on the analyses, any required chemical adjustments are made. The formatted slurry is then transferred from the SRAT to the SME.
5. Waste recycle is added to the SME slurry, followed by concentration, fresh frit addition, and further concentration.
6. Based on analytical results, the SME contents are either further adjusted by trim chemical addition, or transferred to the Melter Feed Tank.

Appendix C

**Rheograms for NCAW Melter Feed Simulant Containing
500, 550 or 600 g Total Oxide/Liter**

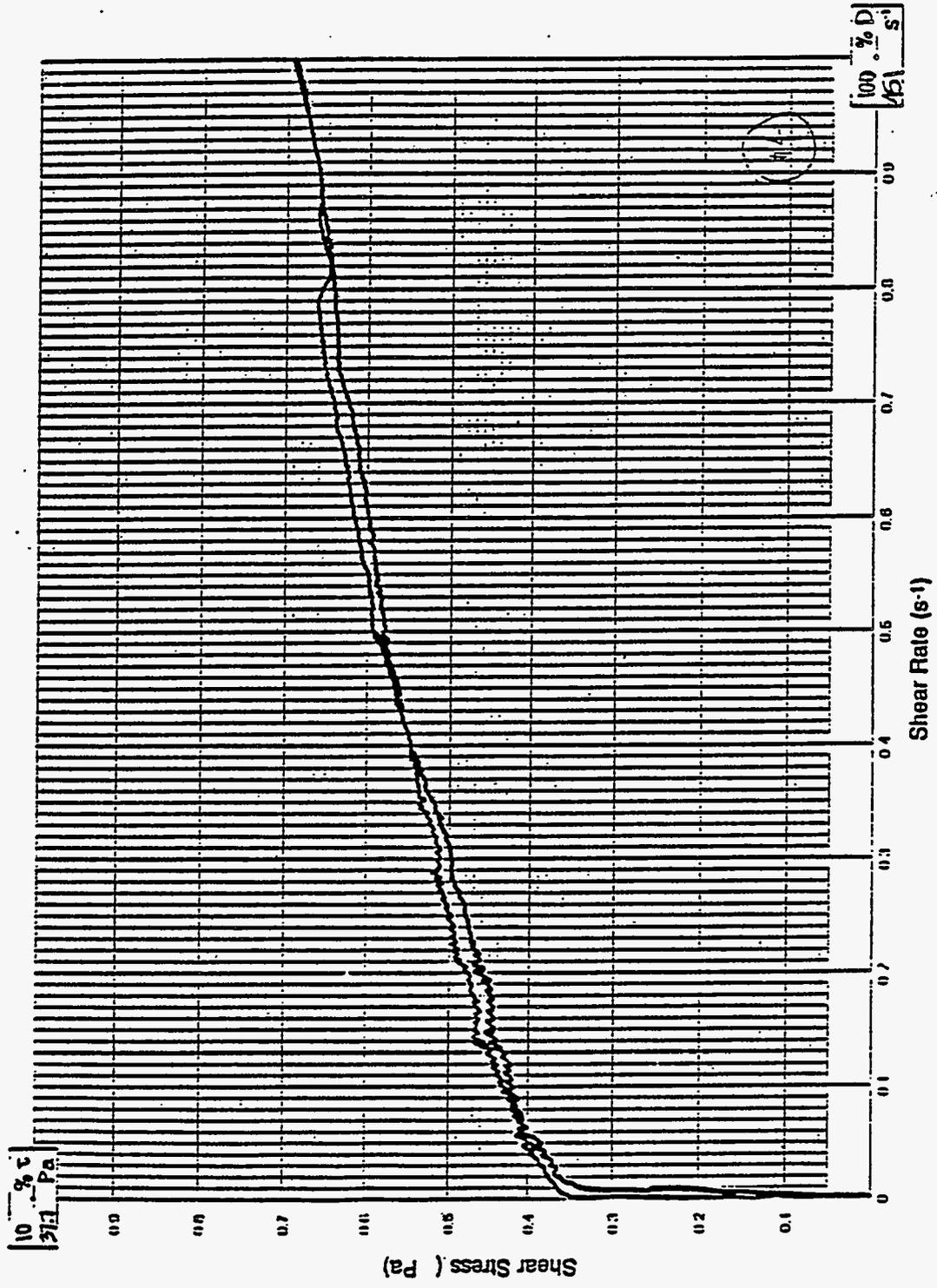


Figure C.1. Rheogram for NCA W Melter Feed Simulant Containing 500 g Total Oxide/Liter

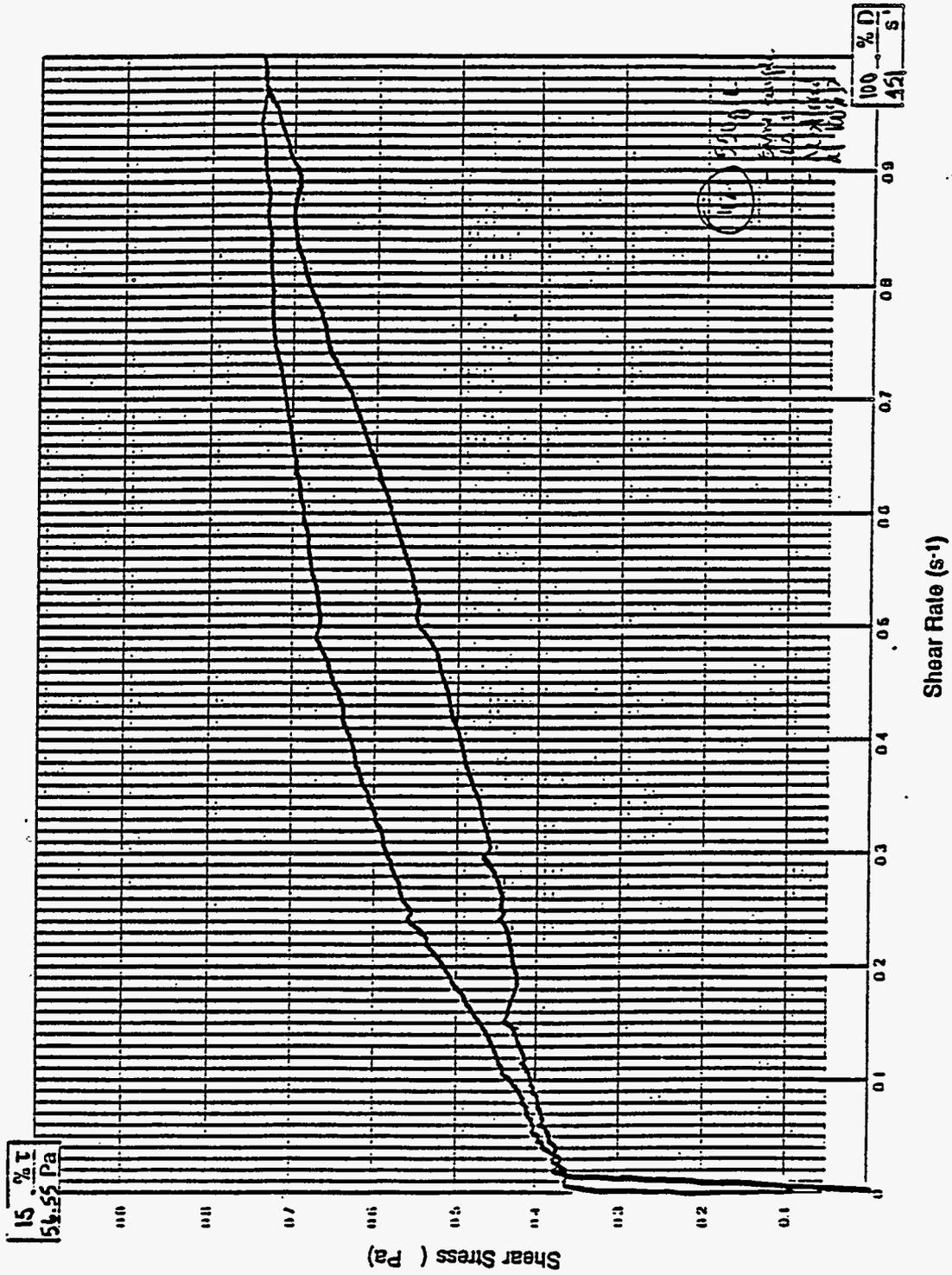


Figure C.2. Rheogram for NCAW Melter Feed Simulant Containing 550 g Total Oxide/Liter

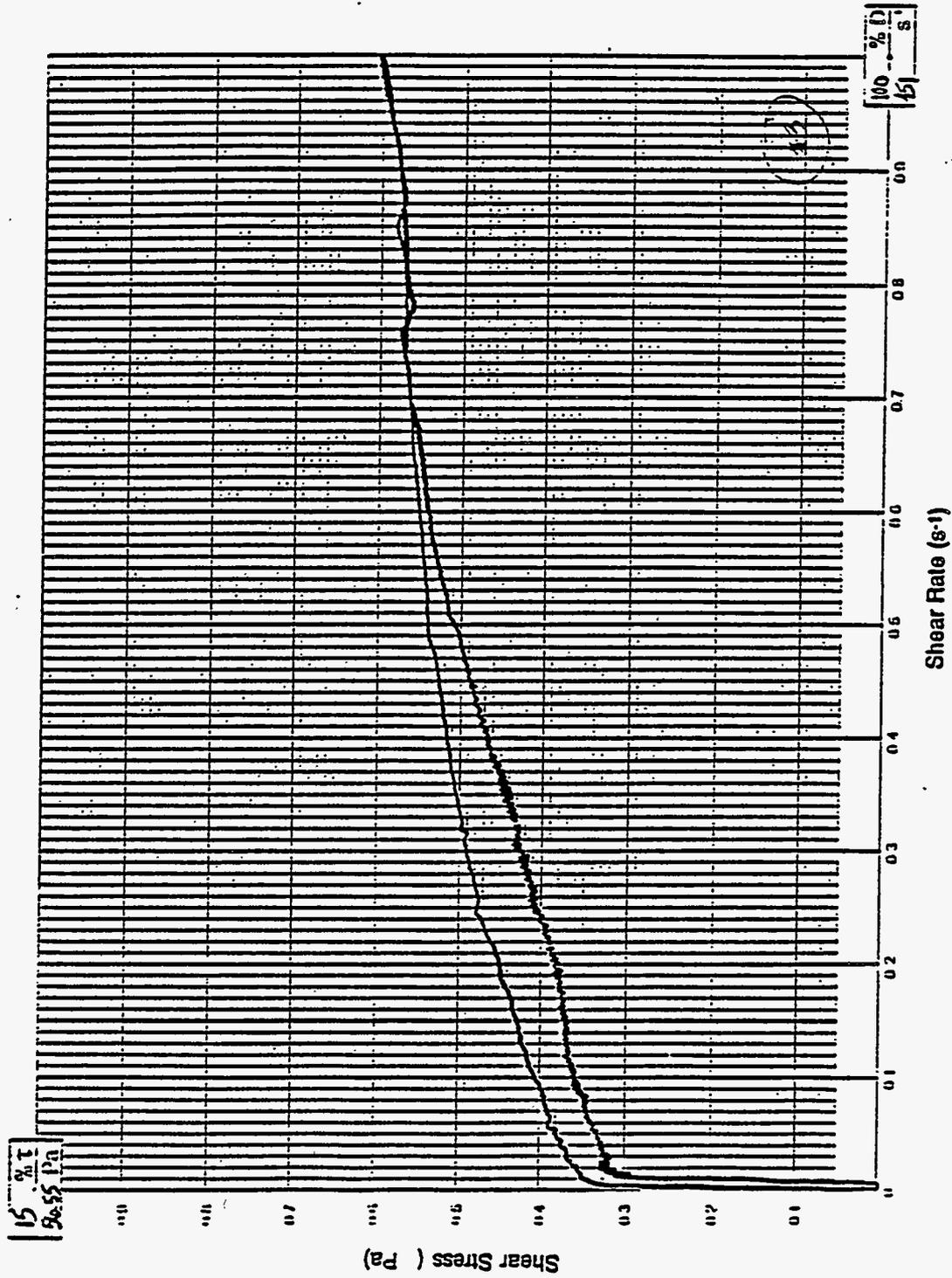


Figure C.3. Rheogram for NCAW Melter Feed Simulant Containing 600 g Total Oxide/Liter

Appendix D

Offgas Profile as a Function of Process Time and Key Events Related to Offgas Generation During FY 1991 Laboratory-Scale Feed Preparation Tests

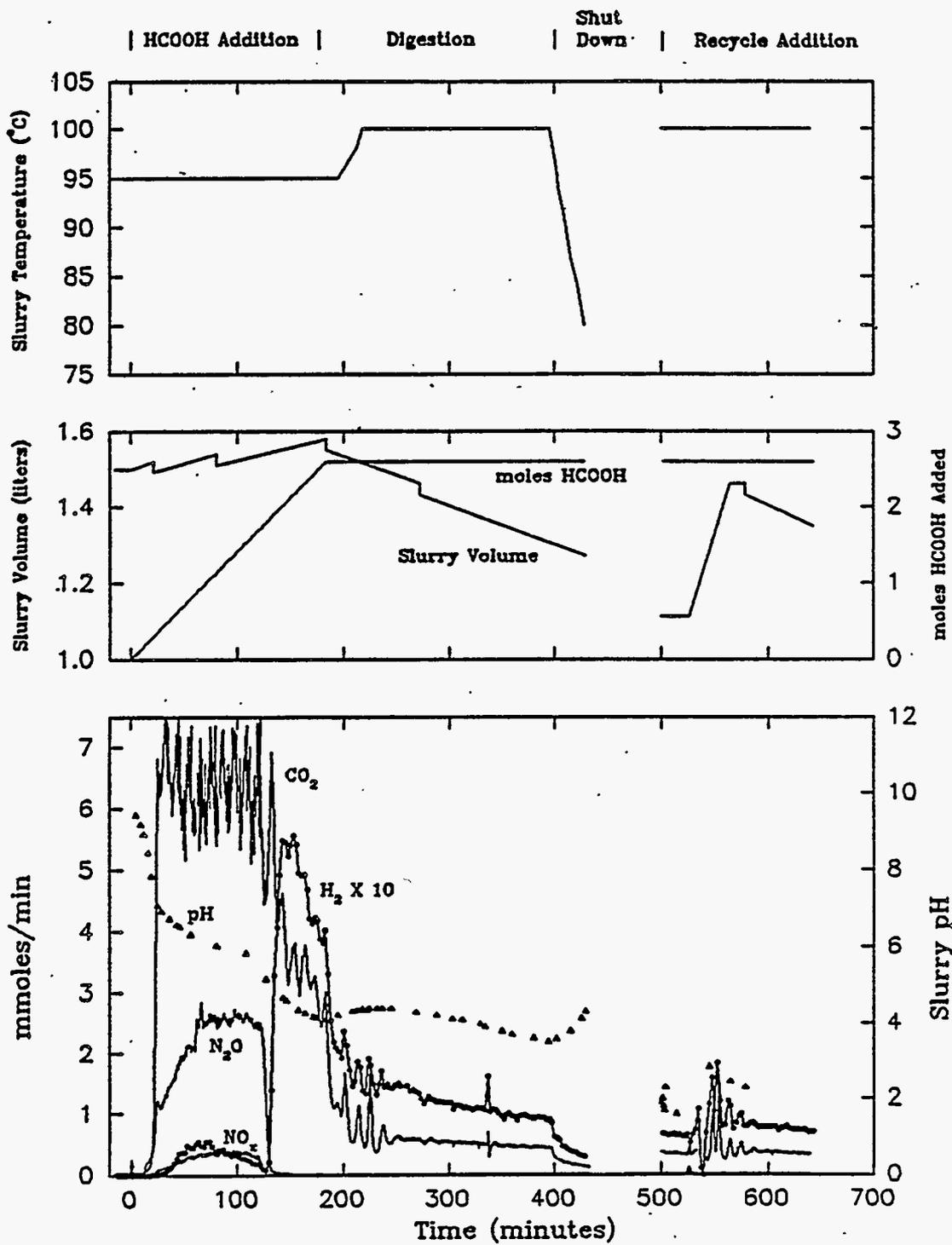


Figure D.1. Offgas Profile for NCAW Slurry Test 1.1: Maximum Amount of Formic Acid Added, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

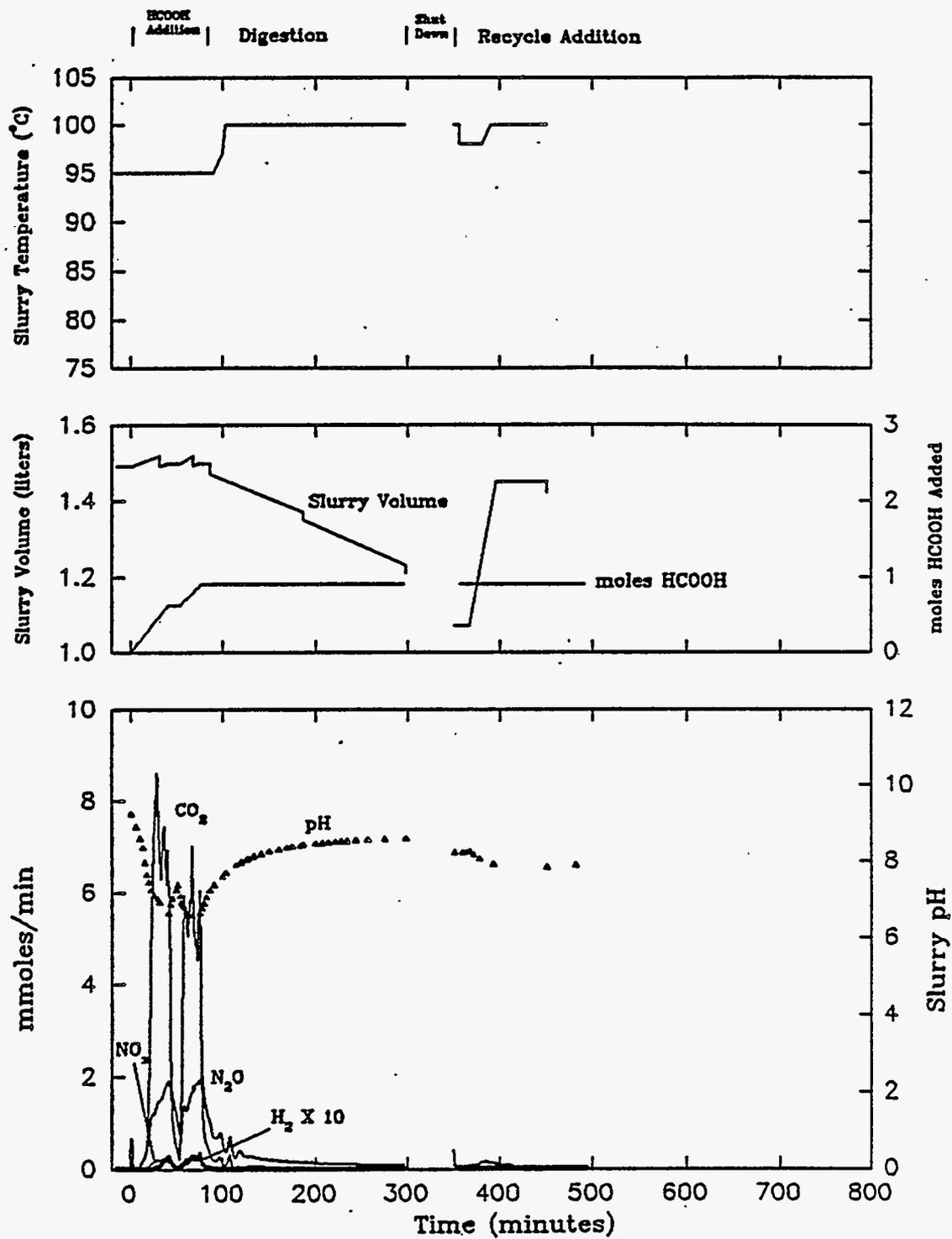


Figure D.2. Offgas Profile for NCAW Slurry Test 1.2: Minimum Amount of Formic Acid Added, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

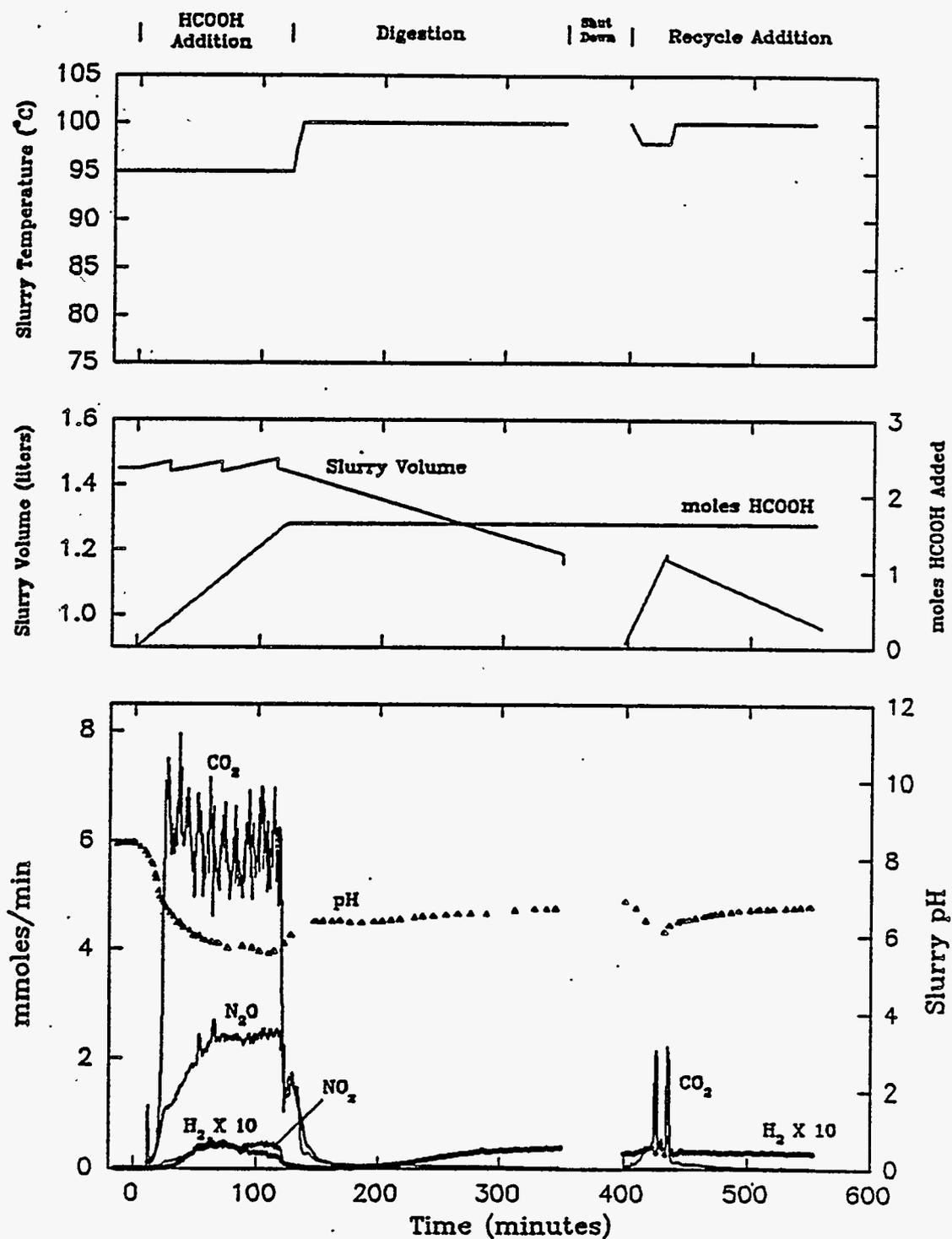


Figure D.3. Offgas Profile for NCAW Slurry Test 1.3: Mid-Amount of Formic Acid Added, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

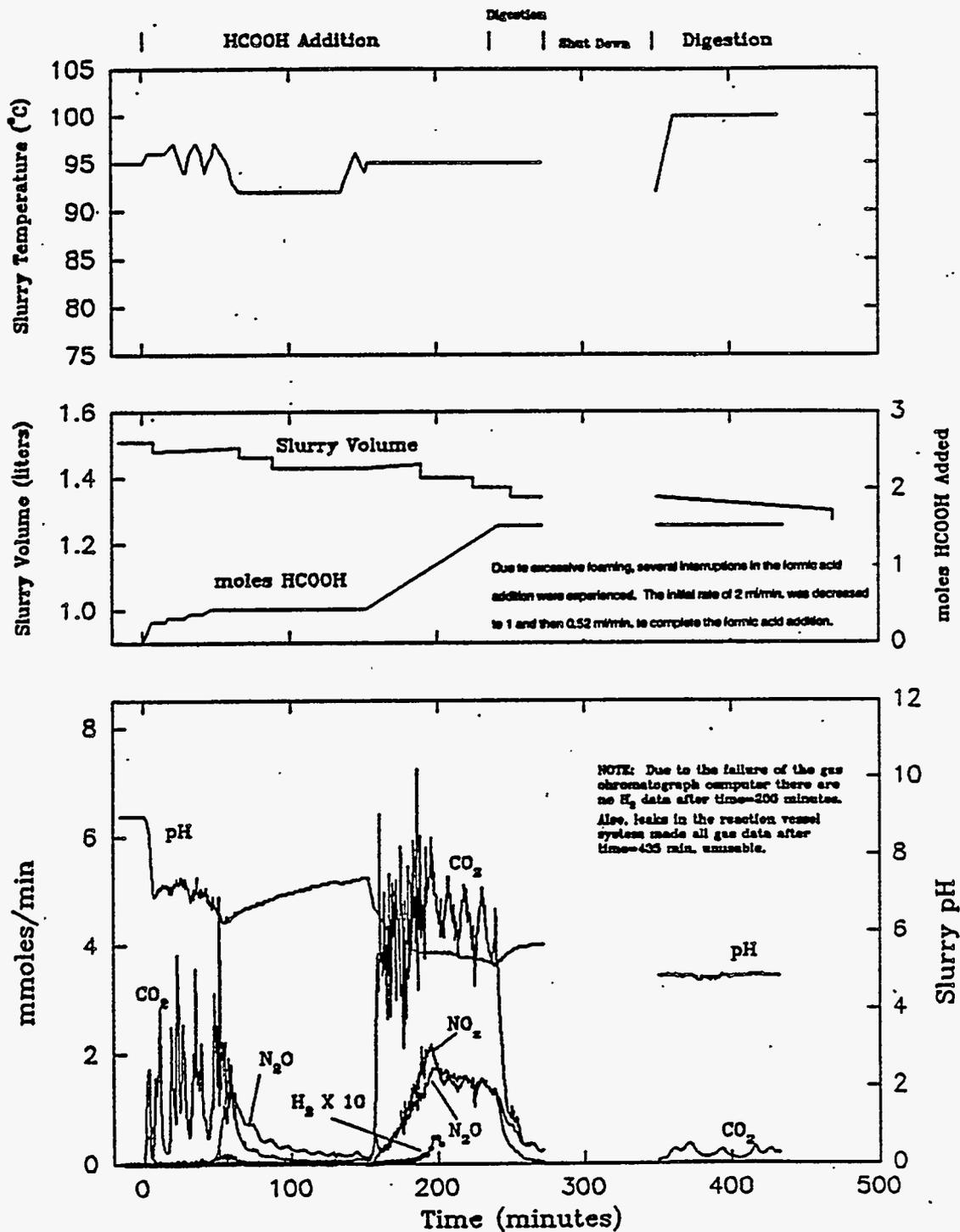


Figure D.4. Offgas Profile for NCAW Slurry Test 2.1: Maximum Formic Acid Addition Rate, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

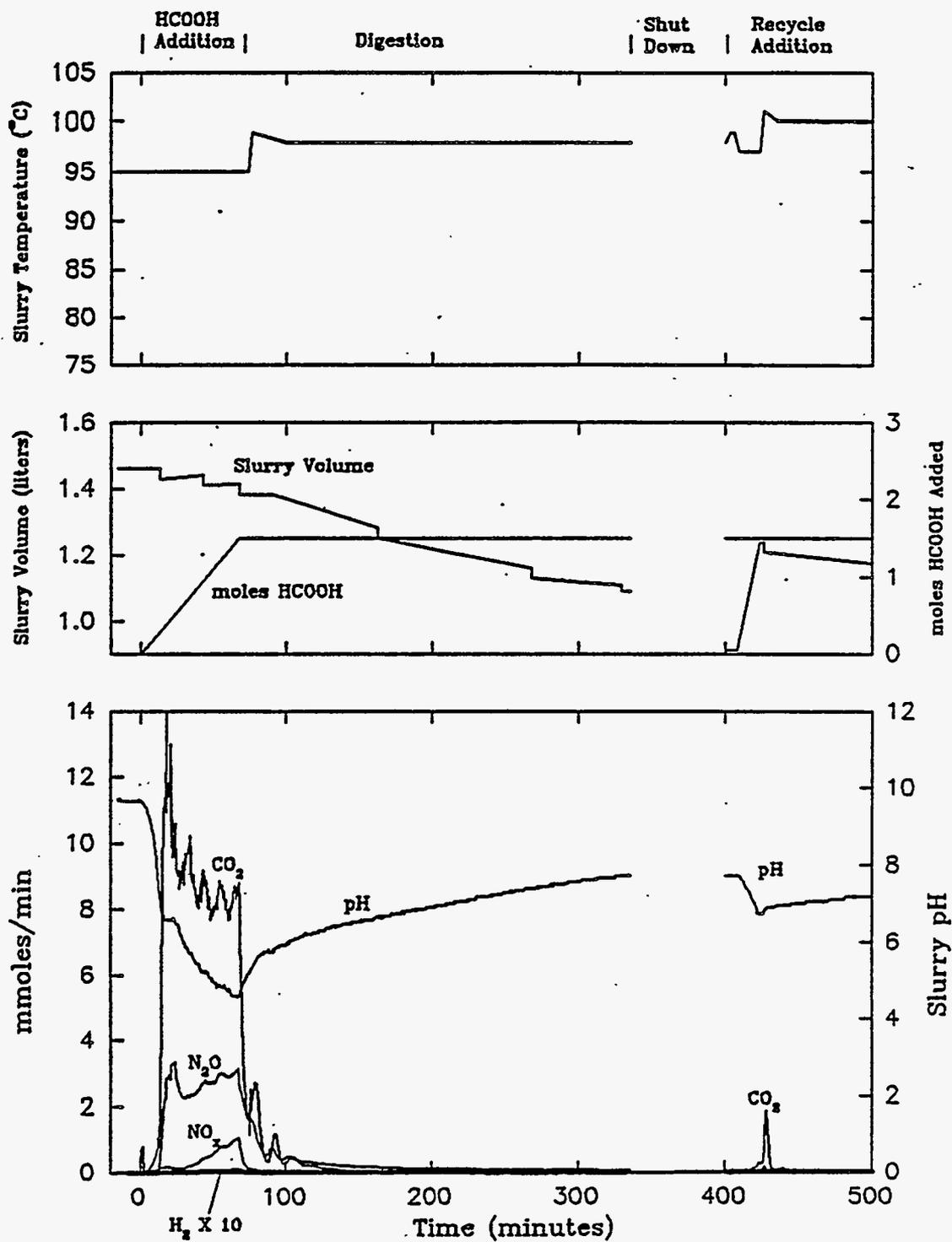


Figure D.5. Offgas Profile for NCAW Slurry Test 2.2: Mid Formic Acid Addition Rate, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

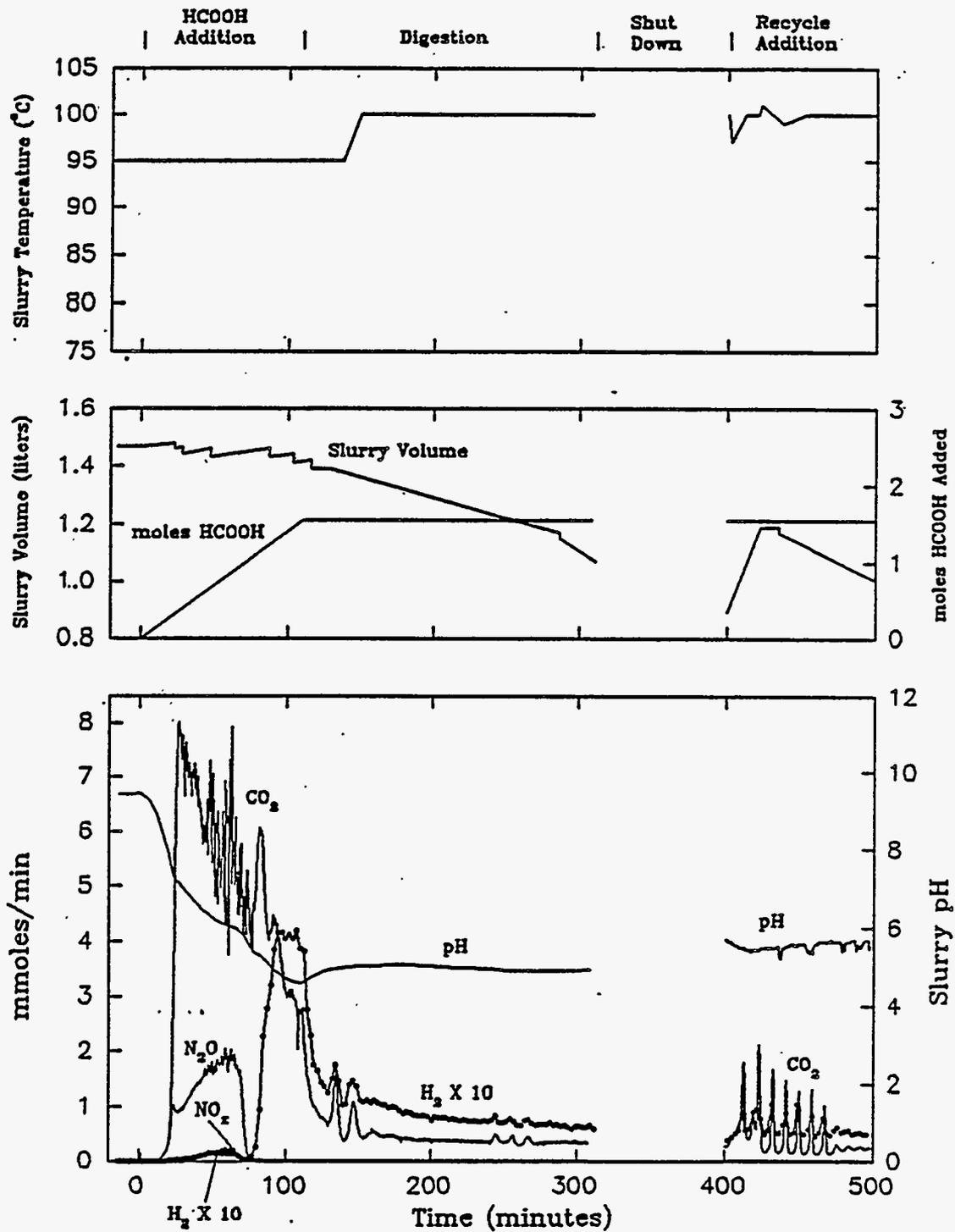


Figure D.6. Offgas Profile for NCAW Slurry Test 3.1: Minimum Amount of Nitrite Added, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

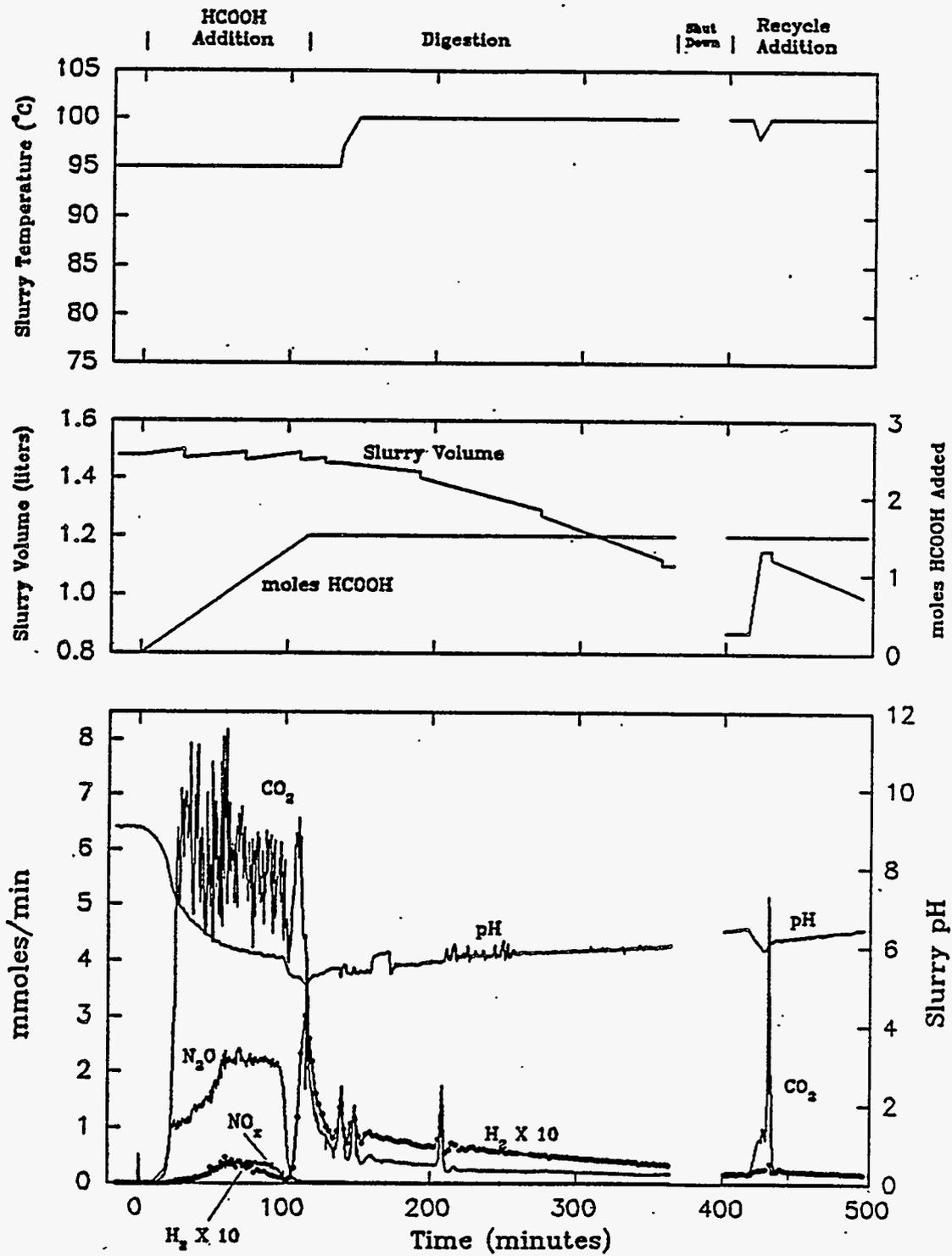


Figure D.7. Offgas Profile for NCAW Slurry Test 3.2: Mid-Amount of Nitrite Added, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

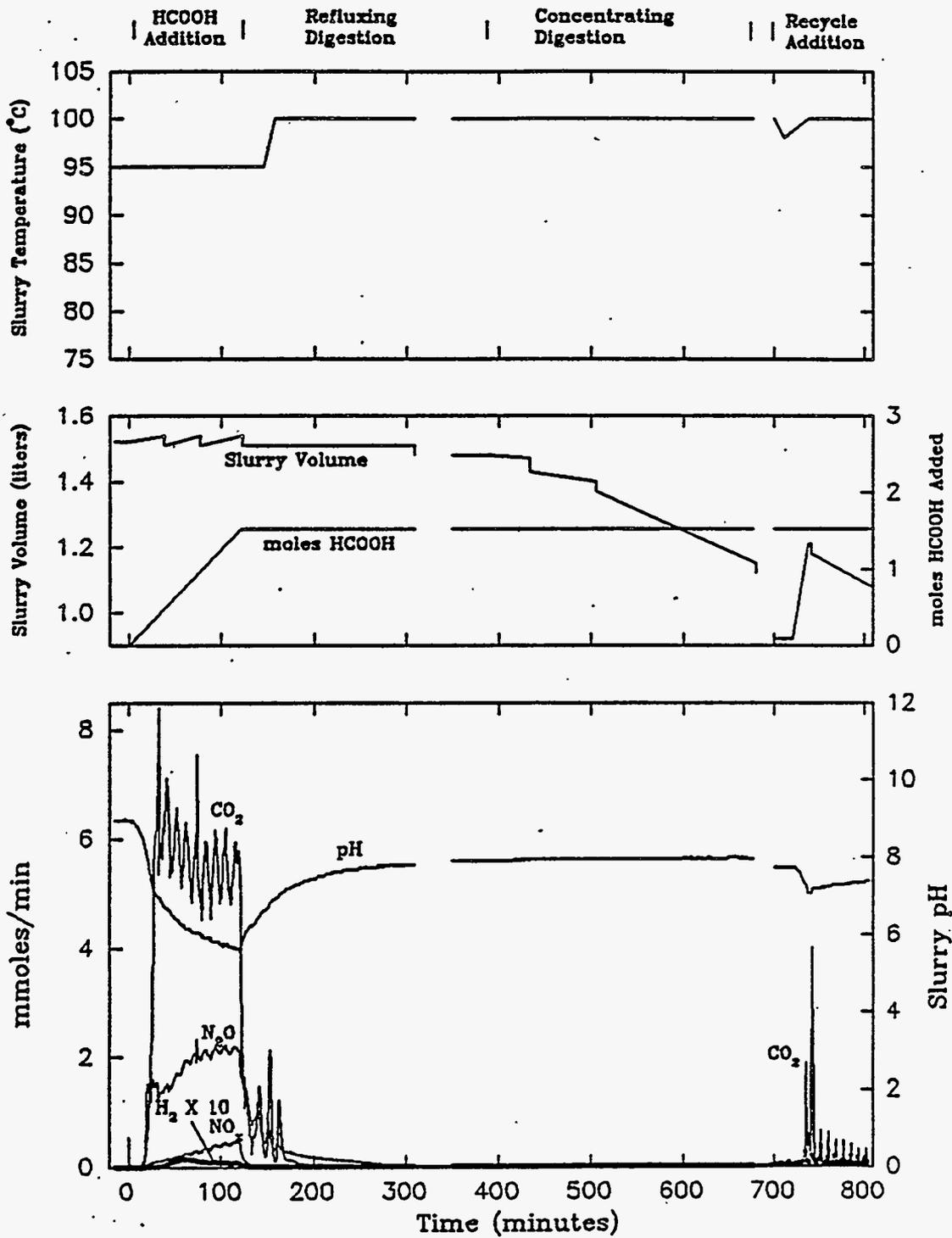


Figure D.8. Offgas Profile for NCAW Slurry Test 4.1: Extended Digestion Period, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

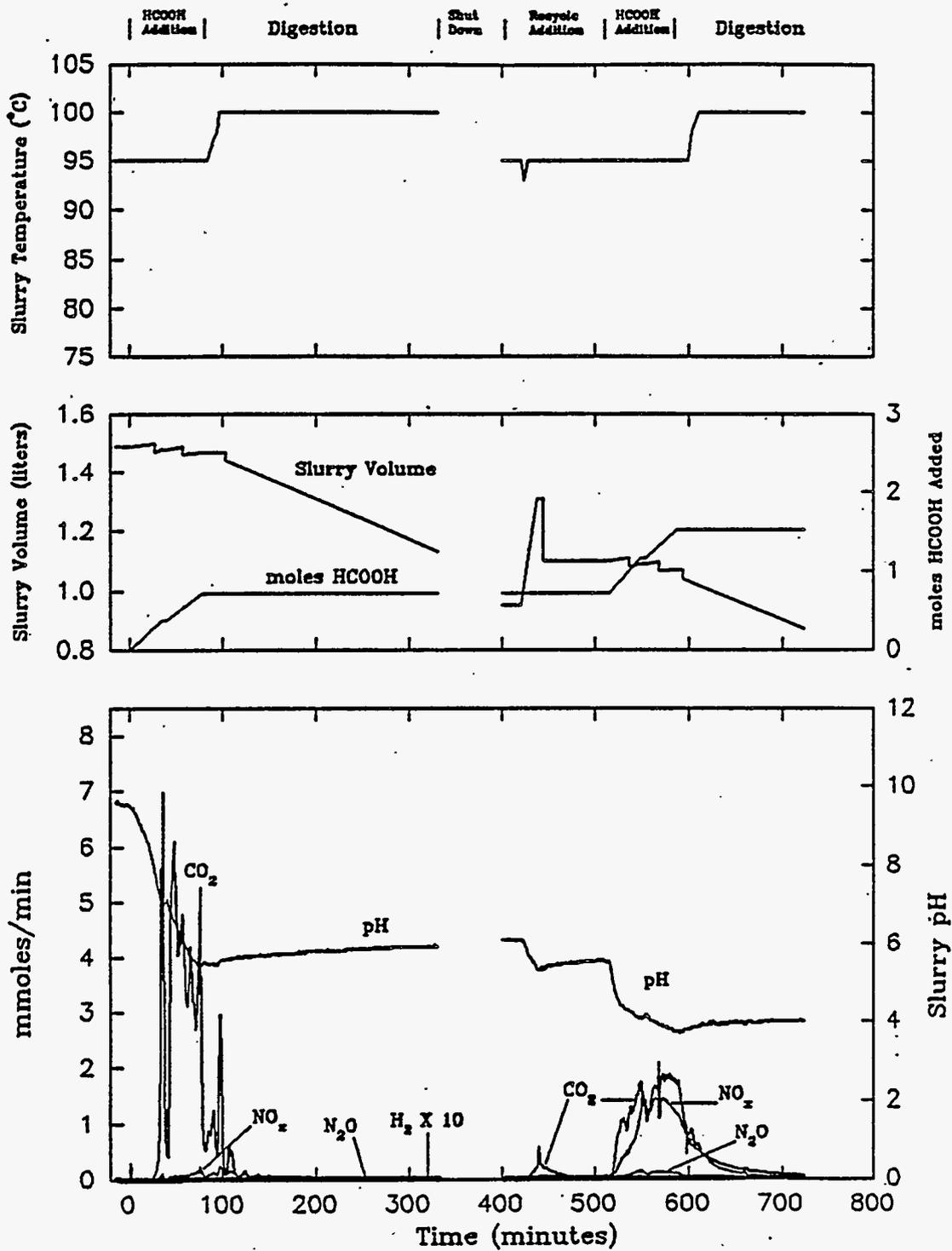


Figure D.9. Offgas Profile for NCAW Slurry Test 5.1: Non-Noble Metal Simulant; Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time (Conducted for Slurry Integrated Performance Testing Only)

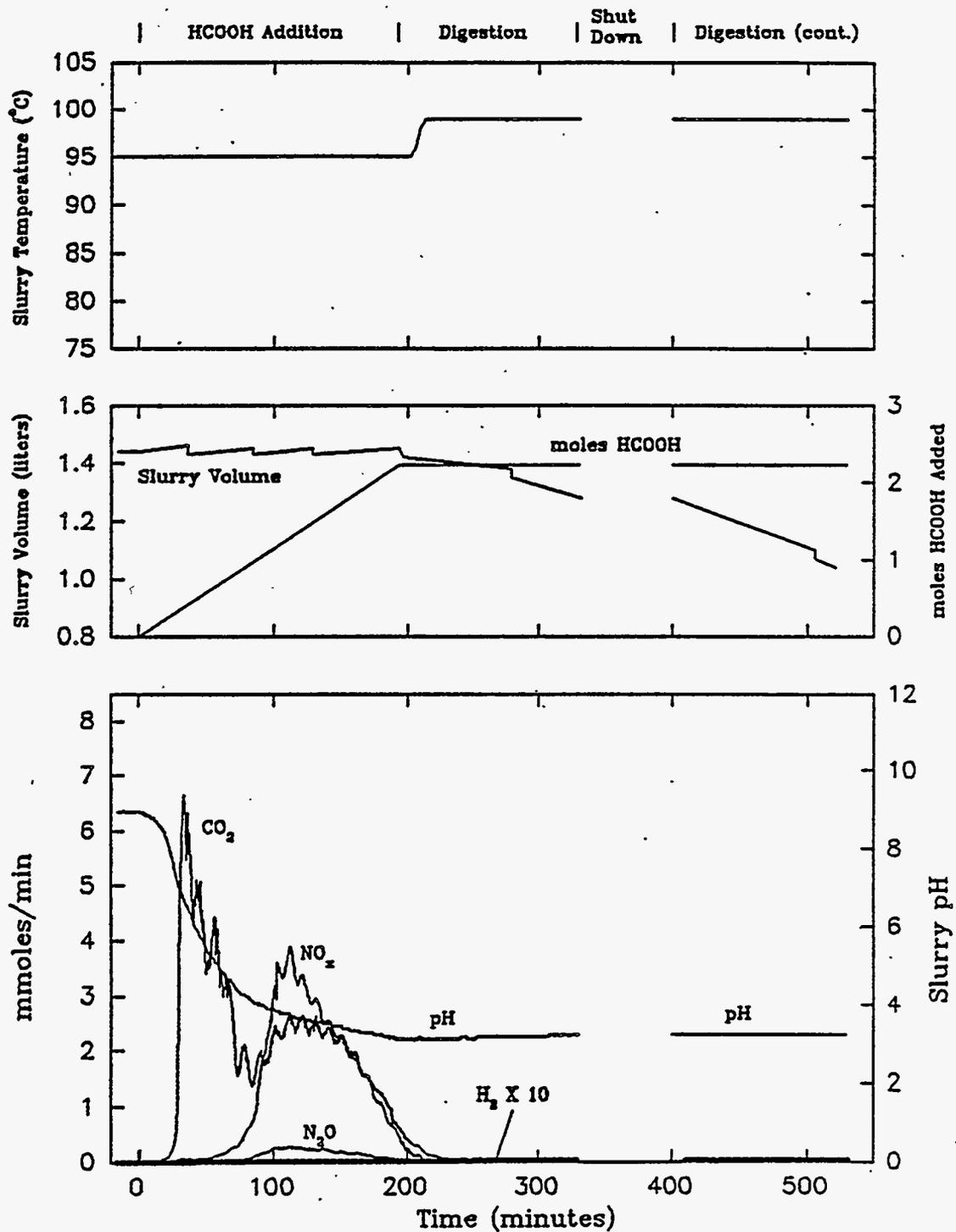


Figure D.10. Offgas Profile for NCAW Slurry Test 5.2: Non-Noble Metal Simulant; Excess Formic Acid, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

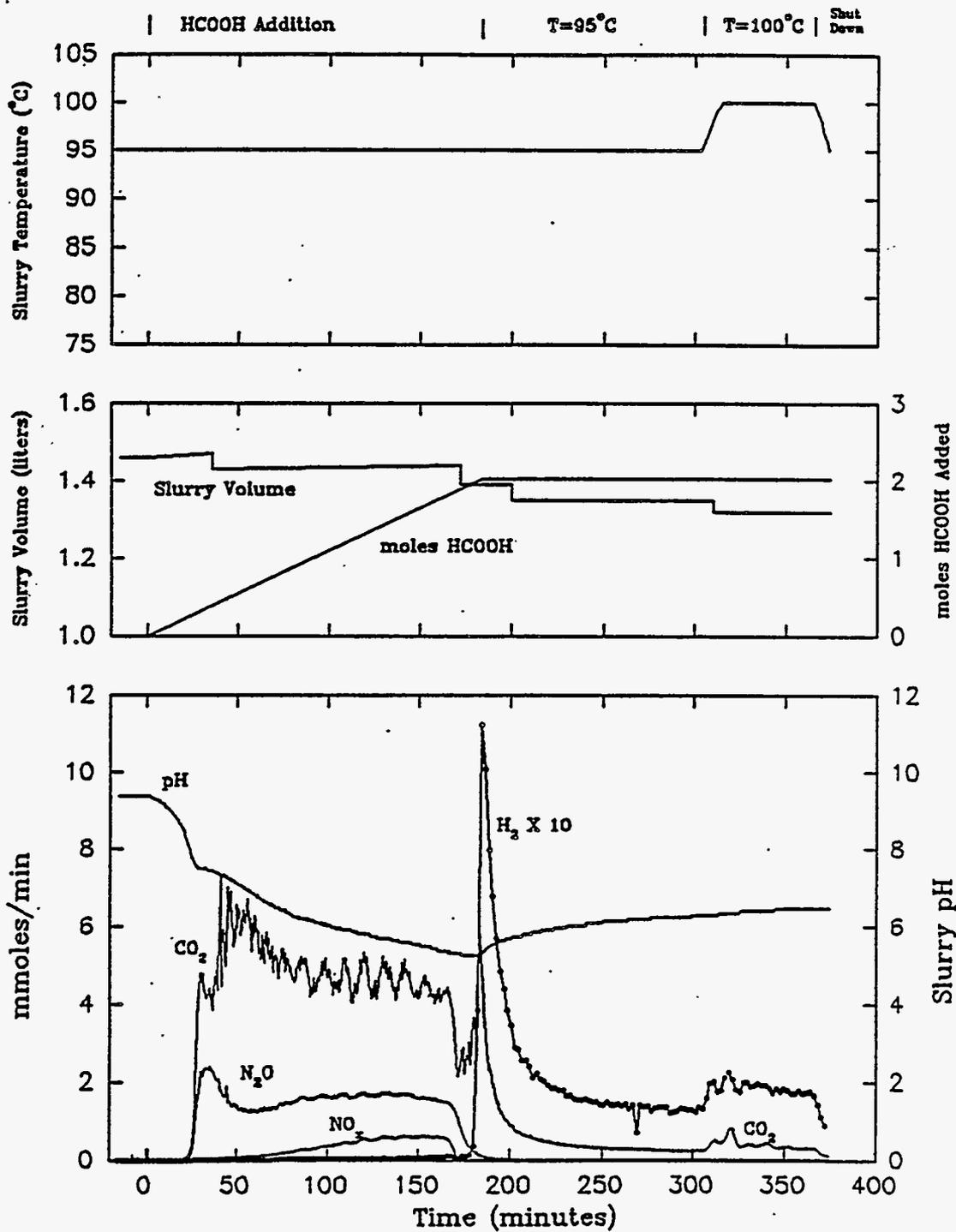


Figure D.11. Offgas Profile for NCAW Slurry Test 6.1: Formic Acid Addition Interrupt, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

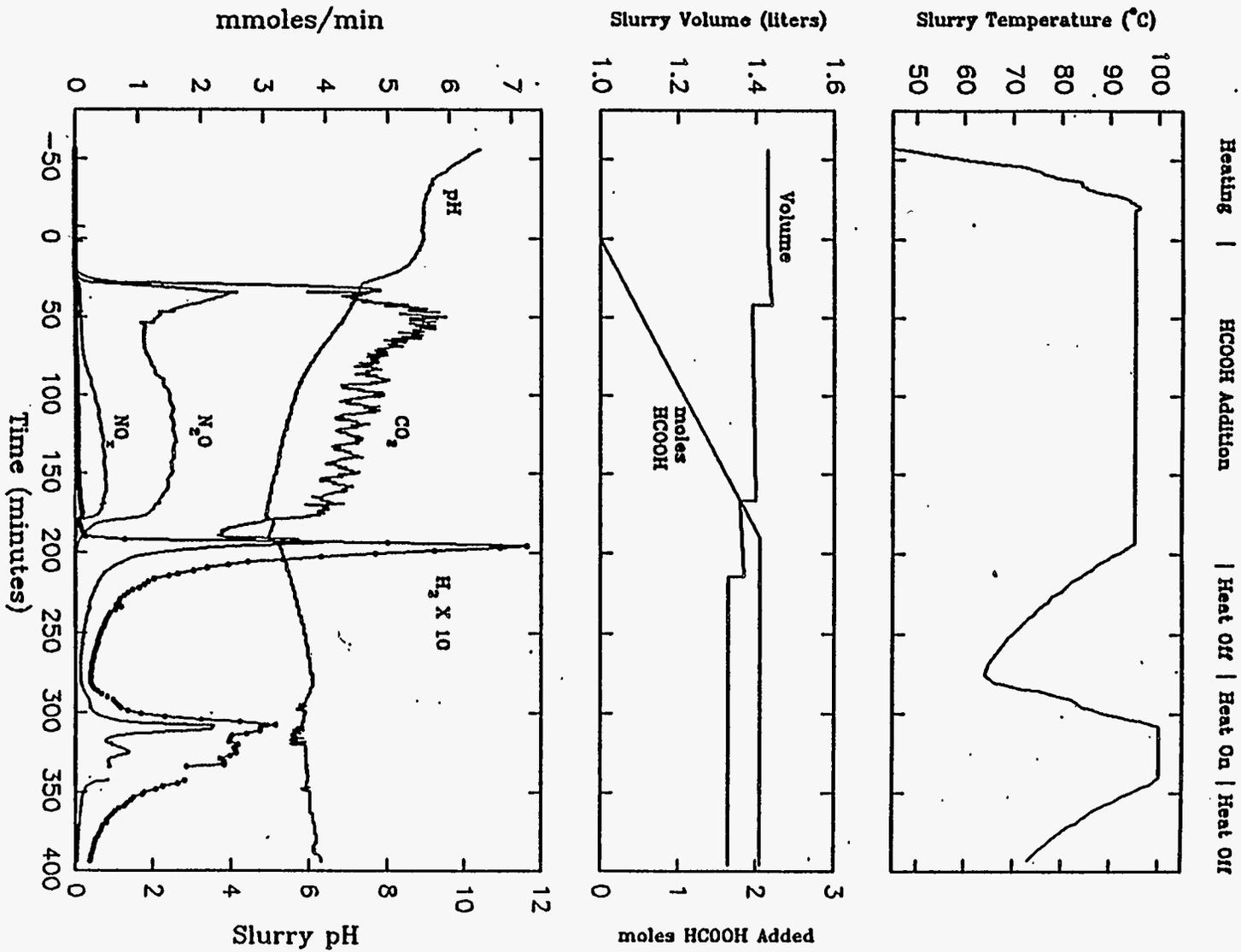


Figure D.12. Offgas Profile for NCAW Slurry Test 6.2: Formic Acid and Heat Source Interrupt, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

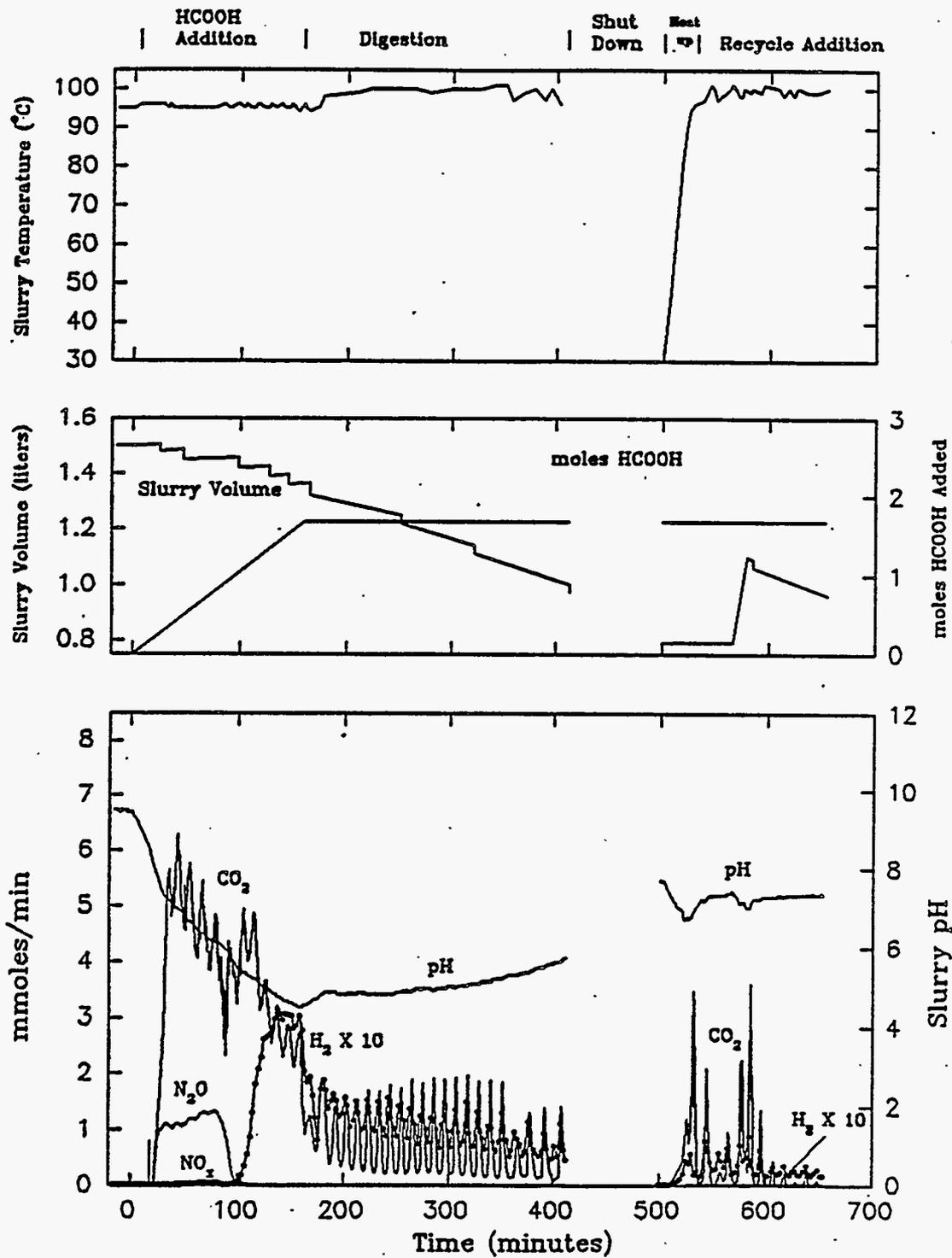


Figure D.13. Offgas Profile for NCAW Slurry Test 7.1: Maximum Nitrate/Minimum Nitrite, Showing Slurry Temperature, Slurry Volume, Amount of Formic Acid Added, Slurry pH, and Concentration of Offgases as a Function of Process Time

Table D.1. Key Test Events Related to Offgas Analysis for FY 1991 Laboratory-Scale Feed Preparation Tests

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

Table D.1. (contd)

Test	Time (minutes)	Event
	16	• HCOOH addition resumes
	17	• severe foaming, HCOOH shut off
	21	• HCOOH addition resumed at 1 mL/min
	22	• HCOOH shut off
	29	• HCOOH addition resumes
	32	• HCOOH shut off
	41	• HCOOH addition resumed at 0.5 mL/min
	46	• HCOOH shut -- shaft seal leaking gas
	152	• HCOOH addition resumed at 0.6 mL/min
	200	• GC computer failed -- no hydrogen data for the remainder of the test
	239	• end of HCOOH addition
	272	• shut down for the day
	350	• resumed slurry digestion next day
	435	• leak in vessel seal found -- remainder of gas data for this test not valid
2.2	0	• HCOOH addition begins at 0.99 mL/min
	1	• HCOOH delivery line submerged in slurry
	68	• end of HCOOH addition
	72	• begin heating up for digestion
	335	• shut down for the day
	400	• begin next day of test
	408	• recycle addition begins
	423	• end of recycle addition
	499	• end of test
3.1	0	• begin HCOOH addition
	75±3	• beginning of hydrogen spike
	110	• end of HCOOH addition
	127	• beginning of digestion
	308	• shut down for the day
	400	• begin next day of test, begin recycle add
	418	• end of recycle addition
	501	• end of test

Table D.1. (contd)

Test	Time (minutes)	Event
3.2	0	• begin HCOOH addition at about 0.53 mL/min
	103±3	• beginning of hydrogen spike
	124	• end of HCOOH addition, begin digestion
	364	• end of digestion, shut down for the day
	400	• begin next day of test
	415	• begin recycle addition
	428	• end of recycle addition
	496	• end of test
4.1	0	• begin HCOOH addition
	122	• end of HCOOH addition
	135	• begin digestion
	308	• shut down for the day
	350	• begin next day, continue digestion
	677	• shut down for the day
	700	• begin next day of test
	720	• begin recycle addition
	737	• end recycle addition
	807	• end of test
5.1	Data taken on 7/1/91	• no gas generation was observed, pH was stable at 9.00
	0 (7/9/91)	• HCOOH addition begins
	35	• approximate end of first HCOOH batch
	40	• approximate beginning of second HCOOH batch
	78	• end of second HCOOH addition
	89	• begin digestion
	331	• shut down for the day
	400	• begin next day of test
	421	• begin recycle addition
	438	• end of recycle addition
	515	• begin HCOOH addition
	549	• end of first HCOOH addition
	554	• begin second HCOOH addition
	587	• end of second HCOOH addition
	599	• begin digestion

Table D.1. (contd)

Test	Time (minutes)	Event
	724	<ul style="list-style-type: none"> • shut down for the day
	Data taken on 7/12/91 (frit addition)	<ul style="list-style-type: none"> • The only gas observed was hydrogen which was constant at about 20 ppm (about 10^{-6} moles/min). • pH initially at 4.3 falls to 4.2 during the addition of a small amount of HCOOH. Then pH rose to 5.6 during frit addition. Slowly climbed to 6.04 over the next 45 minutes.
5.2	0	<ul style="list-style-type: none"> • begin HCOOH addition
	194	<ul style="list-style-type: none"> • end of HCOOH addition
	204	<ul style="list-style-type: none"> • begin digestion
	330	<ul style="list-style-type: none"> • shut down for the day
	400	<ul style="list-style-type: none"> • begin next day of test -- continue digestion
	530	<ul style="list-style-type: none"> • end of test
6.1	0	<ul style="list-style-type: none"> • begin HCOOH addition
	178±3	<ul style="list-style-type: none"> • beginning of hydrogen spike
	184	<ul style="list-style-type: none"> • end of HCOOH addition
	310	<ul style="list-style-type: none"> • increased slurry temperature to 100°C
	365	<ul style="list-style-type: none"> • shut off vessel heater
	374	<ul style="list-style-type: none"> • end of test
6.2	0	<ul style="list-style-type: none"> • begin HCOOH addition
	186±4	<ul style="list-style-type: none"> • beginning of hydrogen spike
	190	<ul style="list-style-type: none"> • end of HCOOH addition
	190	<ul style="list-style-type: none"> • shut off vessel heater
	275	<ul style="list-style-type: none"> • reactivated vessel heater
	308	<ul style="list-style-type: none"> • slurry reaches 100°C
	340	<ul style="list-style-type: none"> • shut off vessel heater
	394	<ul style="list-style-type: none"> • end of test
7.1	0	<ul style="list-style-type: none"> • begin HCOOH addition
	94±3	<ul style="list-style-type: none"> • beginning of hydrogen spike
	160	<ul style="list-style-type: none"> • end of HCOOH addition
	412	<ul style="list-style-type: none"> • end of digestion, shut down for the day
	500	<ul style="list-style-type: none"> • begin increasing slurry temperature from 31°C

Table D.1. (contd)

<u>Test</u>	<u>Time (minutes)</u>	<u>Event</u>
	565	• begin recycle addition
	580	• end recycle addition
	653	• end of test

Appendix E

Comparison of H₂, N₂O, NO_x and CO₂ Generation Rates During Processing with FY 1991 Laboratory-Scale Feed Preparation Test Variables

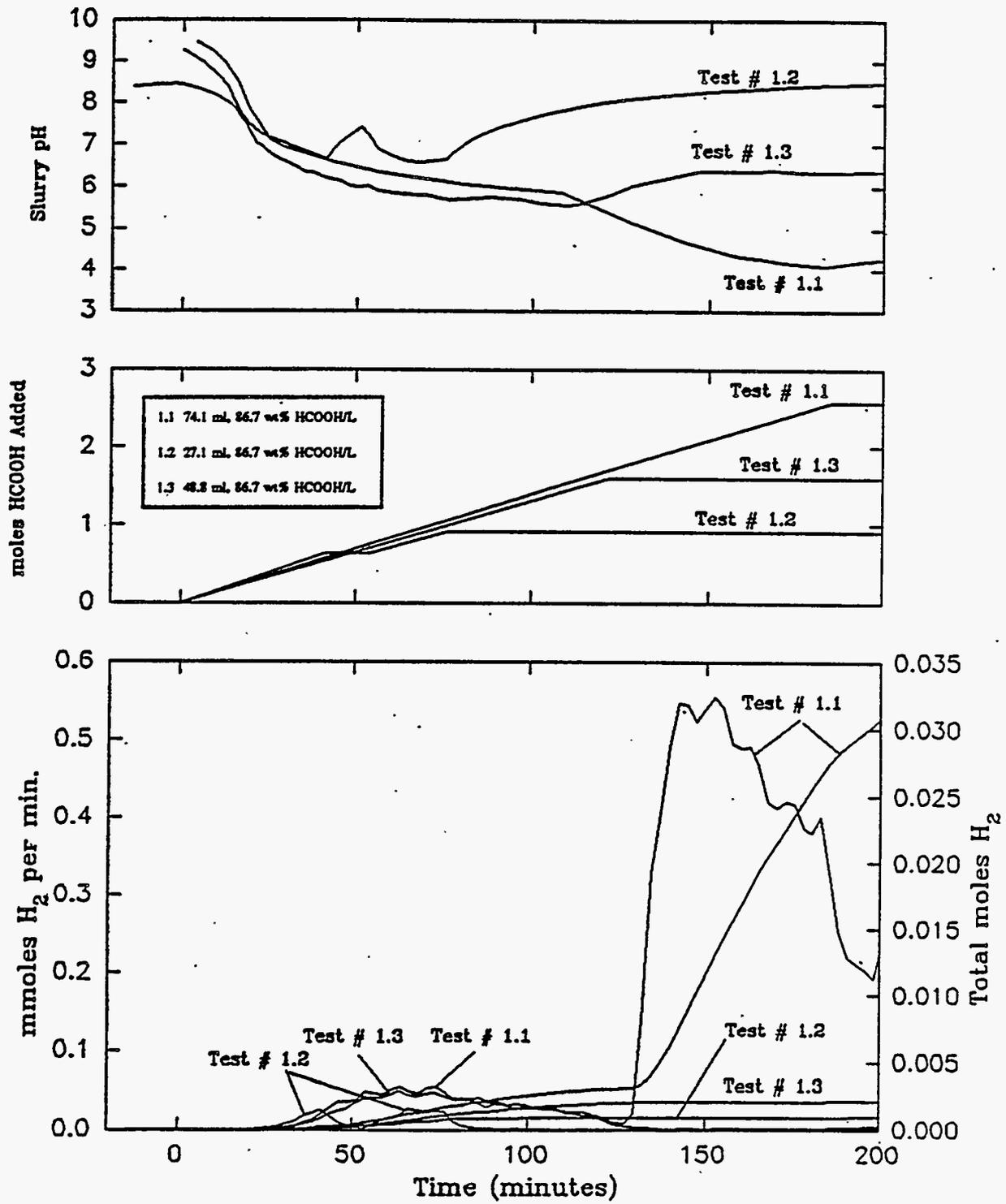


Figure E.1a. Comparison of the H₂ Generation Rate with Amount of Formic Acid Added to the NCAW Simulant as a Function of Process Time for Tests 1.1, 1.2, and 1.3

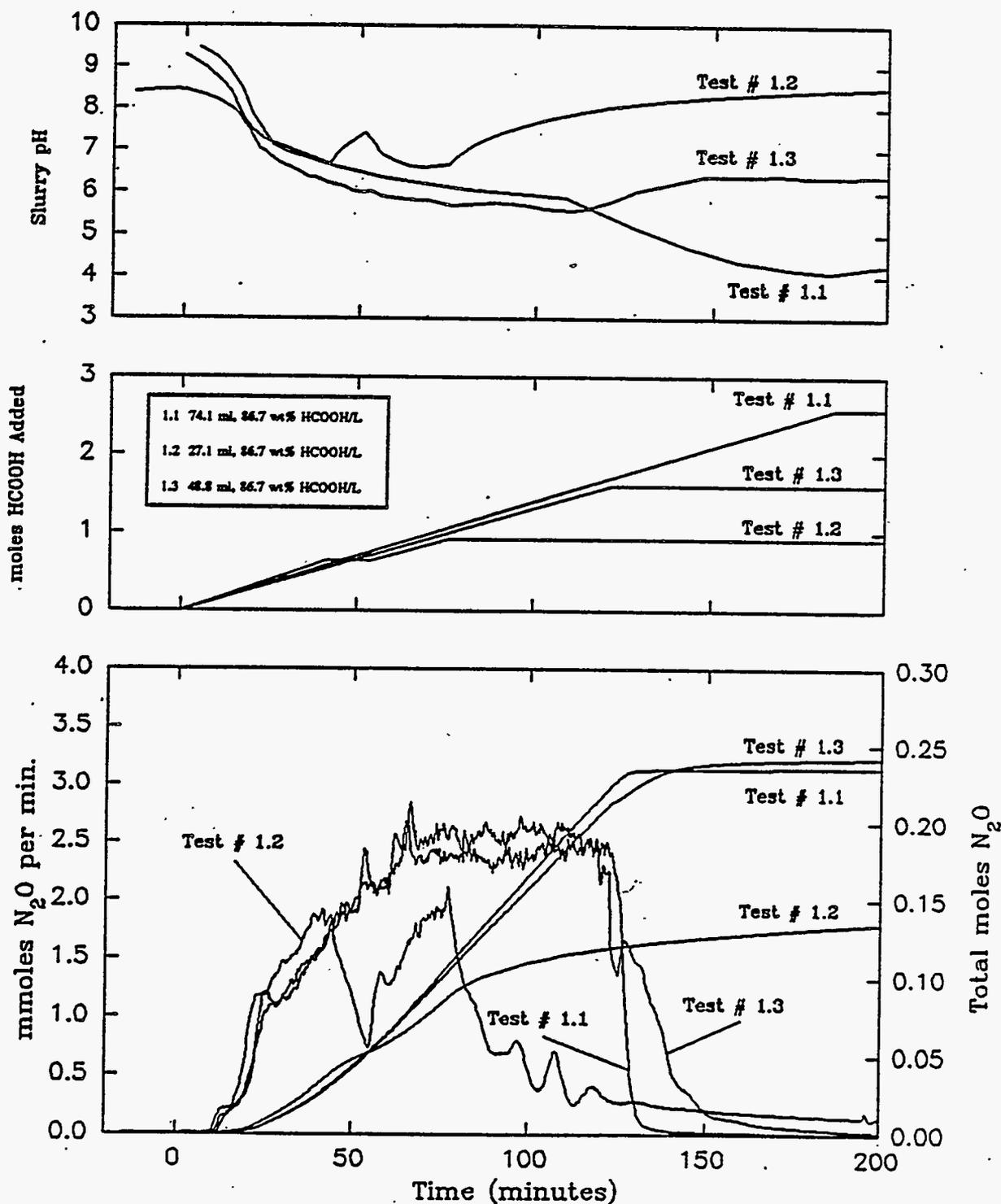


Figure E.1b. Comparison of the N₂O Generation Rate with Amount of Formic Acid Added to the NCAW Simulant as a Function of Process Time for Tests 1.1, 1.2, and 1.3

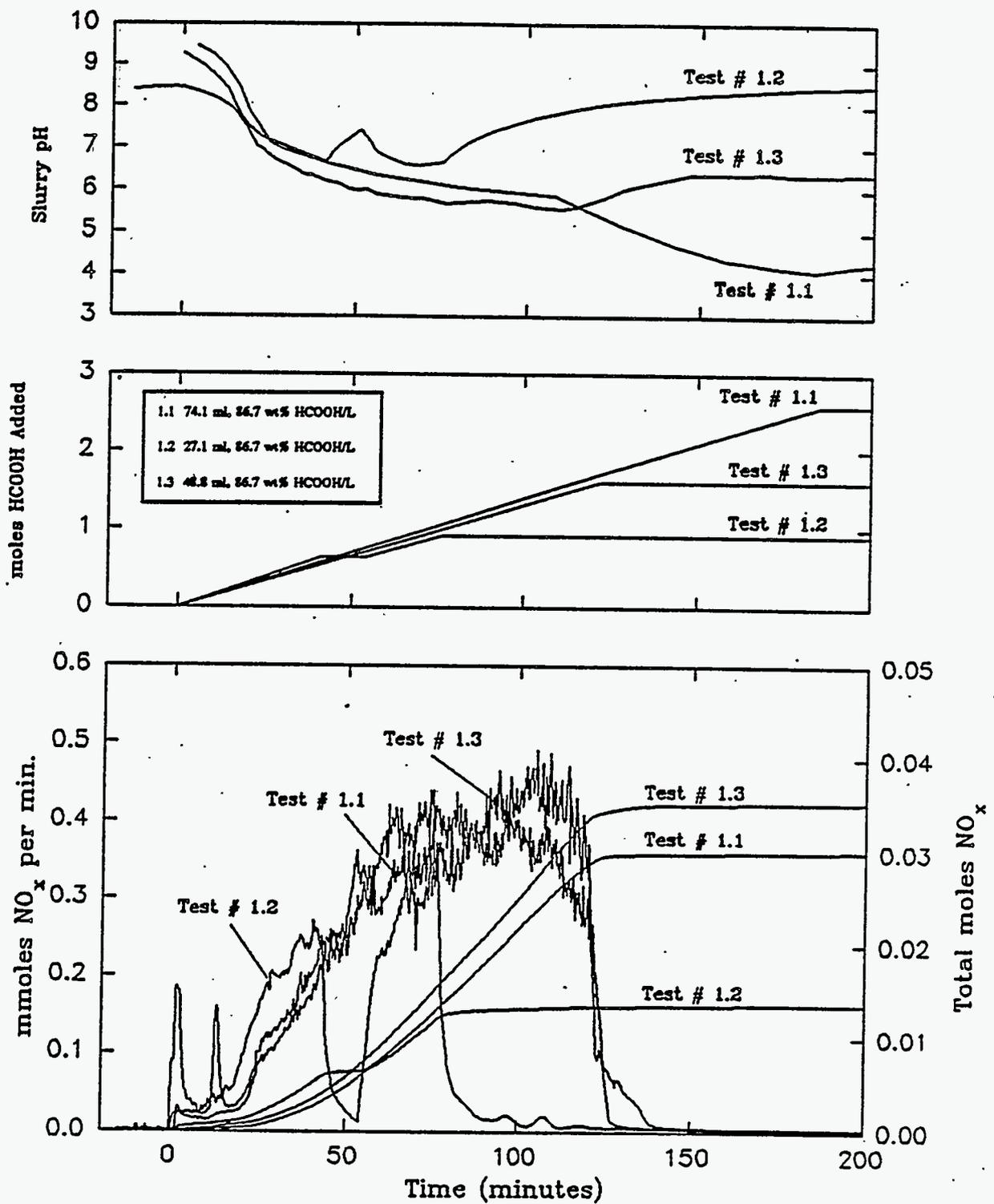


Figure E.1c. Comparison of the NO_x Generation Rate with Amount of Formic Acid Added to the NCAW Simulant as a Function of Process Time for Tests 1.1, 1.2, and 1.3

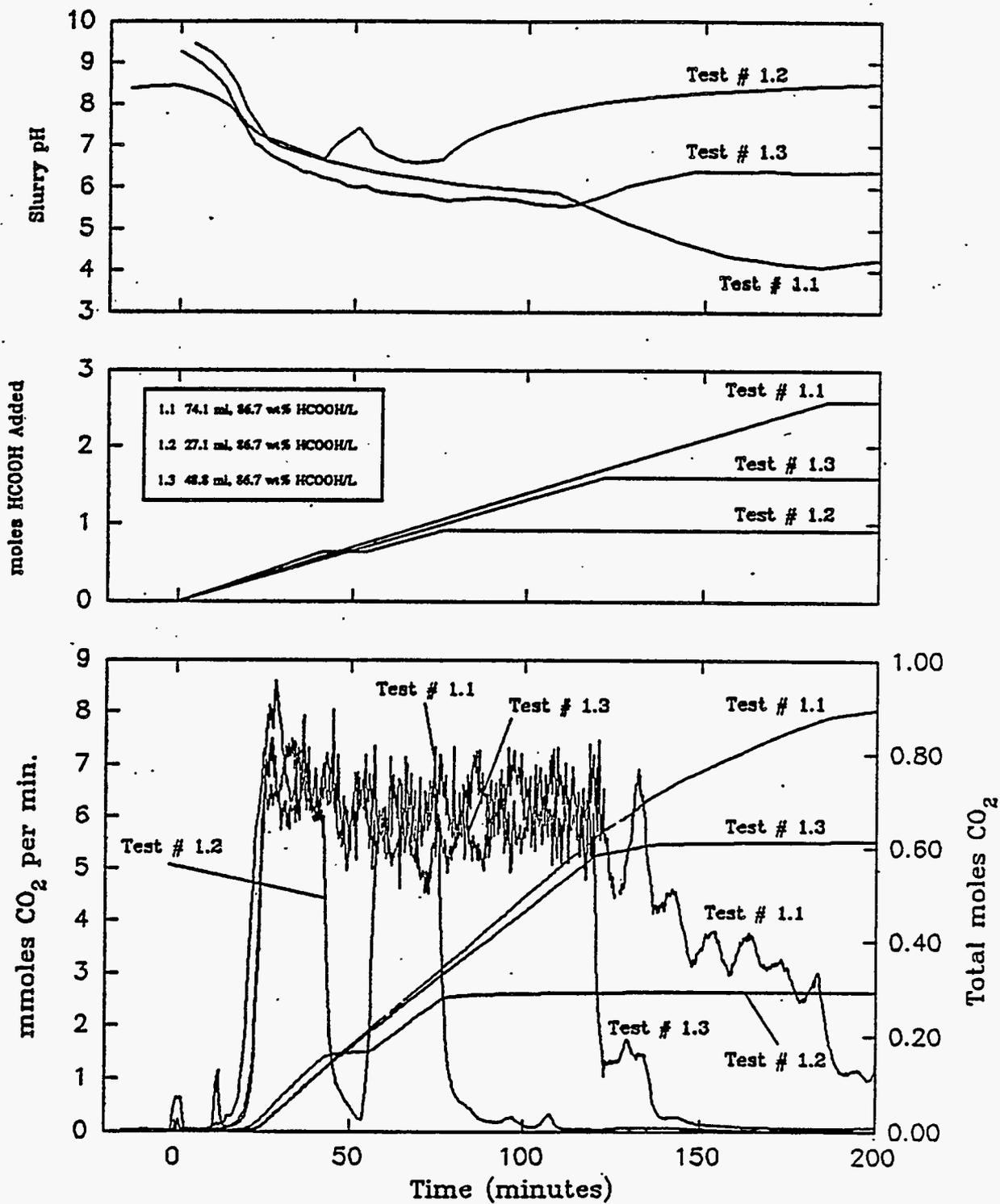


Figure E.1d. Comparison of the CO₂ Generation Rate with Amount of Formic Acid Added to the NCAW Simulant as a Function of Process Time for Tests 1.1, 1.2, and 1.3

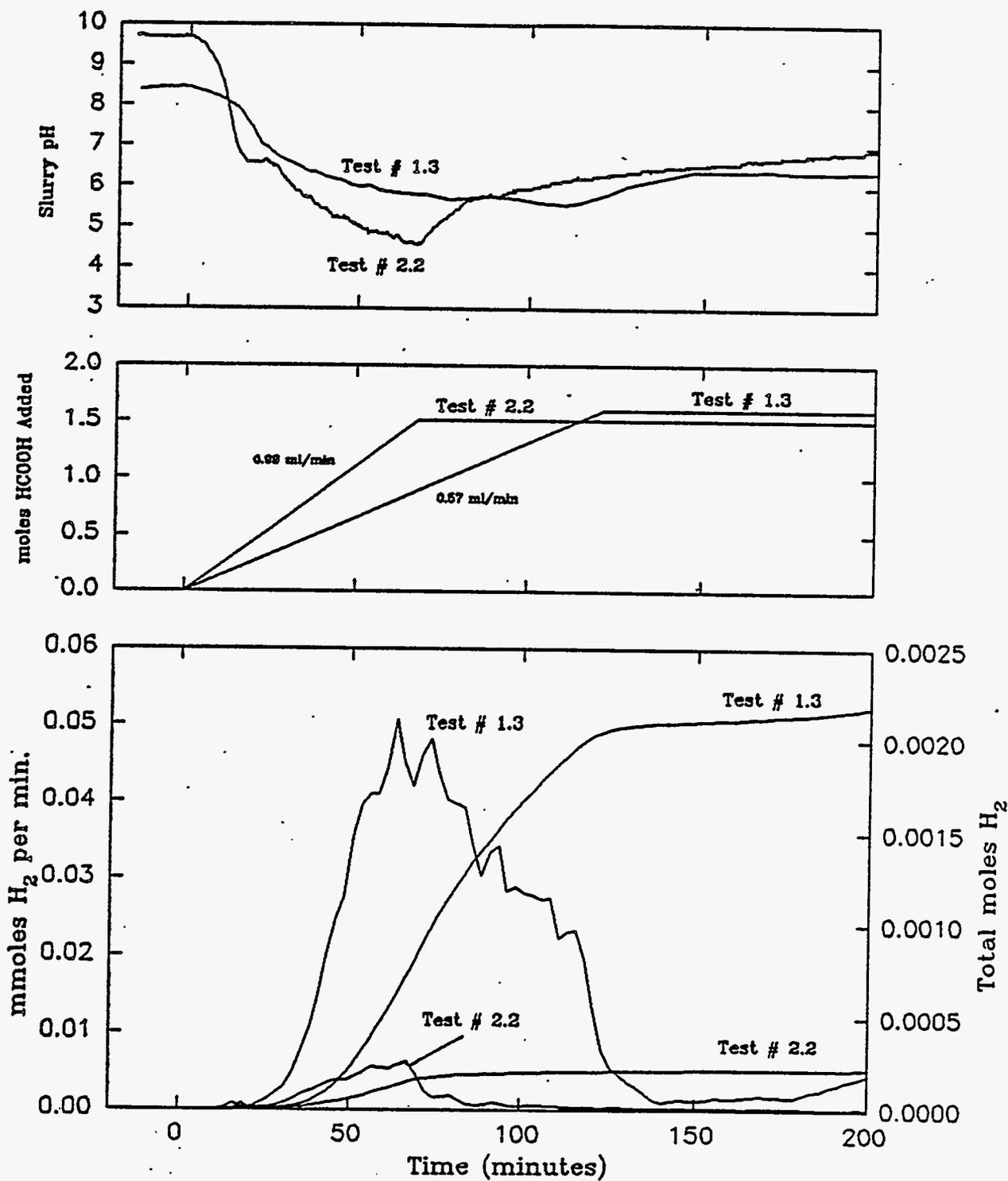


Figure E.2a. Comparison of the H₂ Generation Rate with Rate of Formic Acid Addition to the NCAW Simulant as a Function of Process Time for Tests 1.3 and 2.2

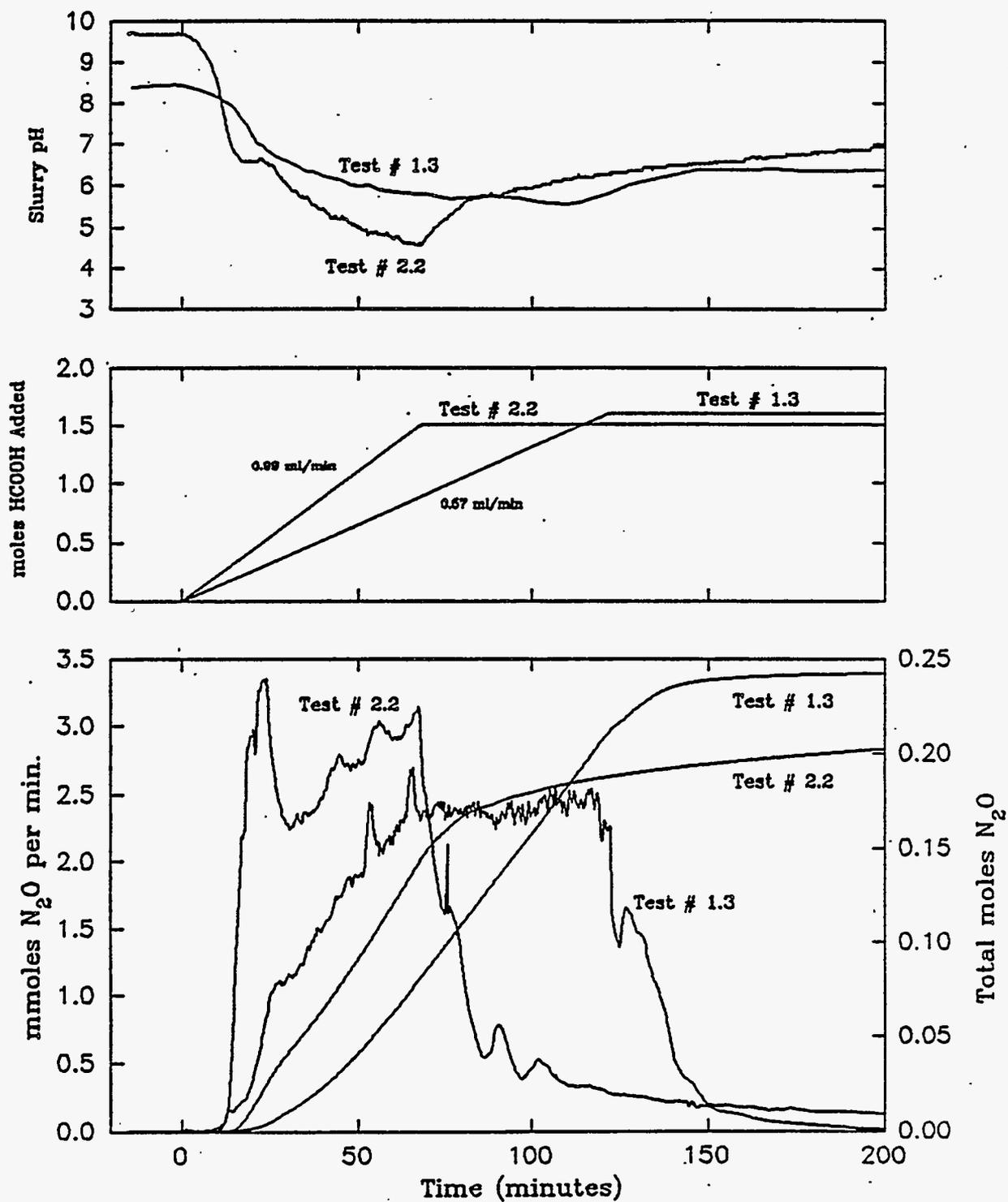


Figure E.2b. Comparison of the N₂O Generation Rate with Rate of Formic Acid Addition to the NCAW Simulant as a Function of Process Time for Tests 1.3 and 2.2

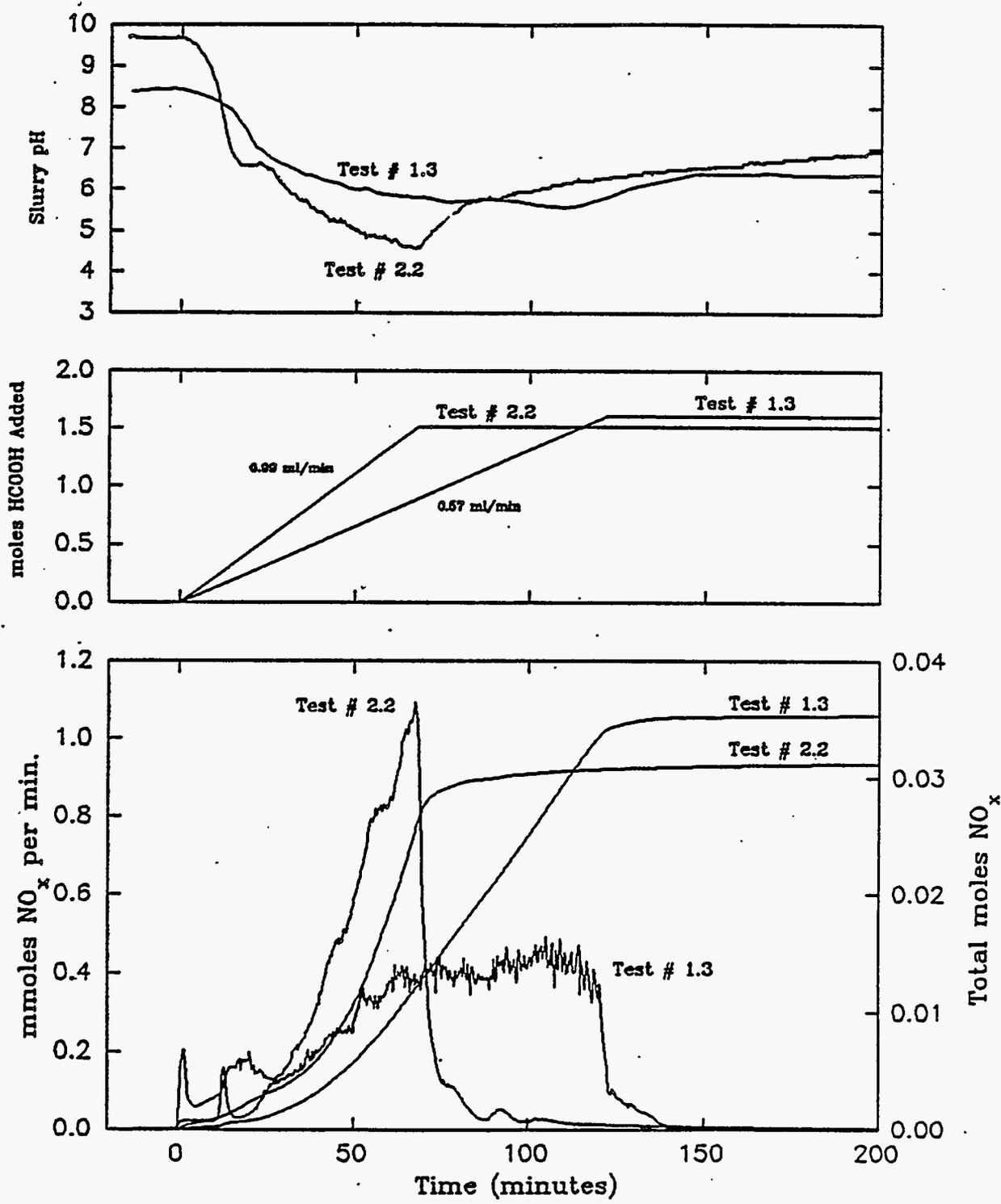


Figure E.2c. Comparison of the NO_x Generation Rate with Rate of Formic Acid Addition to the NCAW Simulant as a Function of Process Time for Tests 1.3 and 2.2

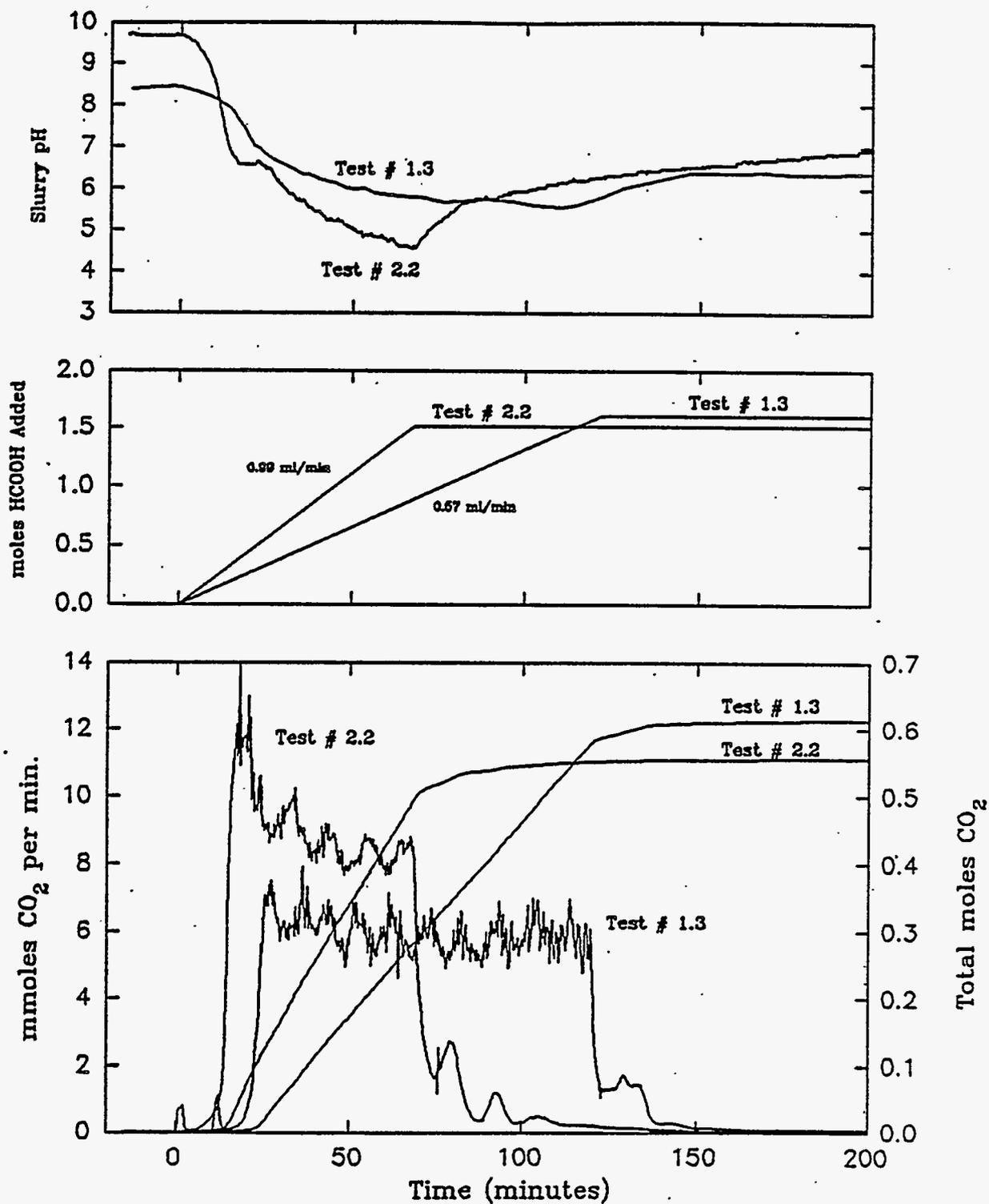


Figure E.2d. Comparison of the CO₂ Generation Rate with Rate of Formic Acid Addition to the NCAW Simulant as a Function of Process Time for Tests 1.3 and 2.2

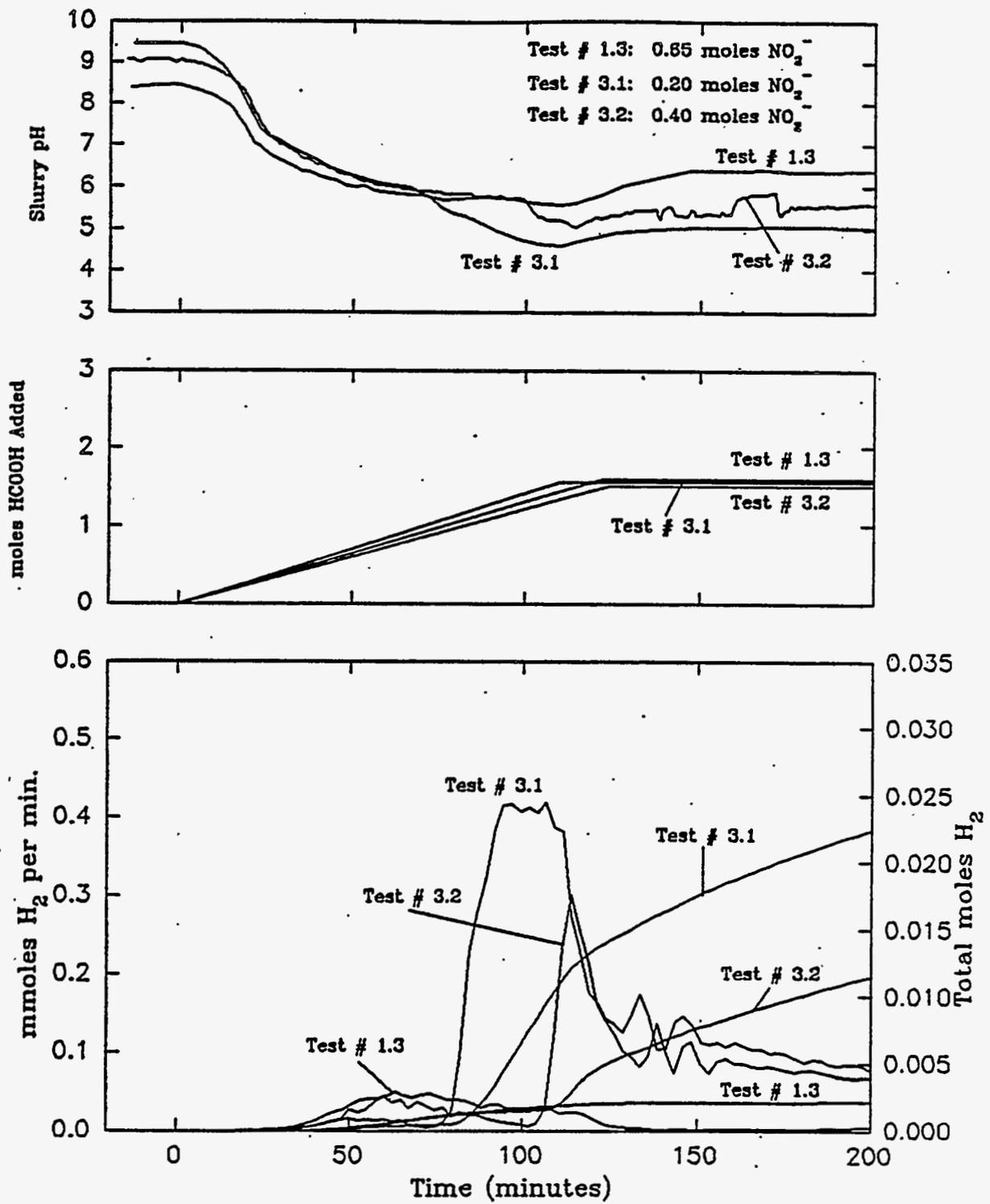


Figure E.3a. Comparison of the H₂ Generation Rate with Amount of Nitrite Added to the NCAW Simulant as a Function of Process Time for Tests 1.3, 3.1, and 3.2

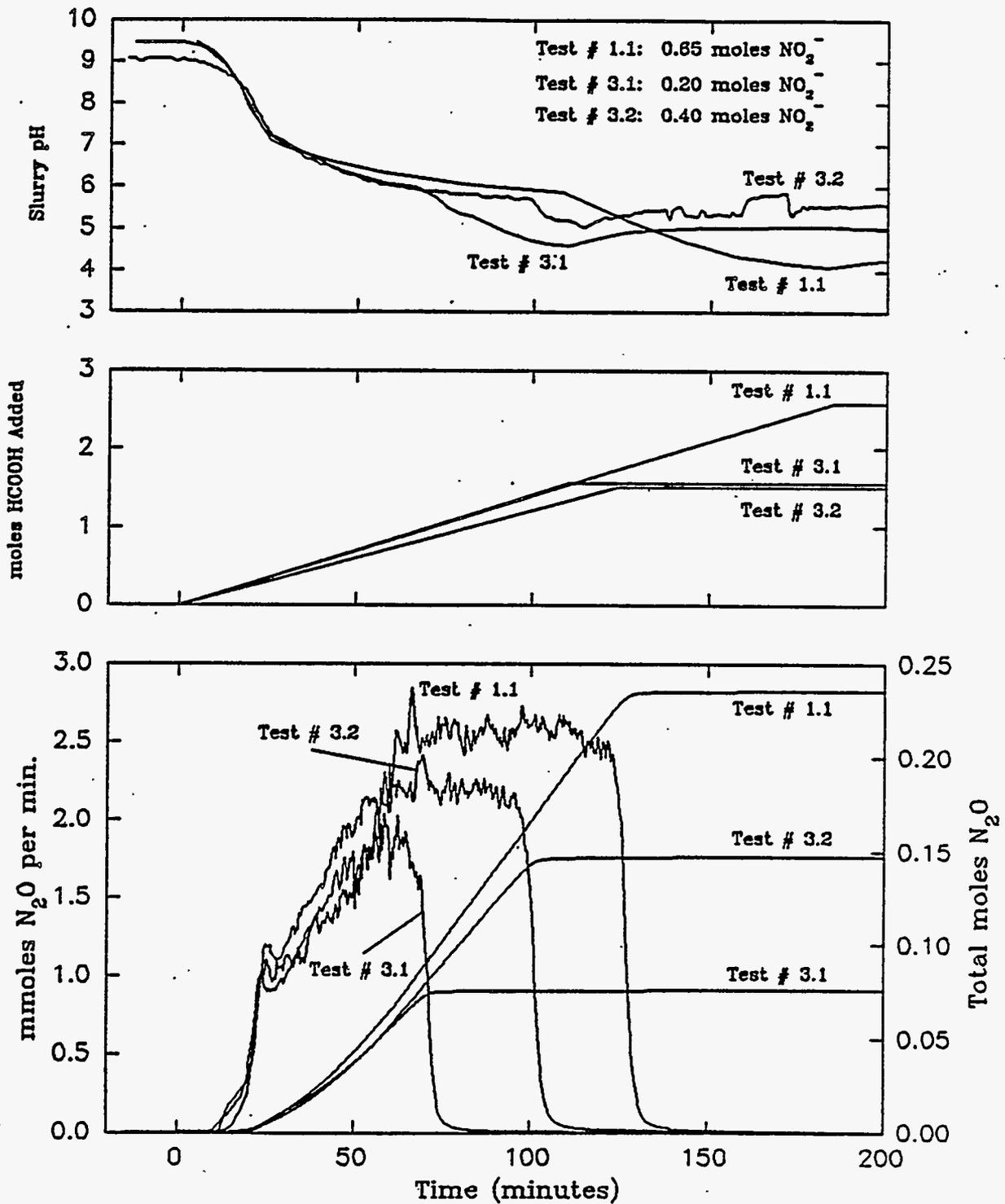


Figure E.3b. Comparison of the N₂O Generation Rate with Amount of Nitrite Added to the NCAW Simulant as a Function of Process Time for Tests 1.3, 3.1, and 3.2

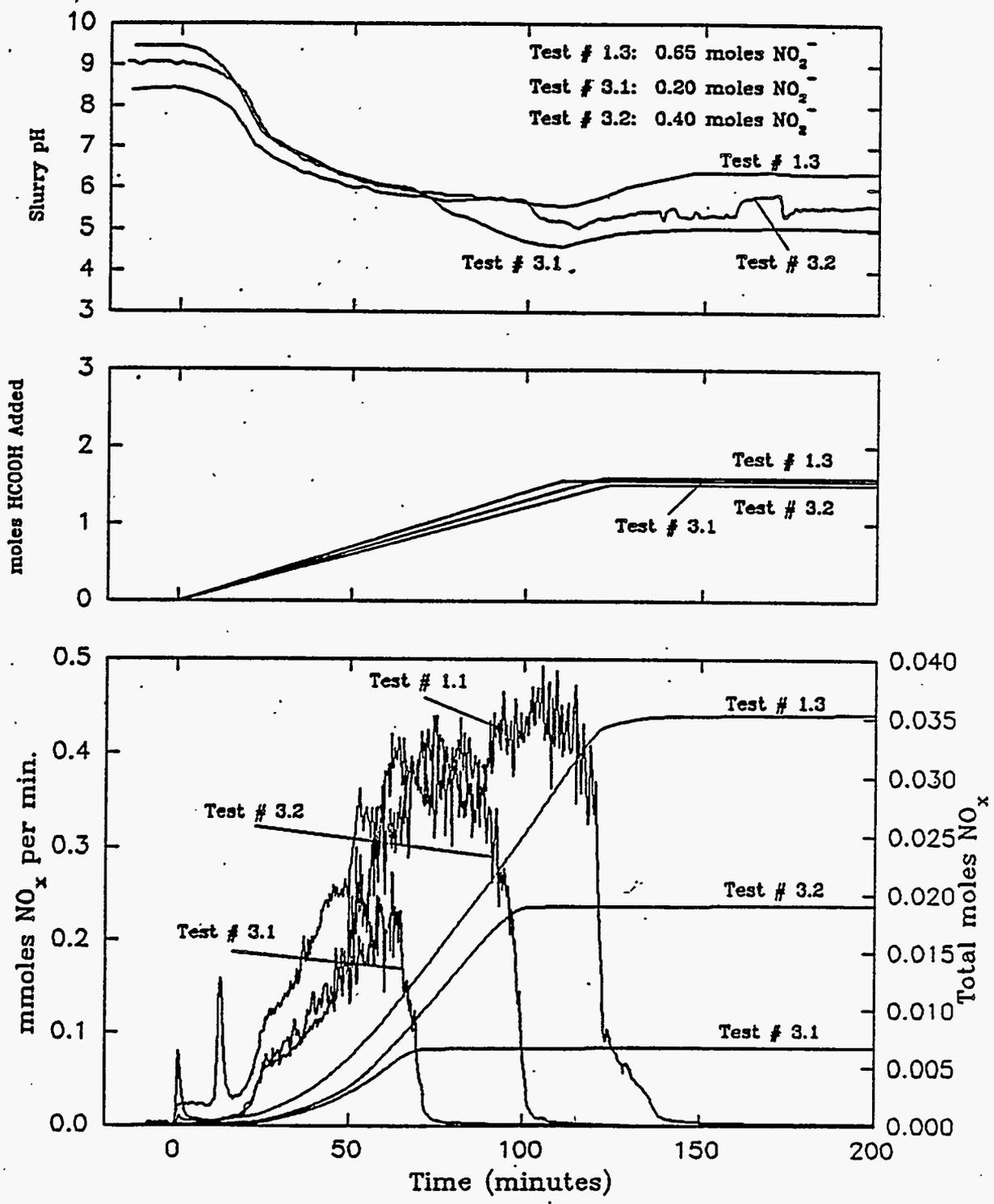


Figure E.3c. Comparison of the NO_x Generation Rate with Amount of Nitrite Added to the NCAW Simulant as a Function of Process Time for Tests 1.3, 3.1, and 3.2

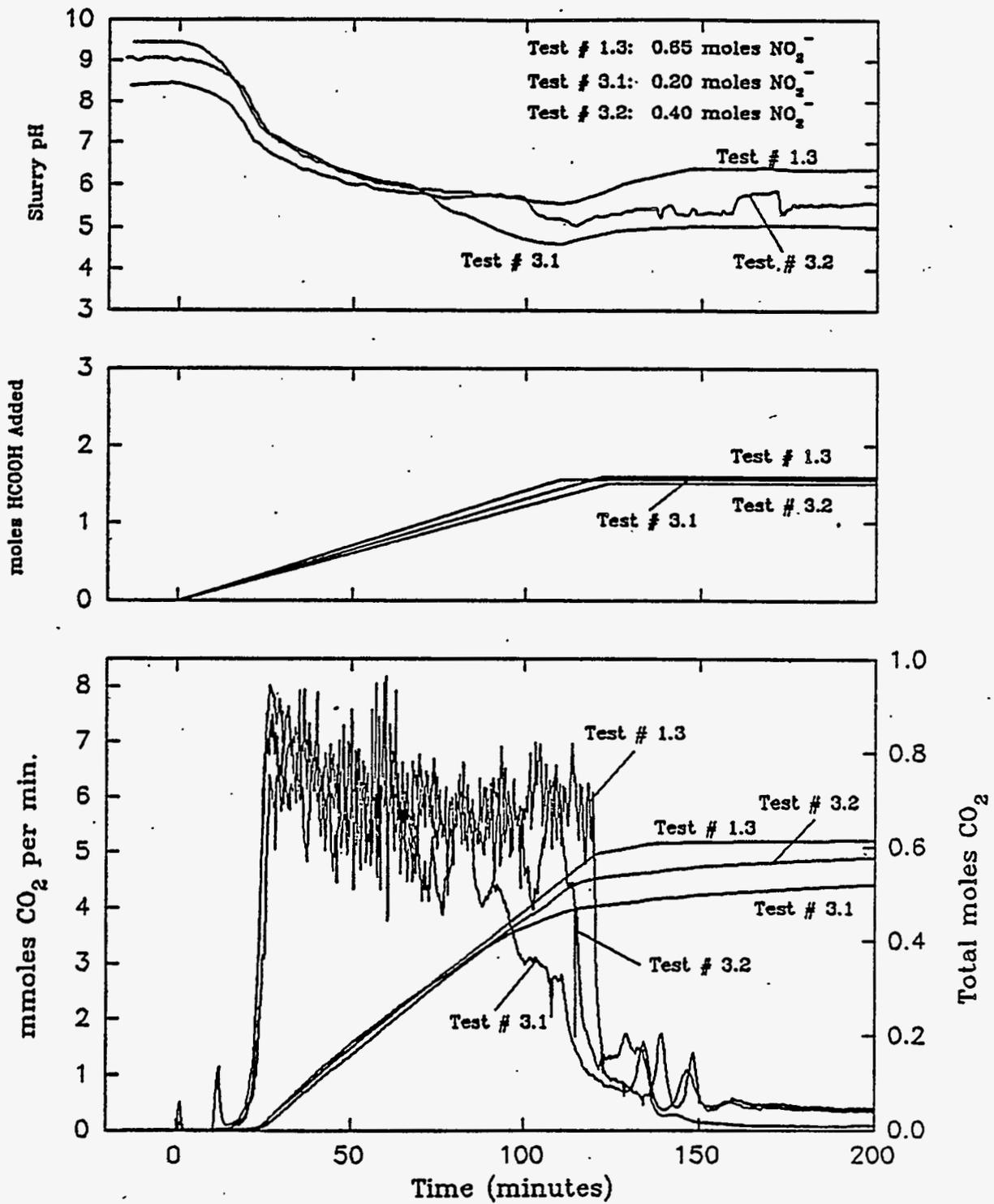


Figure E.3d. Comparison of the CO₂ Generation Rate with Amount of Nitrite Added to the NCAW Simulant as a Function of Process Time for Tests 1.3, 3.1, and 3.2

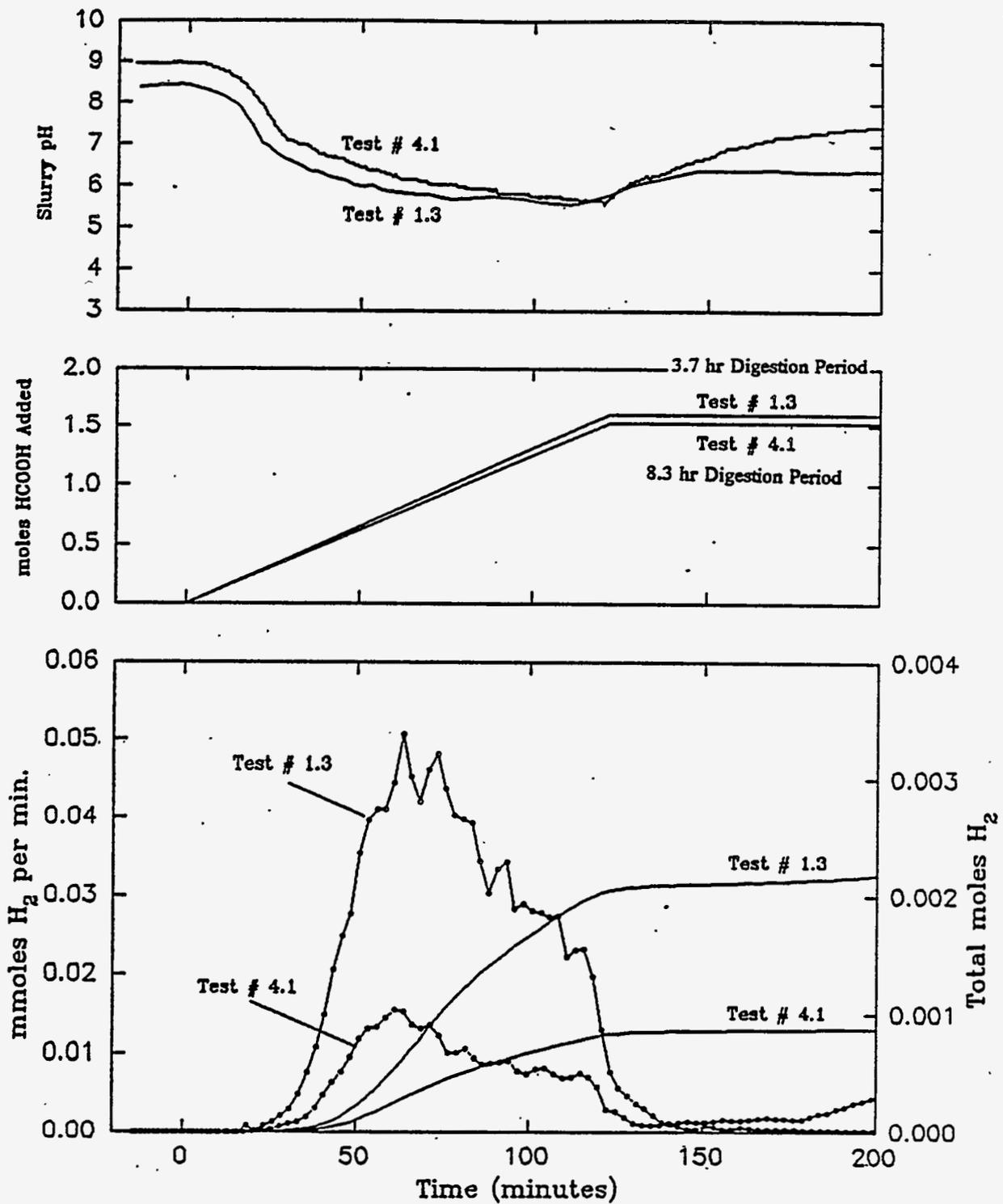


Figure E.4a. Comparison of the H₂ Generation Rate with Extended Digestion Period for NCAW Simulant as Function of Process Time for Tests 1.3 and 4.1

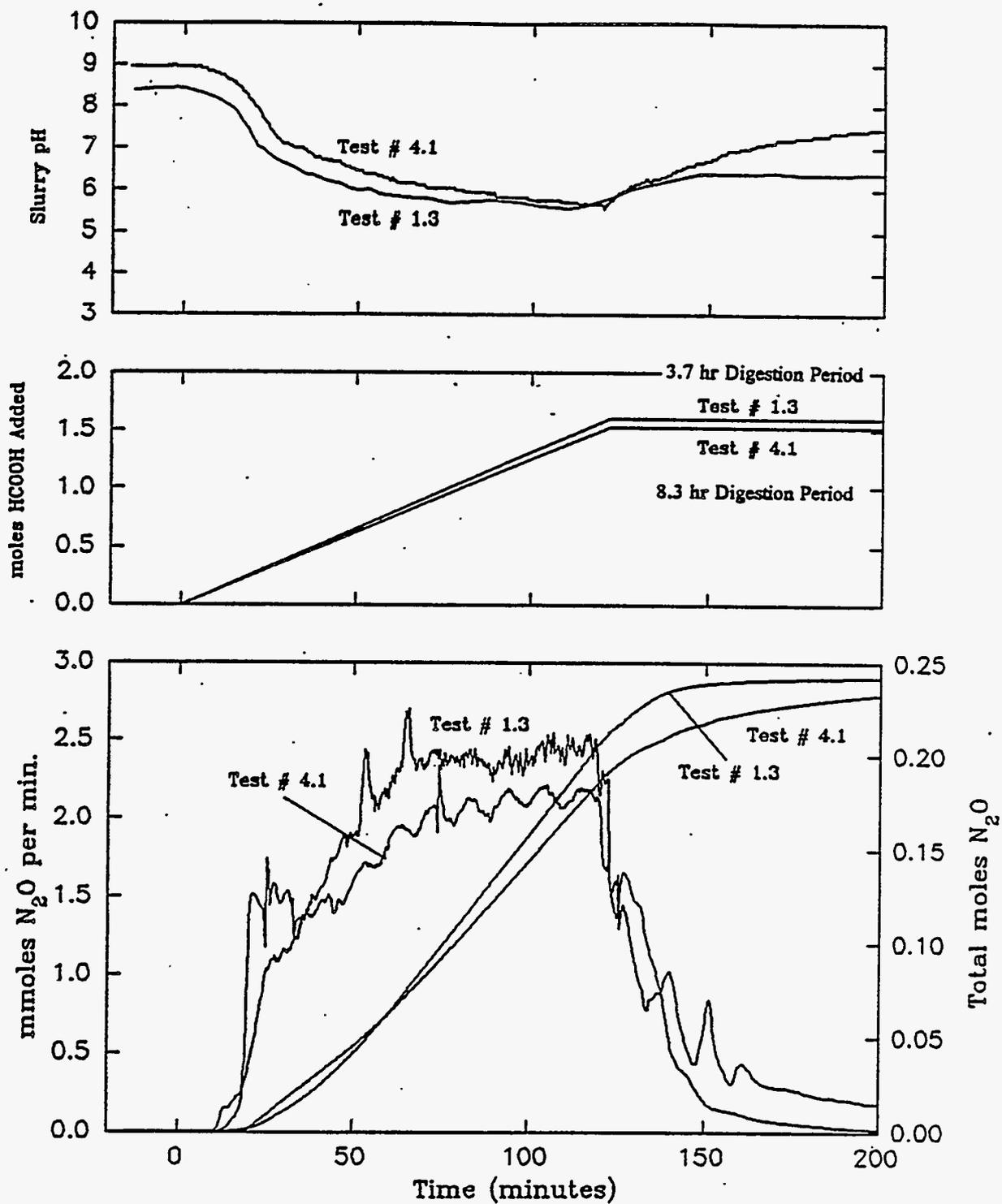


Figure E.4b. Comparison of the N₂O Generation Rate with Extended Digestion Period for NCAW Simulant as a Function of Process Time for Tests 1.3 and 4.1

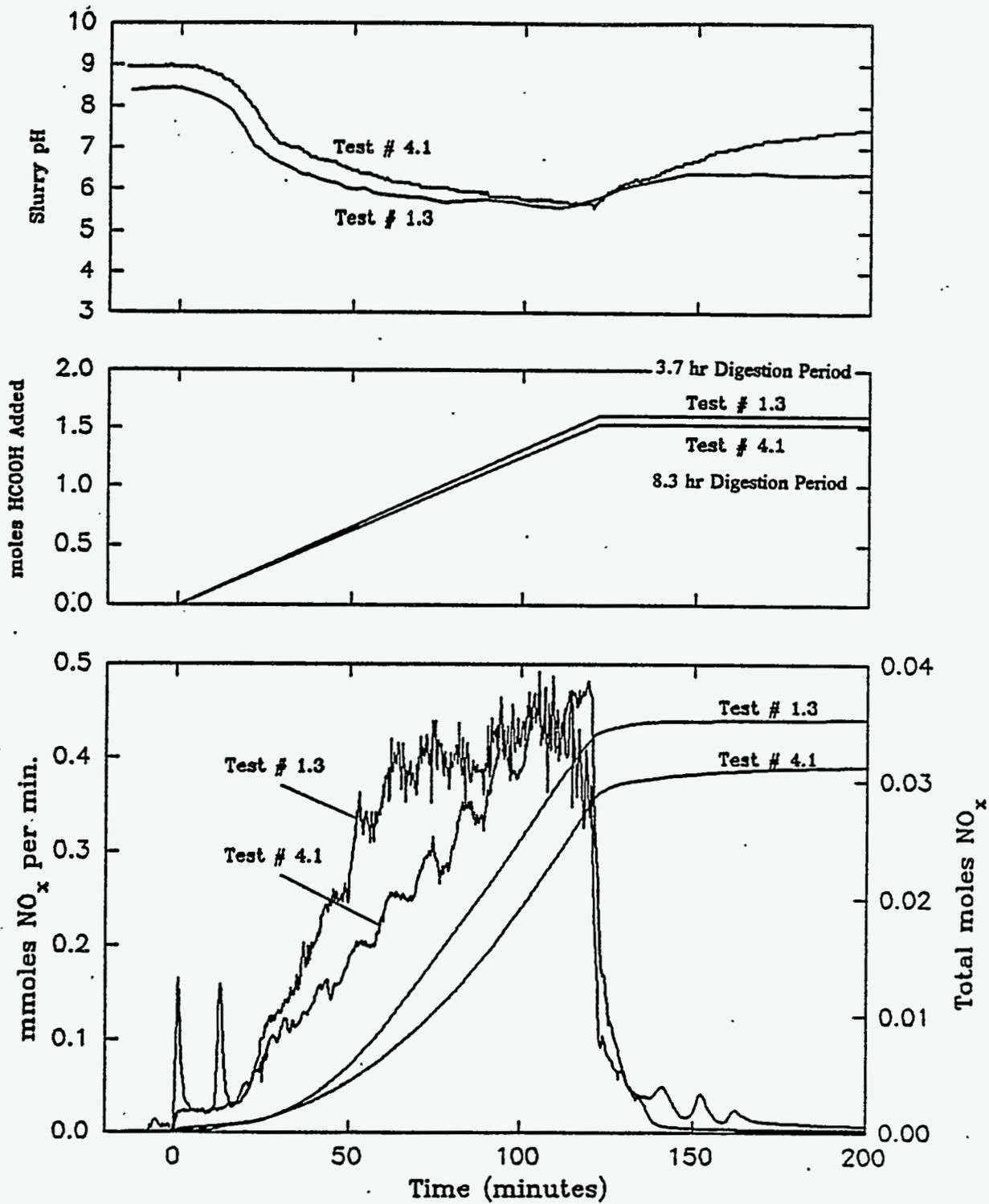


Figure E.4c. Comparison of the NO_x Generation Rate with Extended Digestion Period for NCAW Simulant as a Function of Process Time for Tests 1.3 and 4.1

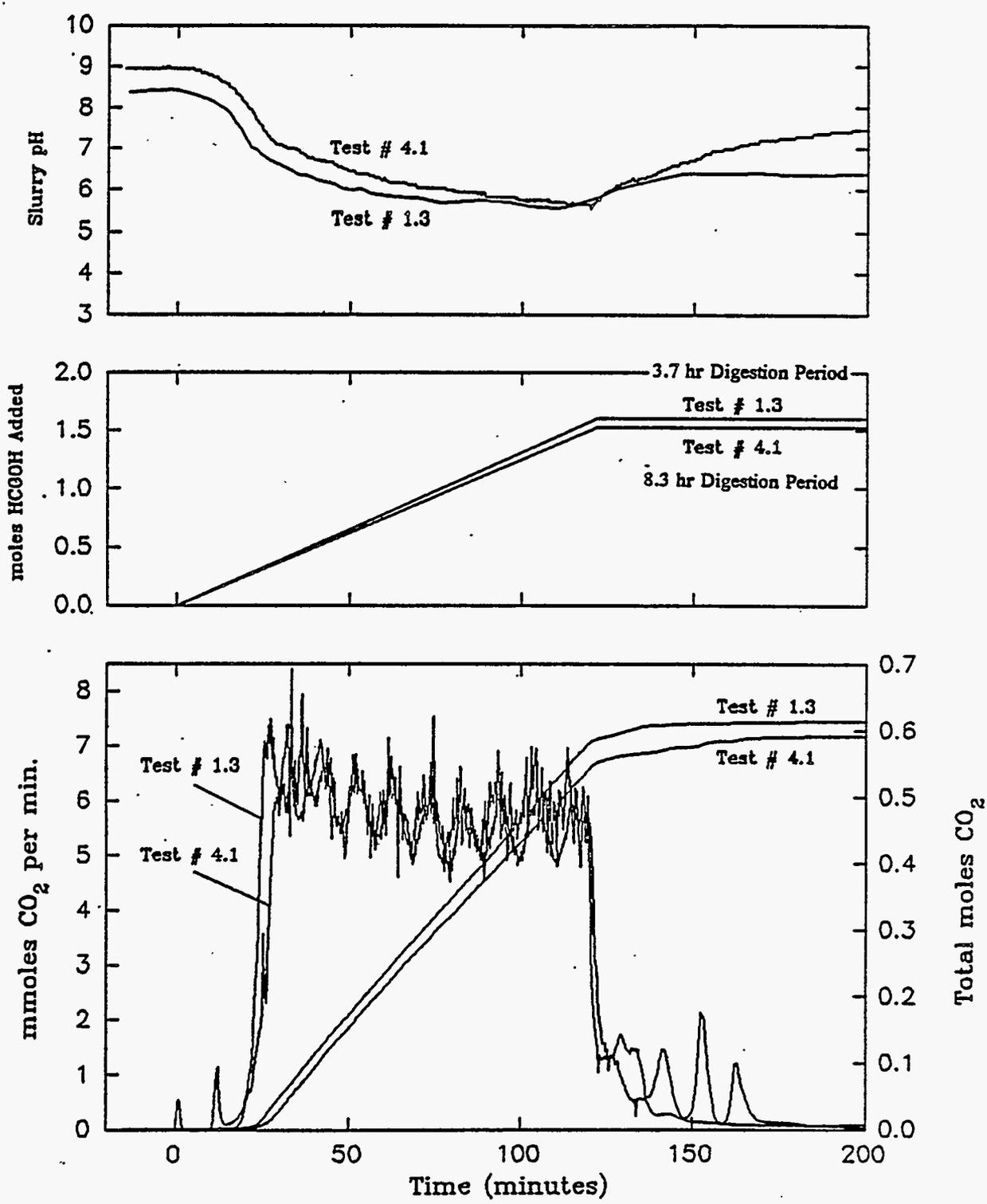


Figure E.4d. Comparison of the CO₂ Generation Rate with Extended Digestion Period for NCAW Simulant as a Function of Process Time for Tests 1.3 and 4.1

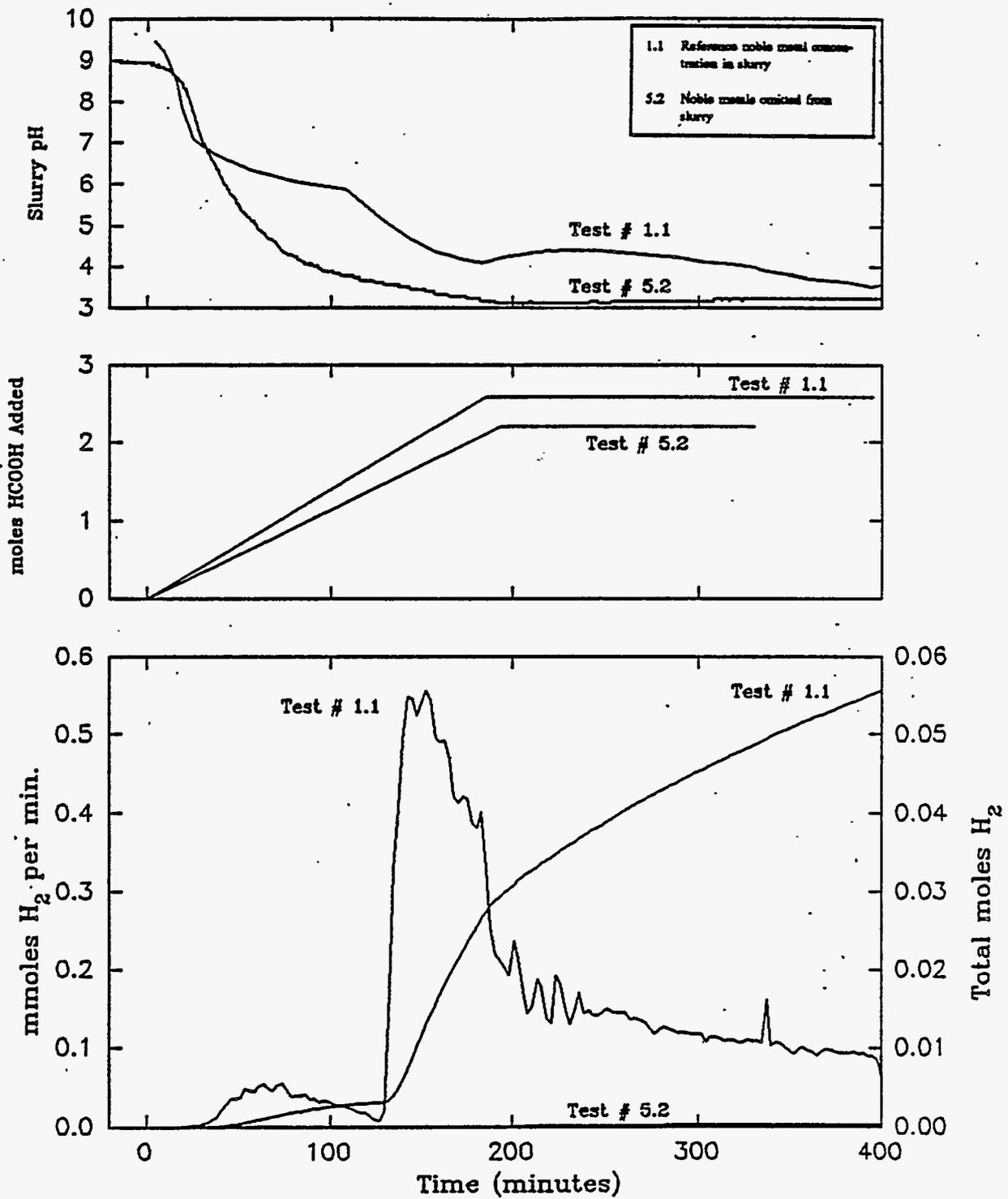


Figure E.5a. Comparison of the H₂ Generation Rate with Noble Metal Content of NCAW Simulant as a Function of Process Time for Tests 1.1 and 5.2

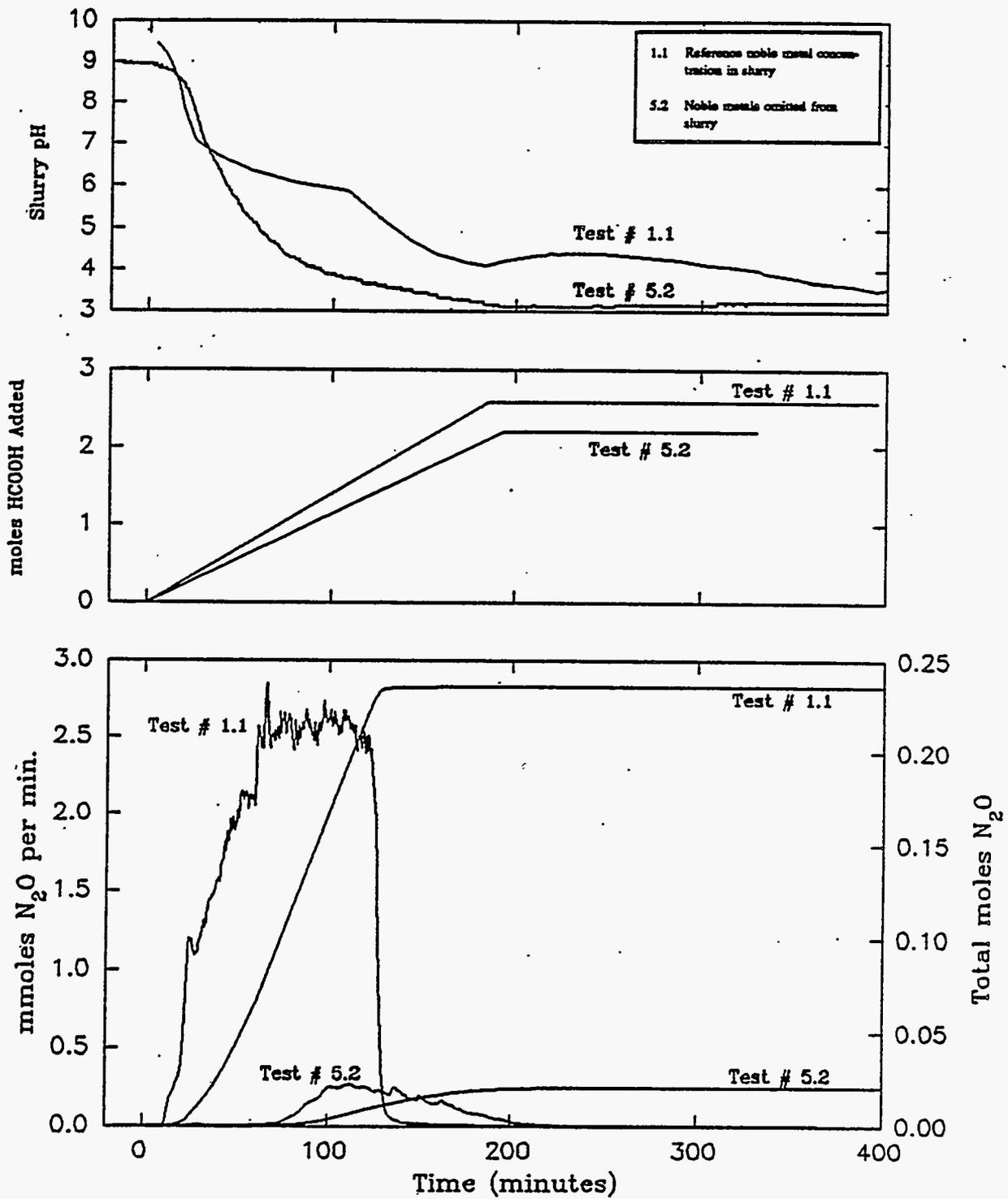


Figure E.5b. Comparison of the N₂O Generation Rate with Noble Metal Content of NCAW Simulant as a Function of Process Time for Tests 1.1 and 5.2

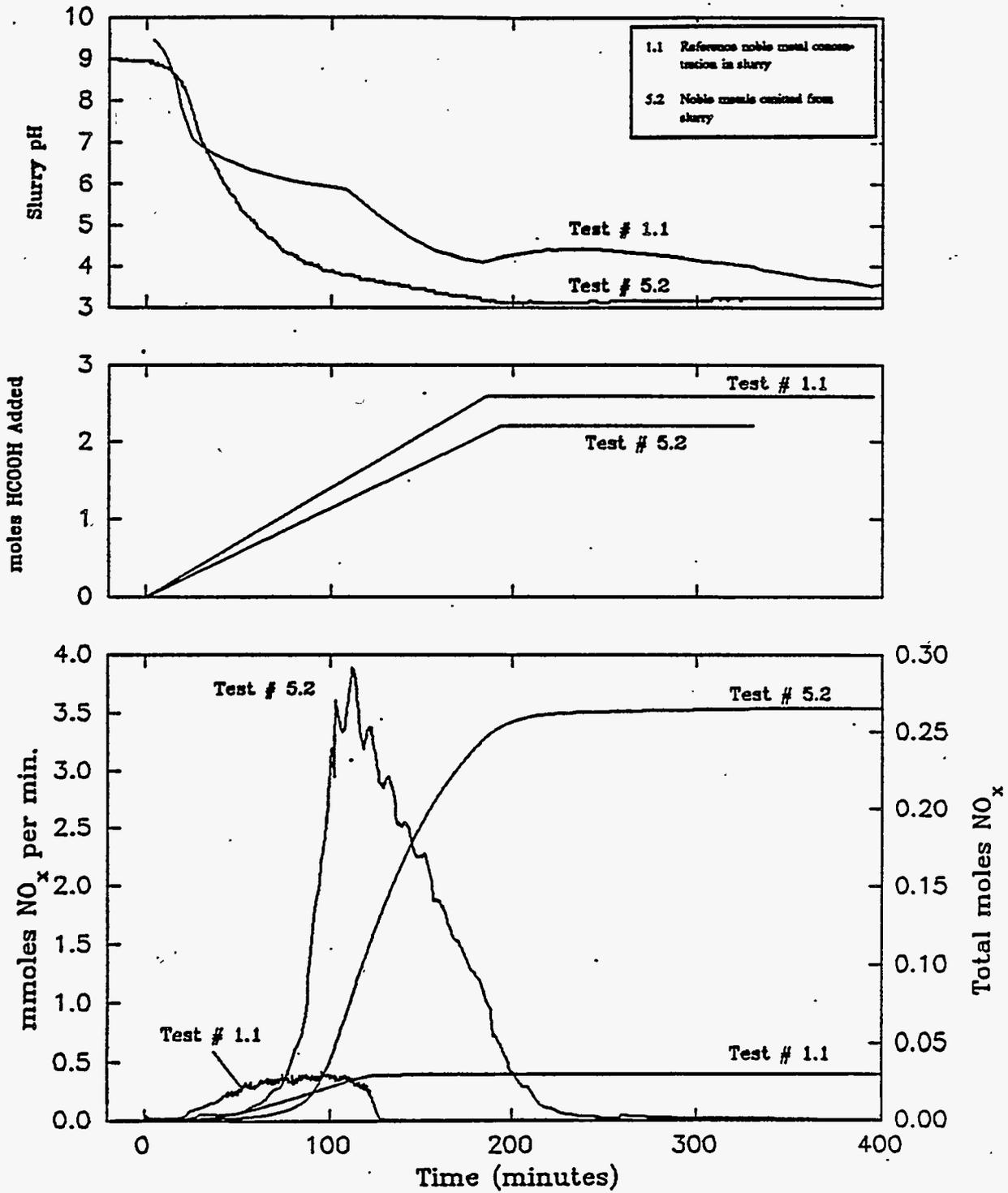


Figure E.5c. Comparison of the NO_x Generation Rate with Noble Metal Content of NCAW Simulant as a Function of Process Time for Tests 1.1 and 5.2

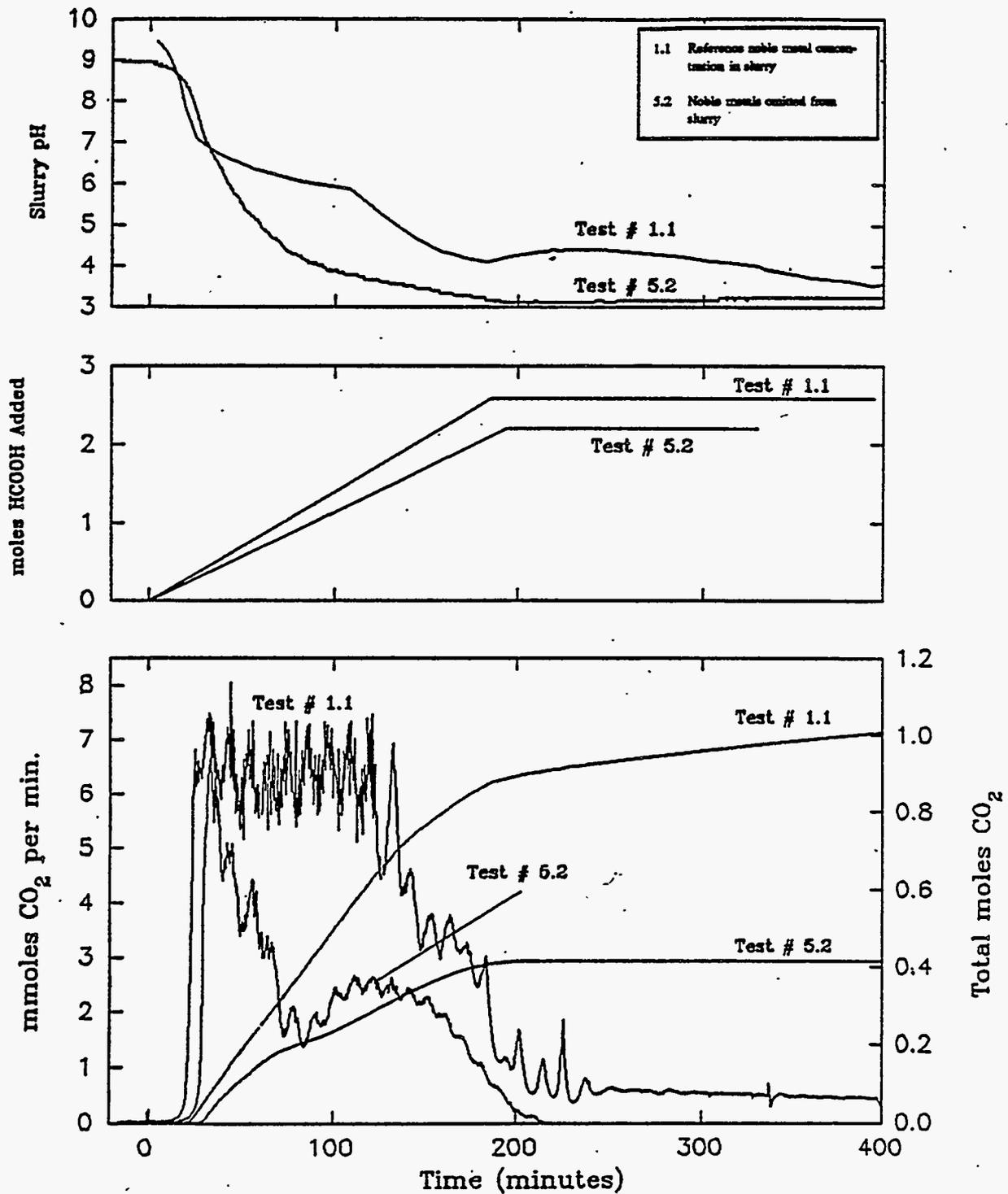


Figure E.5d. Comparison of the CO₂ Generation Rate with Noble Metal Content of NCAW Simulant as a Function of Process Time for Tests 1.1 and 5.2

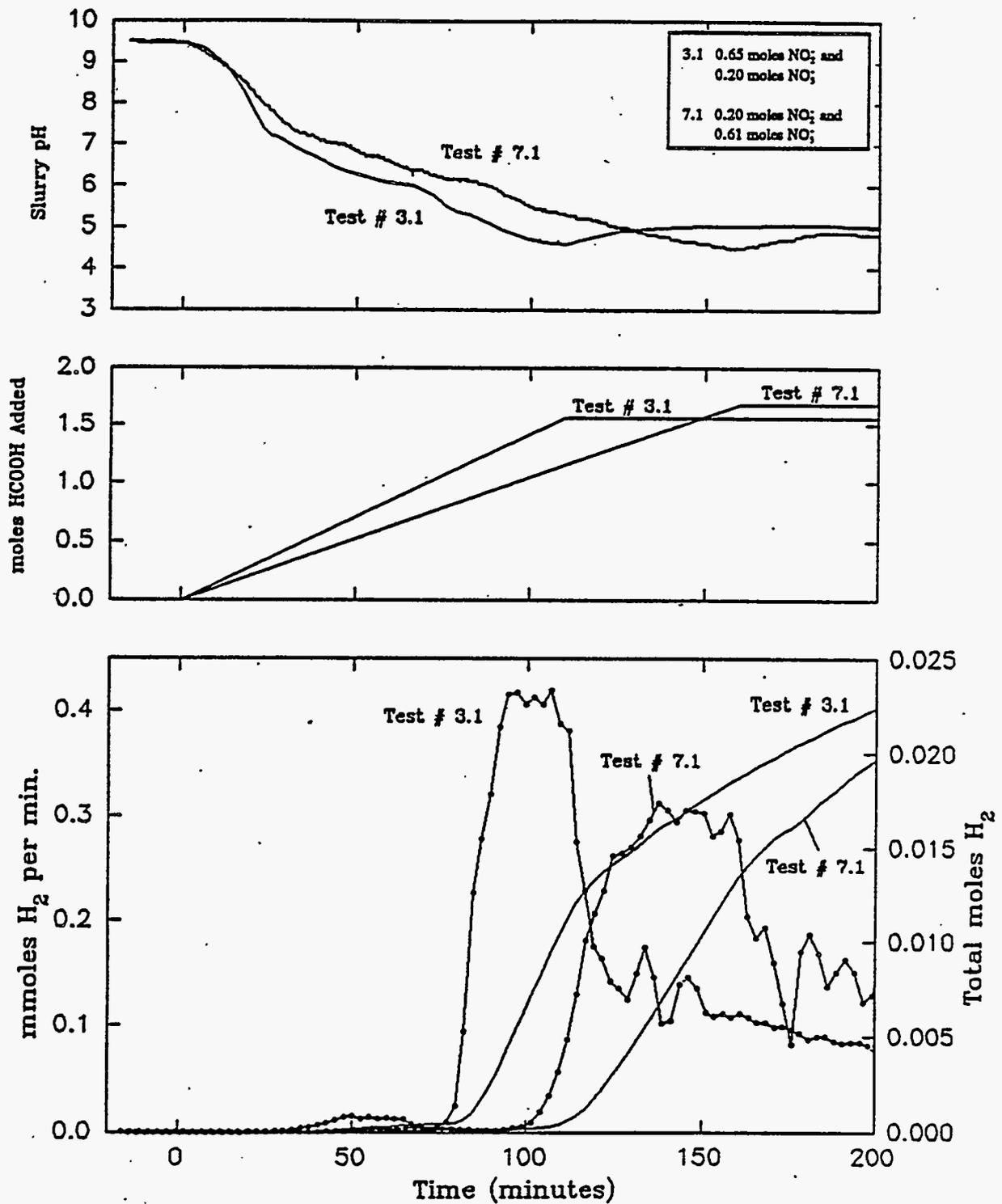


Figure E.6a. Comparison of the H₂ Generation rate with Minimum Nitrite, Maximum Nitrate Content of NCAW Simulant as a Function of Process Time for Tests 3.1 and 7.1

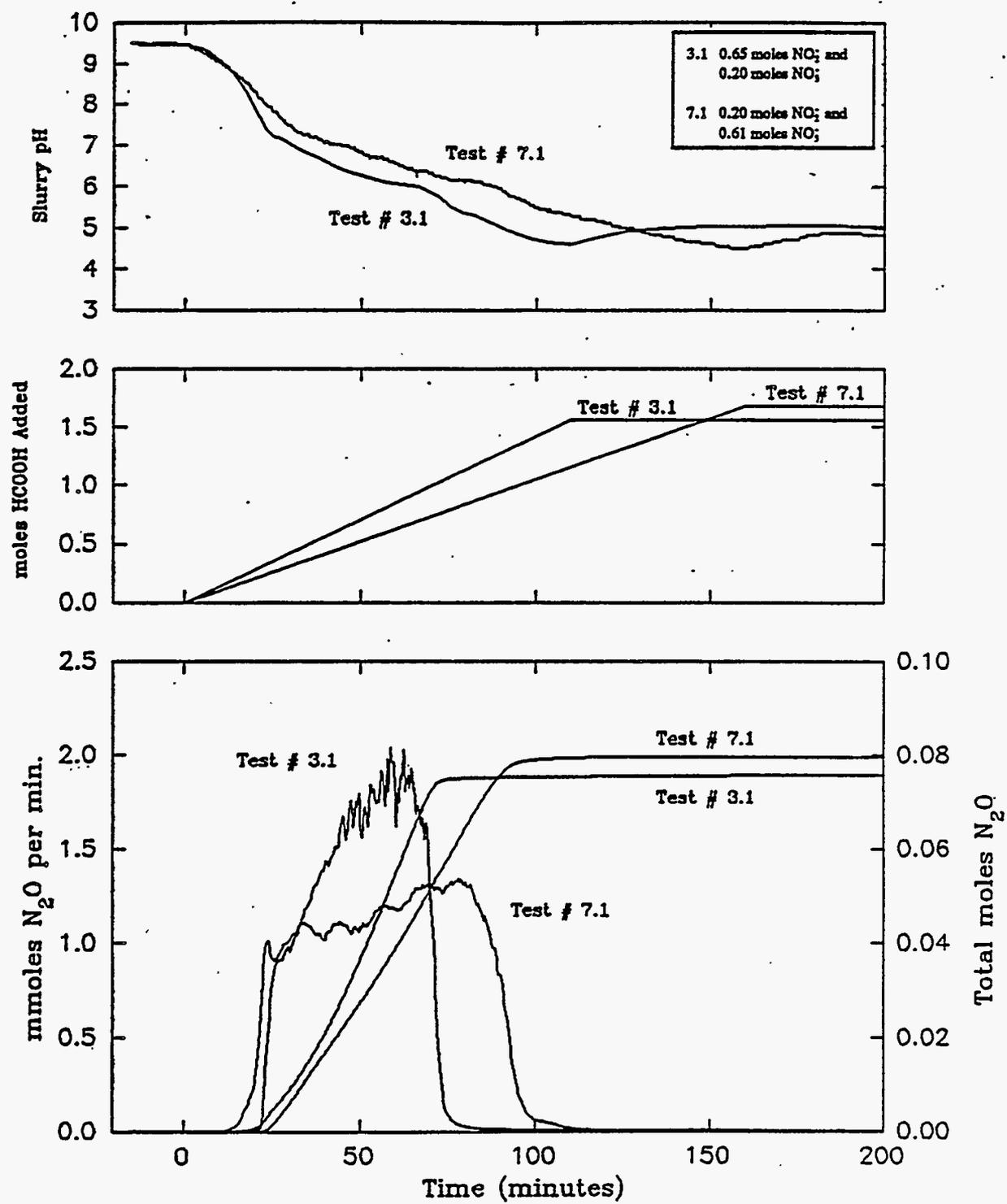


Figure E.6b. Comparison of the N₂O Generation Rate with Minimum Nitrite, Maximum Nitrate Content of NCAW Simulant as a Function of Process Time for Tests 3.1 and 7.1

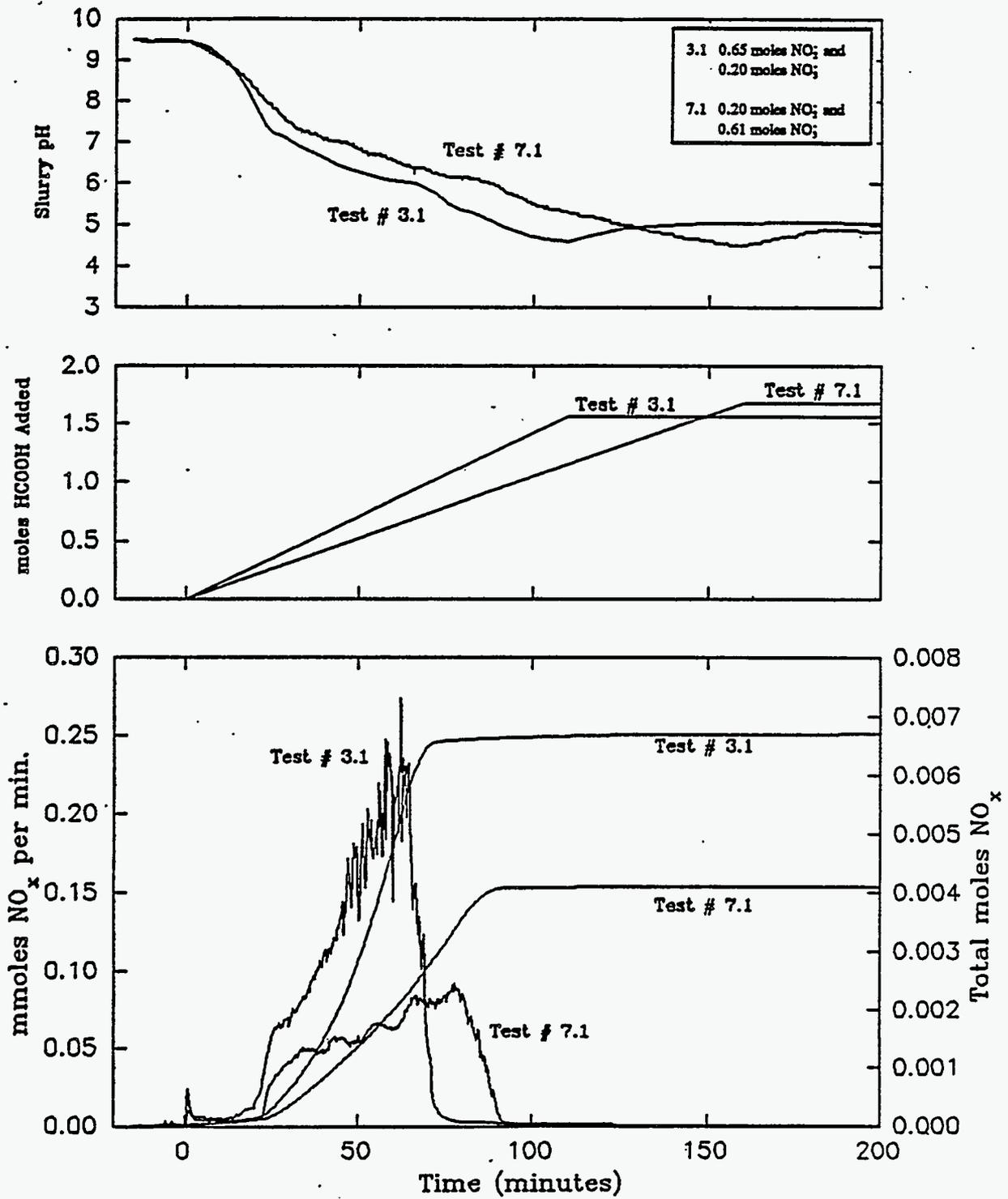


Figure E.6c. Comparison of the NO_x Generation Rate with Minimum Nitrite, Maximum Nitrate Content of NCAW Simulant as a Function of Process Time for Tests 3.1 and 7.1

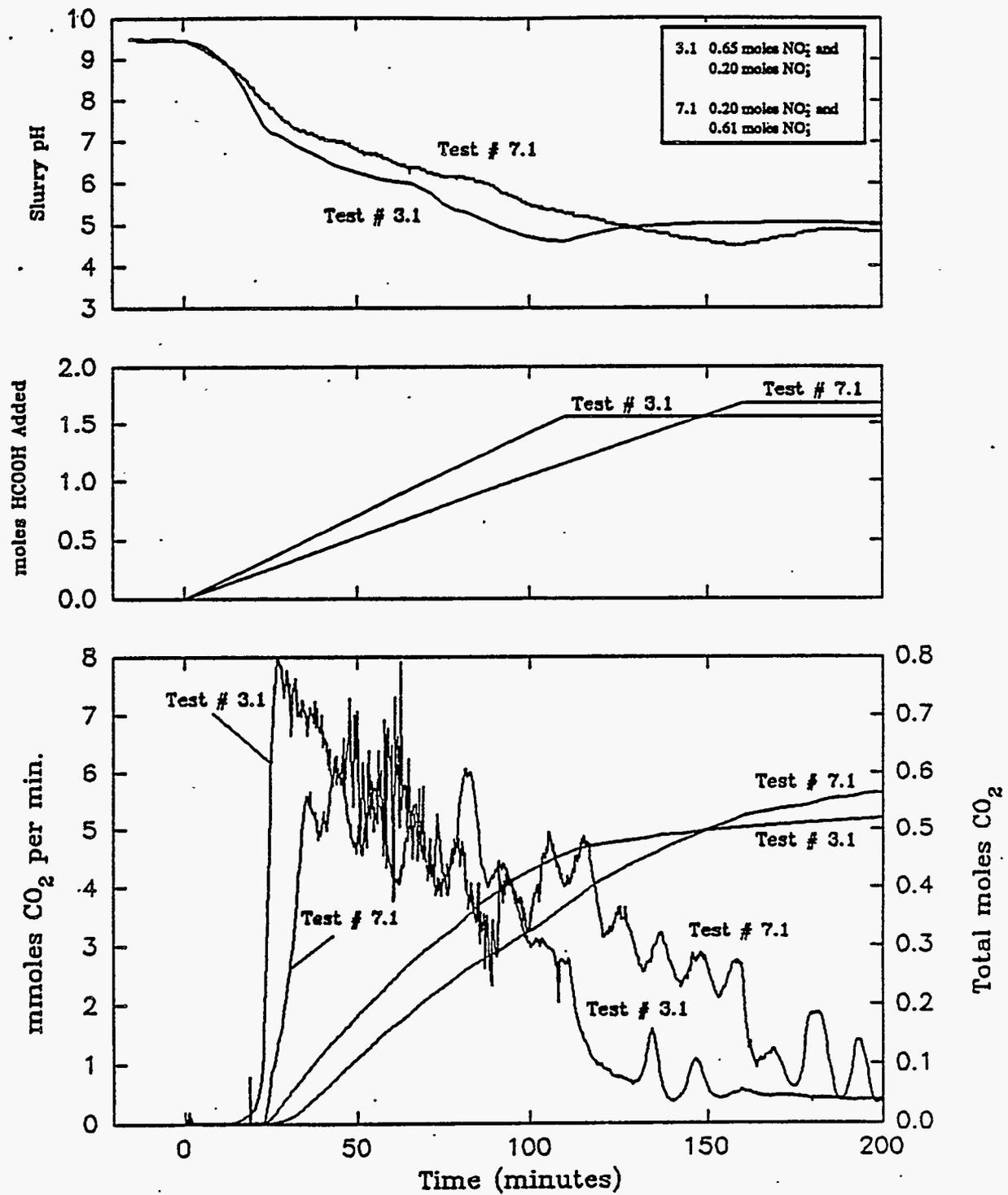


Figure E.6d. Comparison of the CO₂ Generation Rate with Minimum Nitrite, Maximum Nitrate Content of NCAW Simulant as a Function of Process Time for Tests 3.1 and 7.1

Appendix F

Hydrogen and CO₂ Generation as a Function of Time During Cool Down and Heat Up Cycles for Selected FY 1991 Laboratory-Scale Feed Preparation Tests

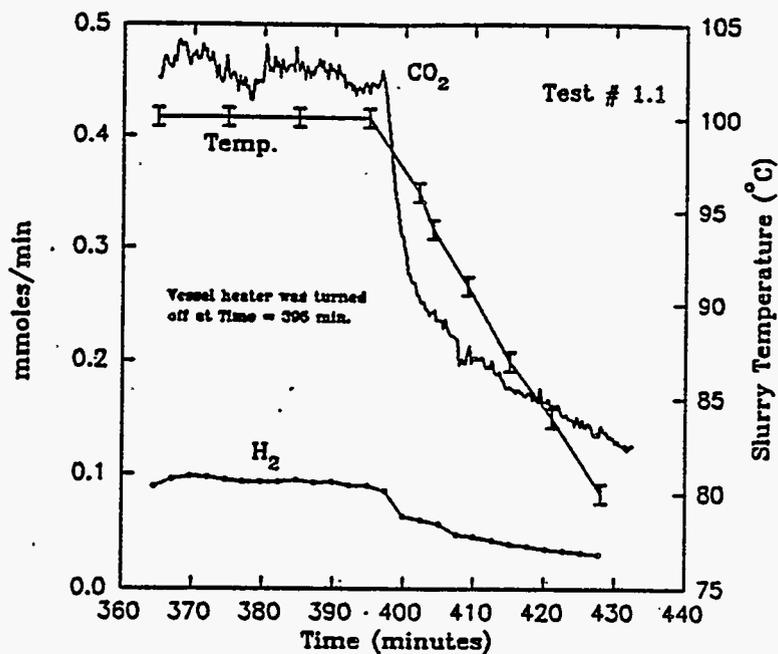


Figure F.1. Hydrogen and CO₂ Generation as a Function of Time During Cool Down After Digestion for Test 1.1: Maximum Amount of Formic Acid Added to the NCAW Simulant

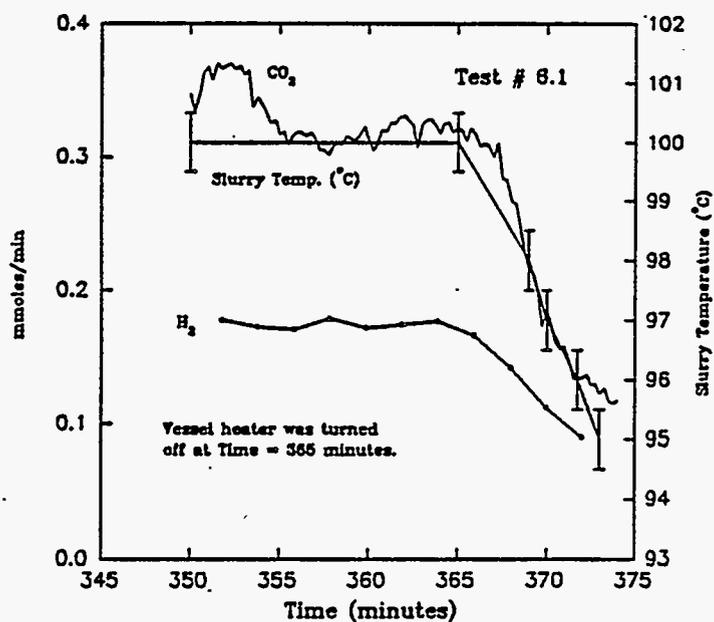


Figure F.2. Hydrogen and CO₂ Generation as a Function of Time During Cool Down After Digestion for Test 6.1

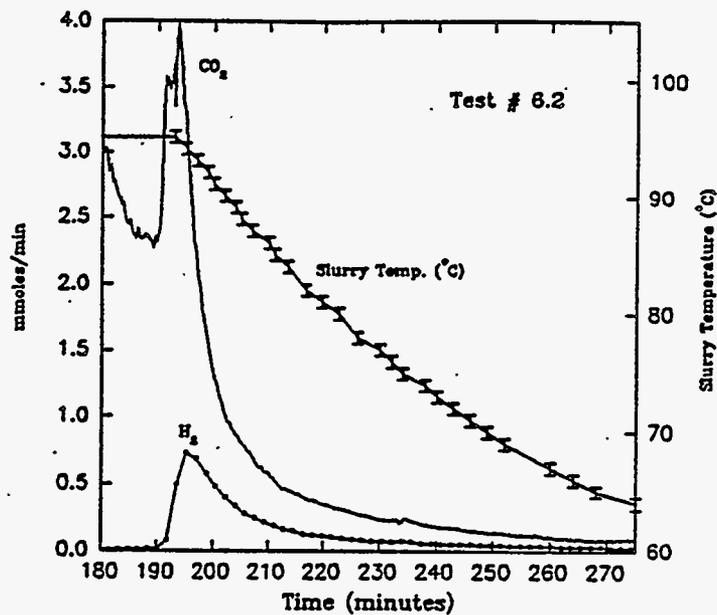


Figure F.3. Hydrogen and CO₂ Generation as a Function of Time During Cool Down Initiated During the H₂ Peak Generation Rate for Test 6.2. Formic acid addition to the NCAW simulant was interrupted also.

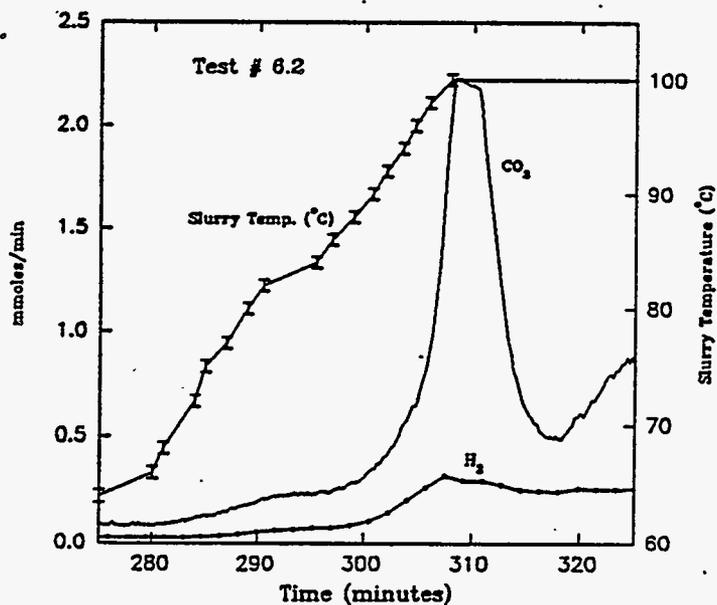


Figure F.4. Hydrogen and CO₂ Generation as a Function of Time During Heat Up After Interruption of Formic Acid Addition and Heat Source Input for Test 6.2

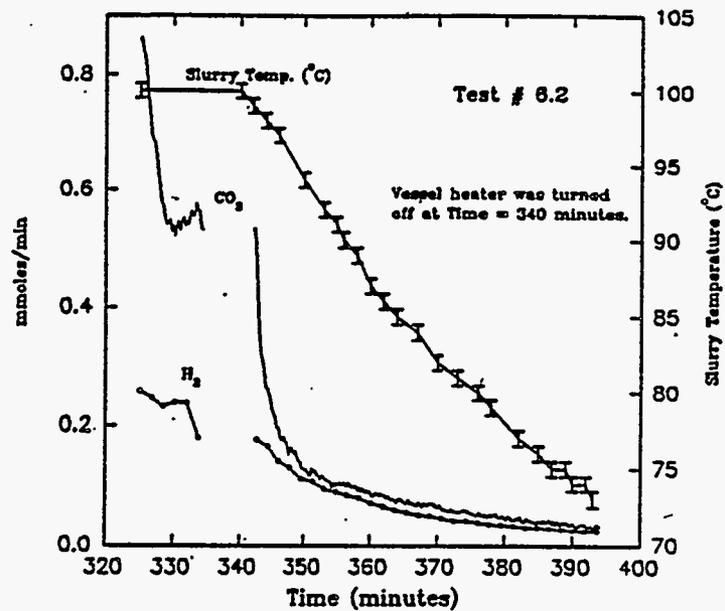


Figure F.5. Hydrogen and CO₂ Generation as a Function of Time During Cool Down Near End of Test for Test 6.2: Formic Acid and Heat Source Interrupted to the NCAW Simulant

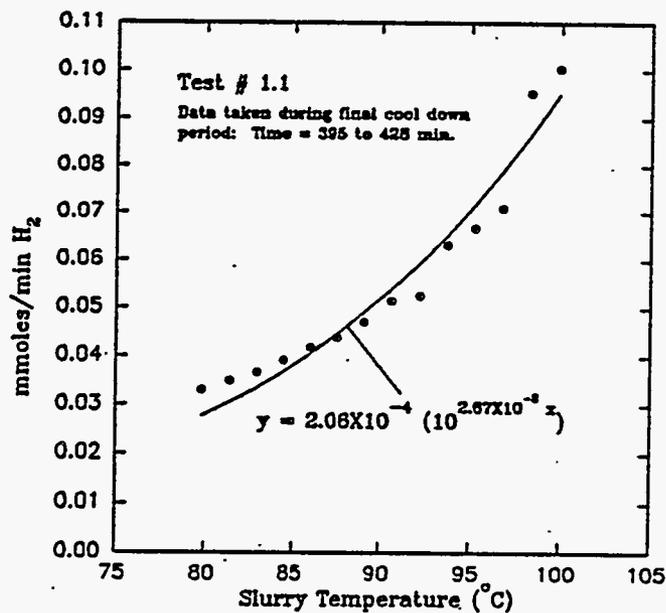


Figure F.6. Hydrogen Generation as a Function of Temperature During Cool Down Near End of Test for Test 1.1: Maximum Amount of Formic Acid Added to the NCAW Simulant

Appendix G

**Thermogravimetric and Differential Scanning Calorimetry
Thermograms of NCAW Slurry, Formated NCAW Slurry
and Formated NCAW Slurry Plus Recycle
Waste Stream Simulant**

G.1

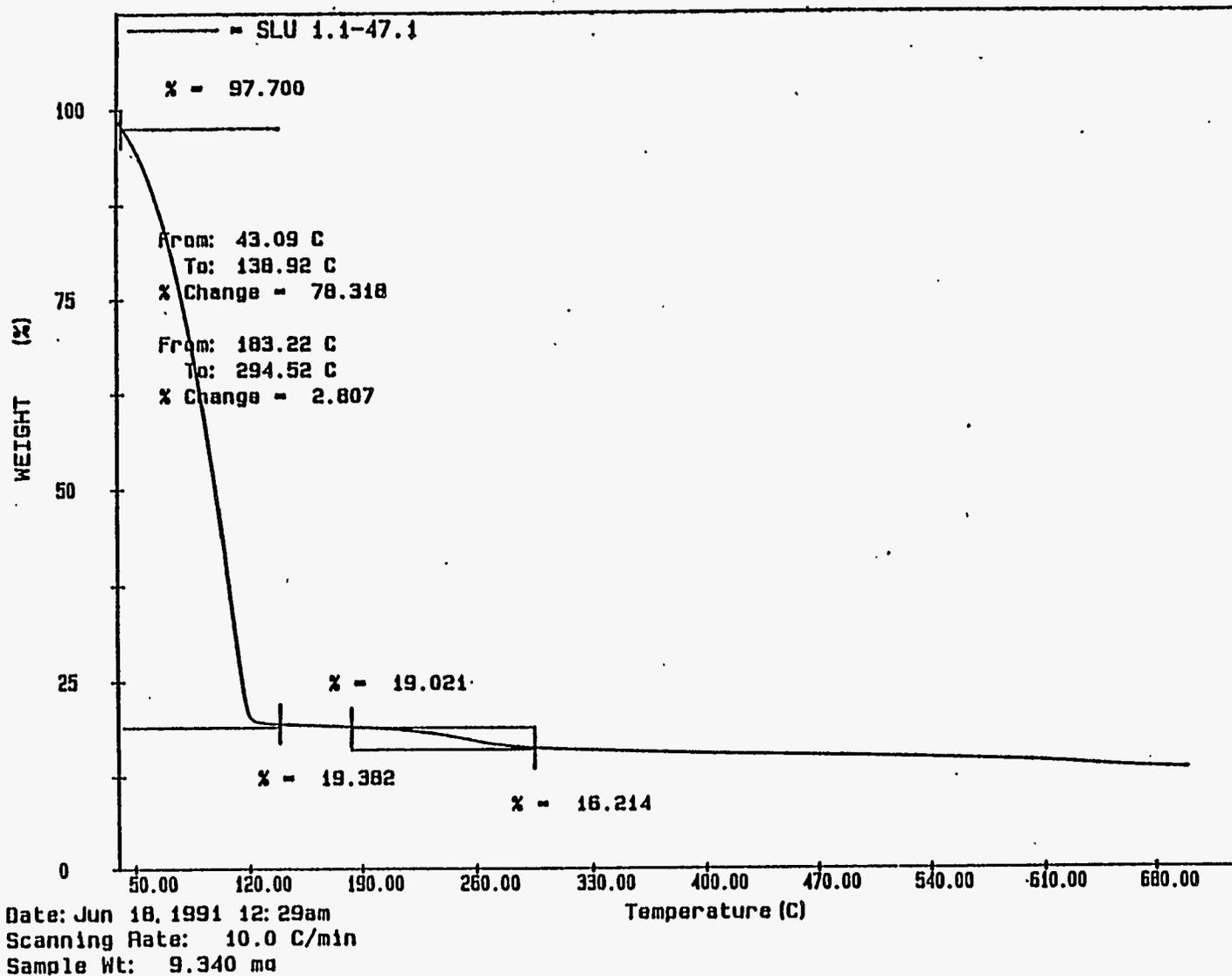
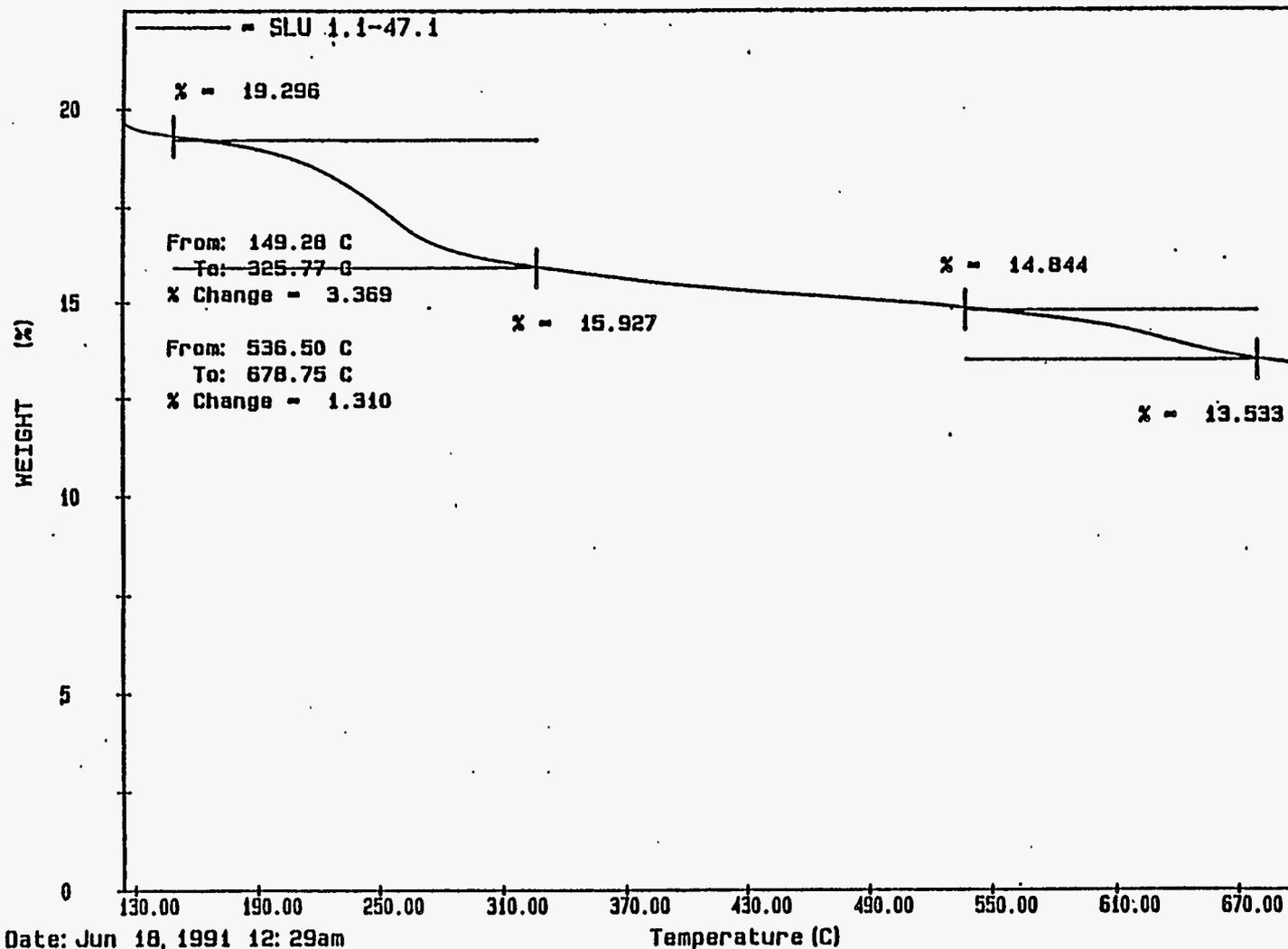


Figure G.1. Weight Loss from 40 to 700°C of Test 1.1 (Maximum Amount of Formic Acid Added) *Formated* NCAW Simulant Plus Recycle Simulant Measured by Thermogravimetric Analysis

G.2



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

Figure G.2. Weight Loss from 120 to 700°C of Test 1.1 (Maximum Amount of Formic Acid Added) *Formatted* NCAW Simulant *Plus Recycle Simulant* Measured by Thermogravimetric Analysis (Same as Figure G1, but Different Scale)

G.3

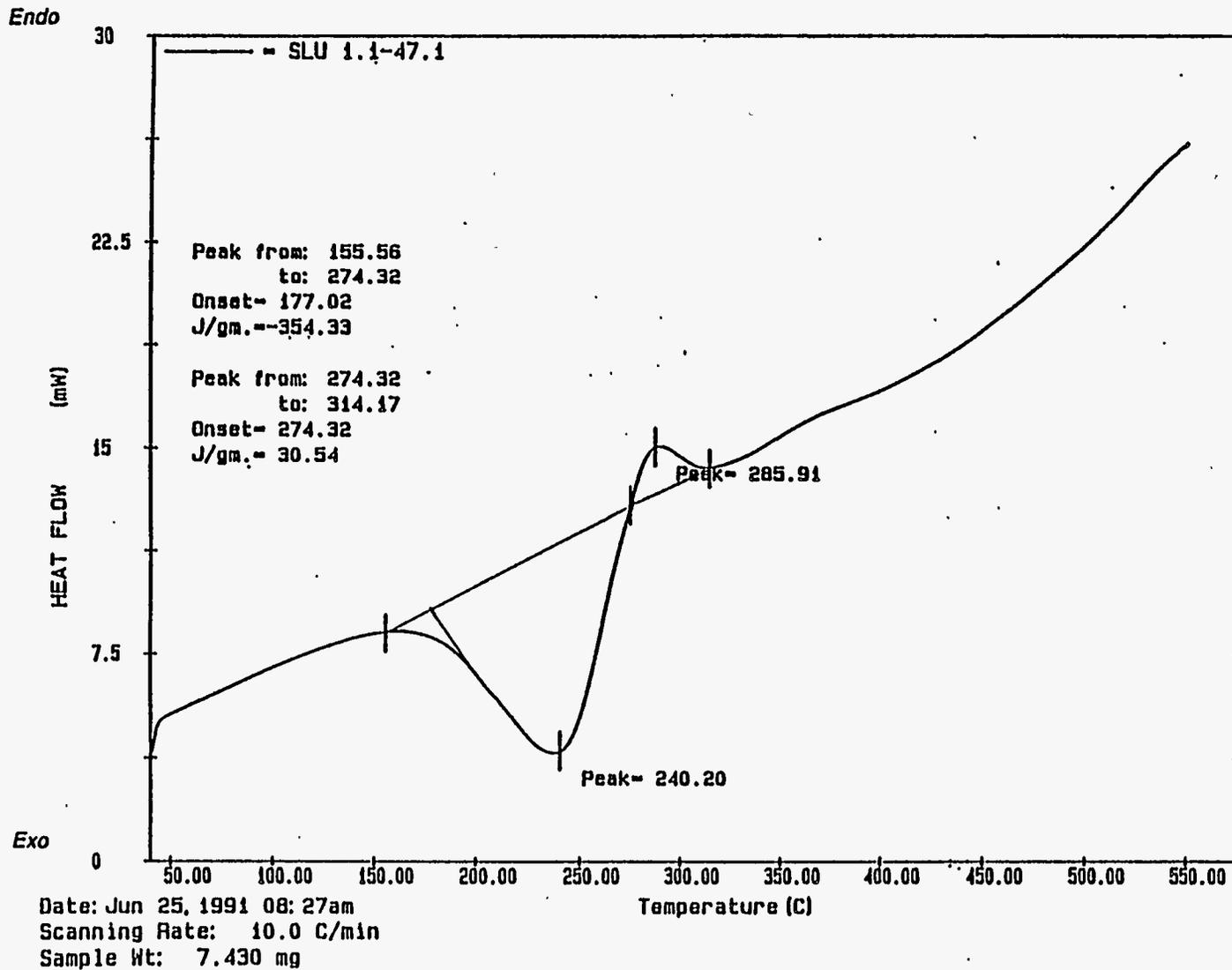


Figure G.3. Heat Flow from 40 to 550°C of Test 1.1 (Maximum Amount of Formic Acid Added) *Formatted* NCAW Simulant Plus Recycle Simulant Measured by Differential Scanning Calorimetry

G.4

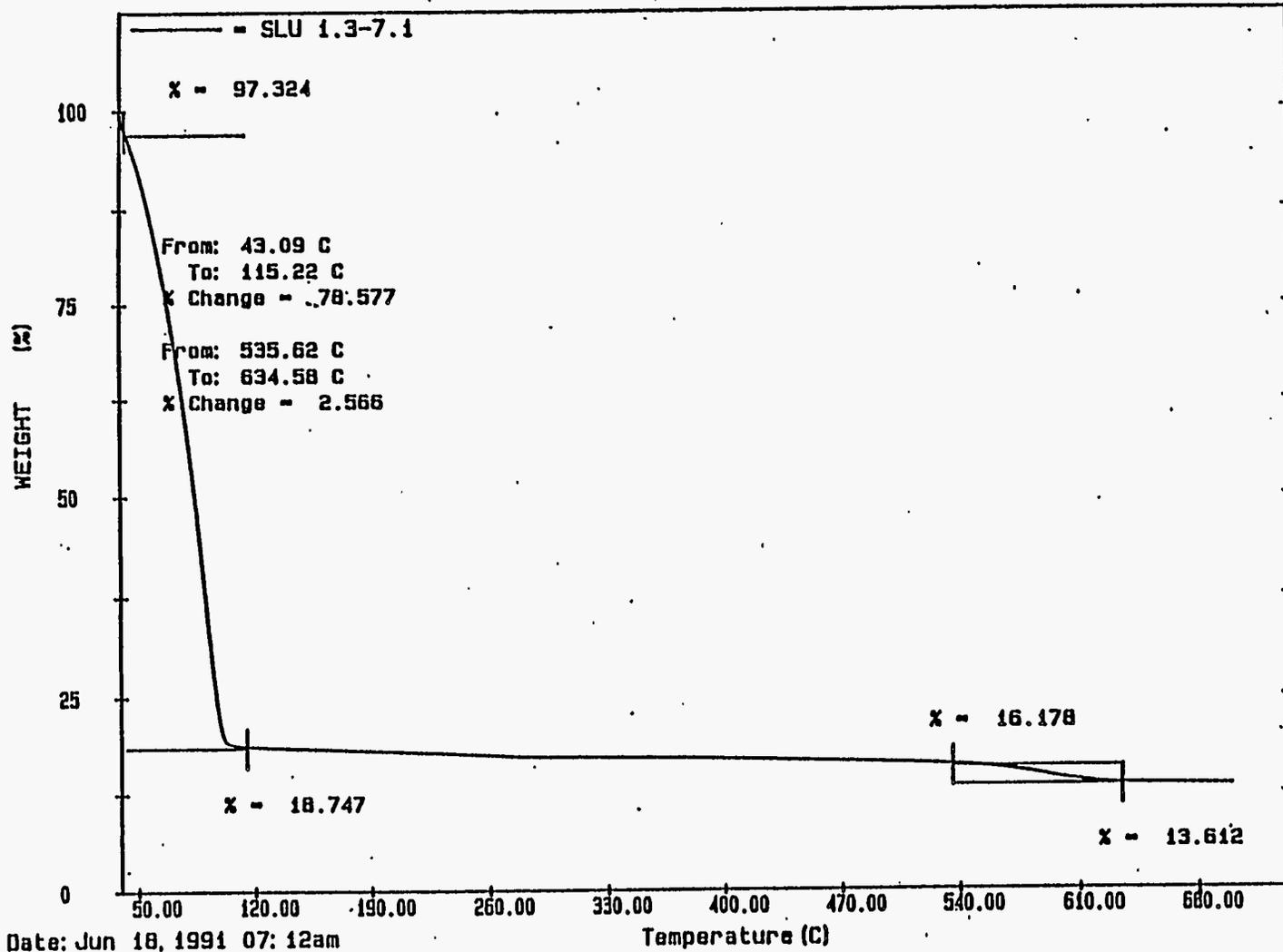


Figure G.4. Weight Loss from 40 to 700°C of Test 1.3 NCAW Simulant Measured by Thermogravimetric Analysis

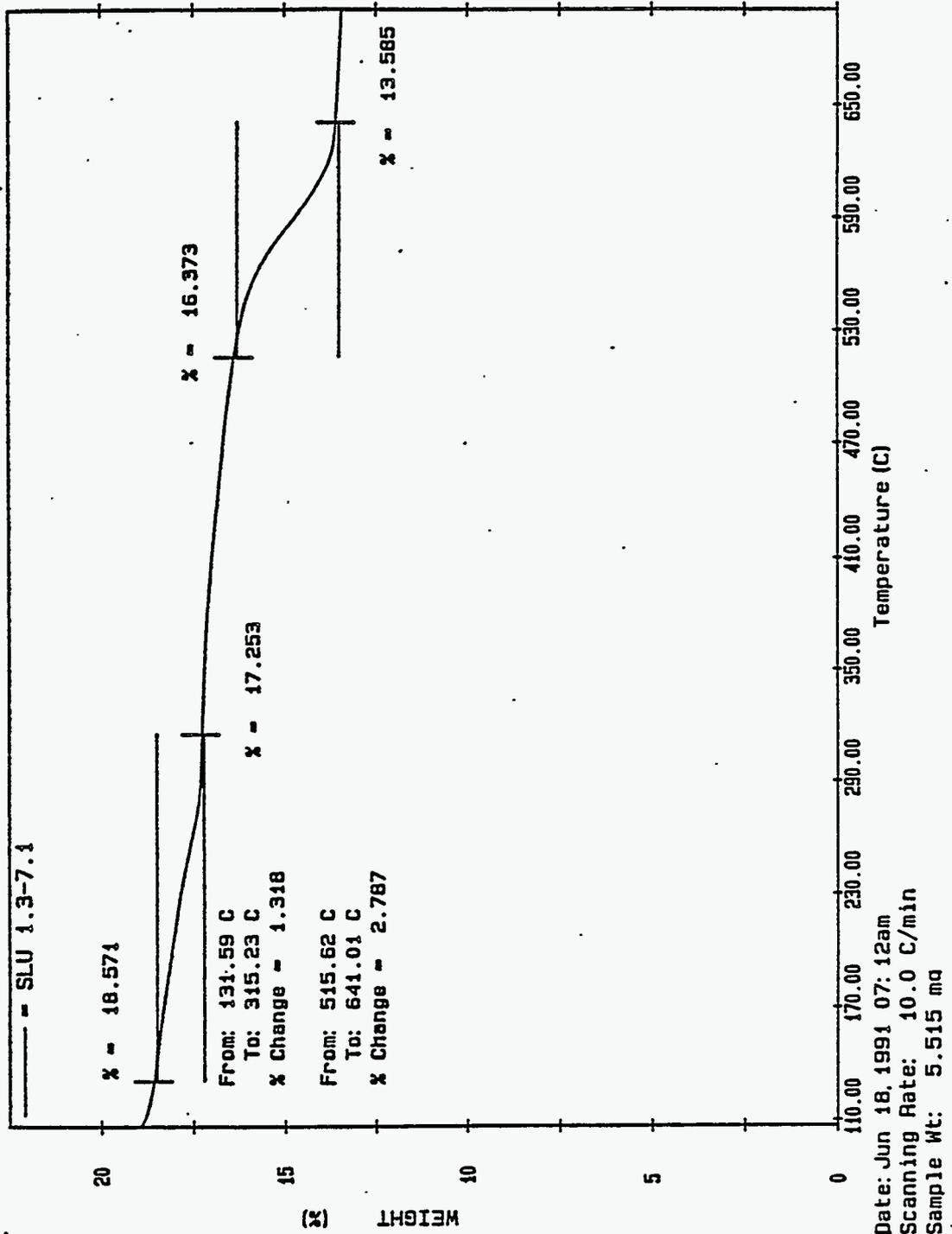


Figure G.5. Weight Loss from 110 to 700°C of Test 1.3 NCAW Simulant Measured by Thermogravimetric Analysis (Same as Figure G4, but Different Scale)

G.6

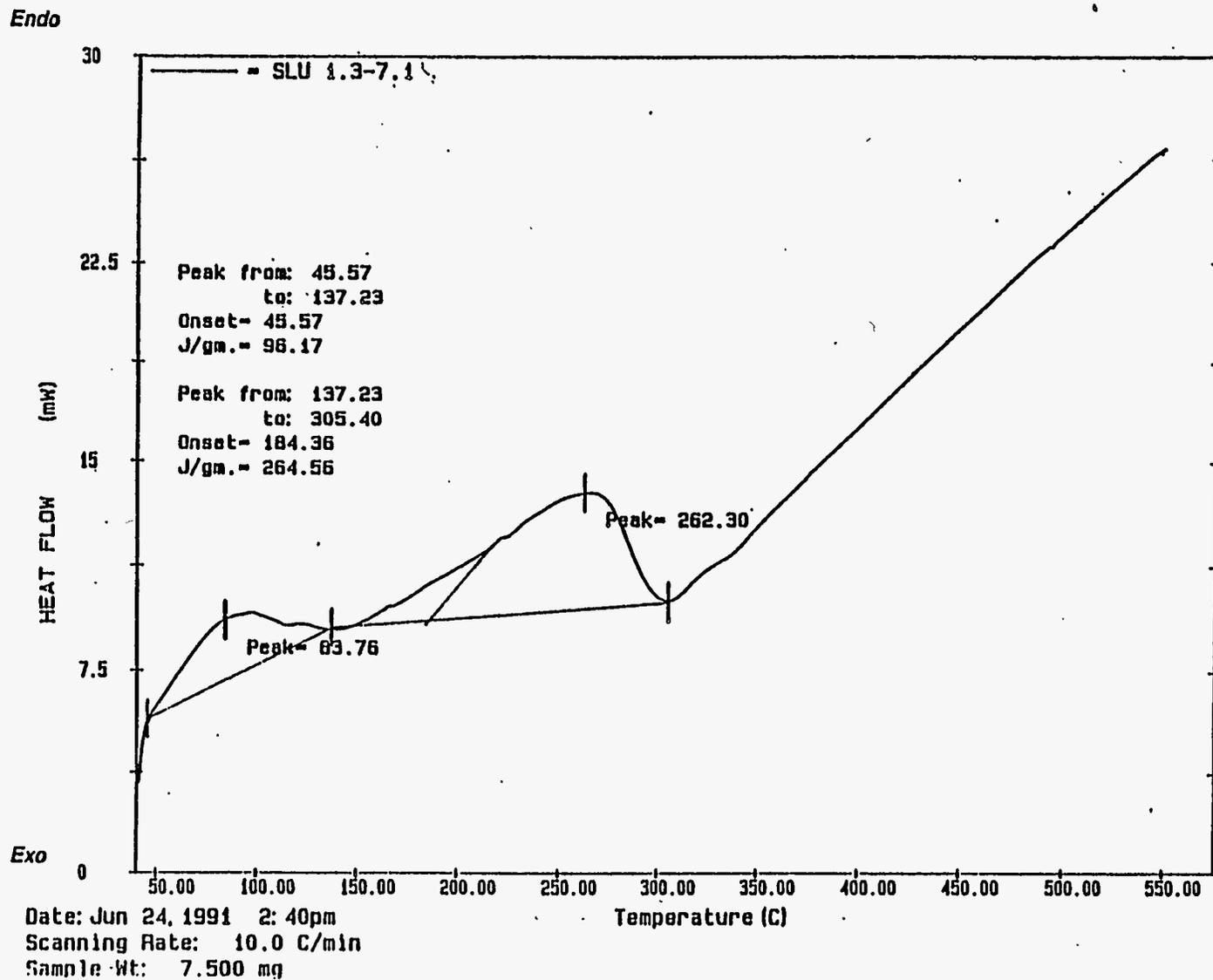


Figure G.6. Heat Flow from 40 to 550°C of Test 1.3 NCAW Simulant Measured by Differential Scanning Calorimetry

G.7

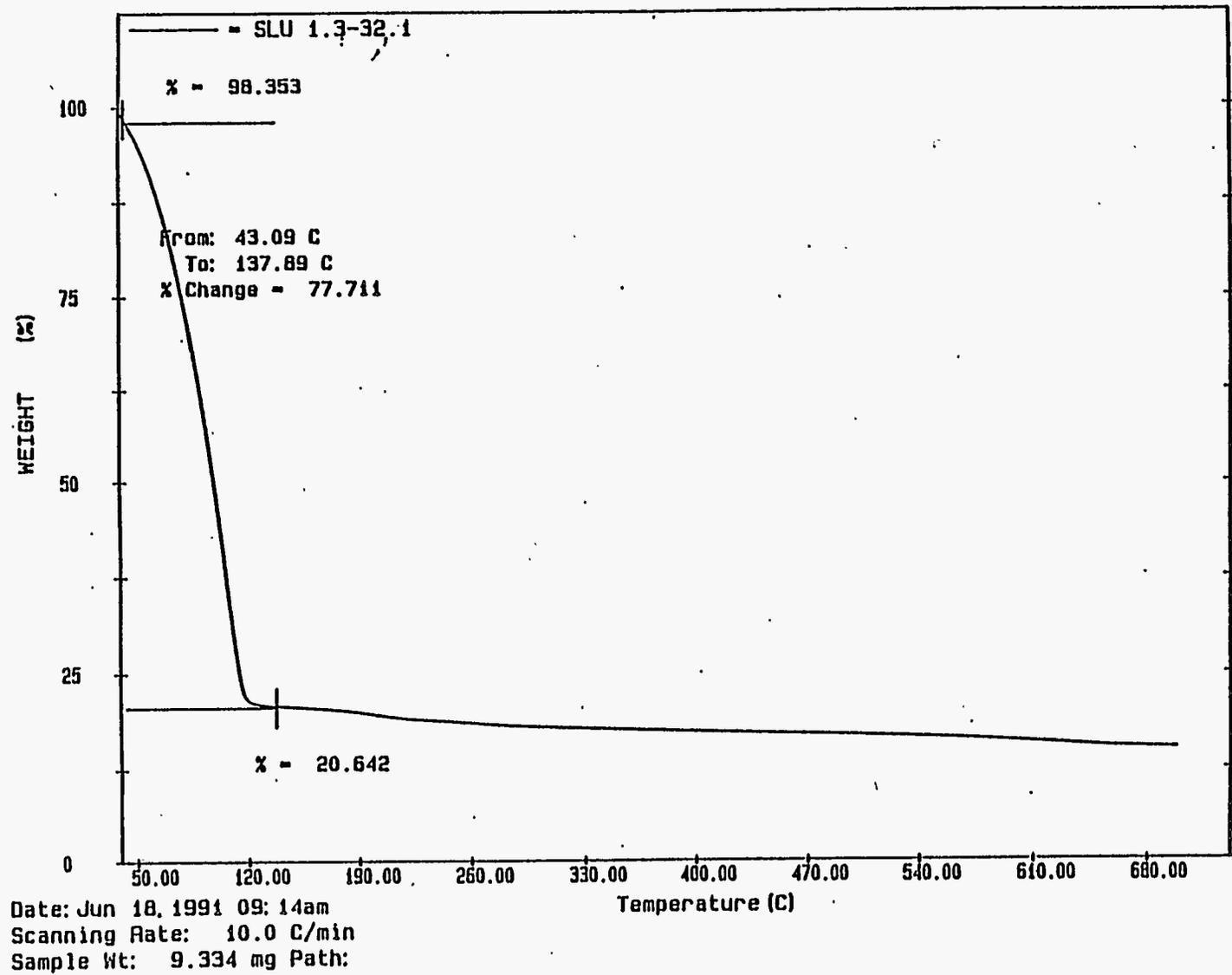


Figure G.7. Weight Loss from 40 to 700°C of Test 1.3 (Mid-Amount of Formic Acid Added) *Formated* NCAW Simulant Measured by Thermogravimetric Analysis

G.8

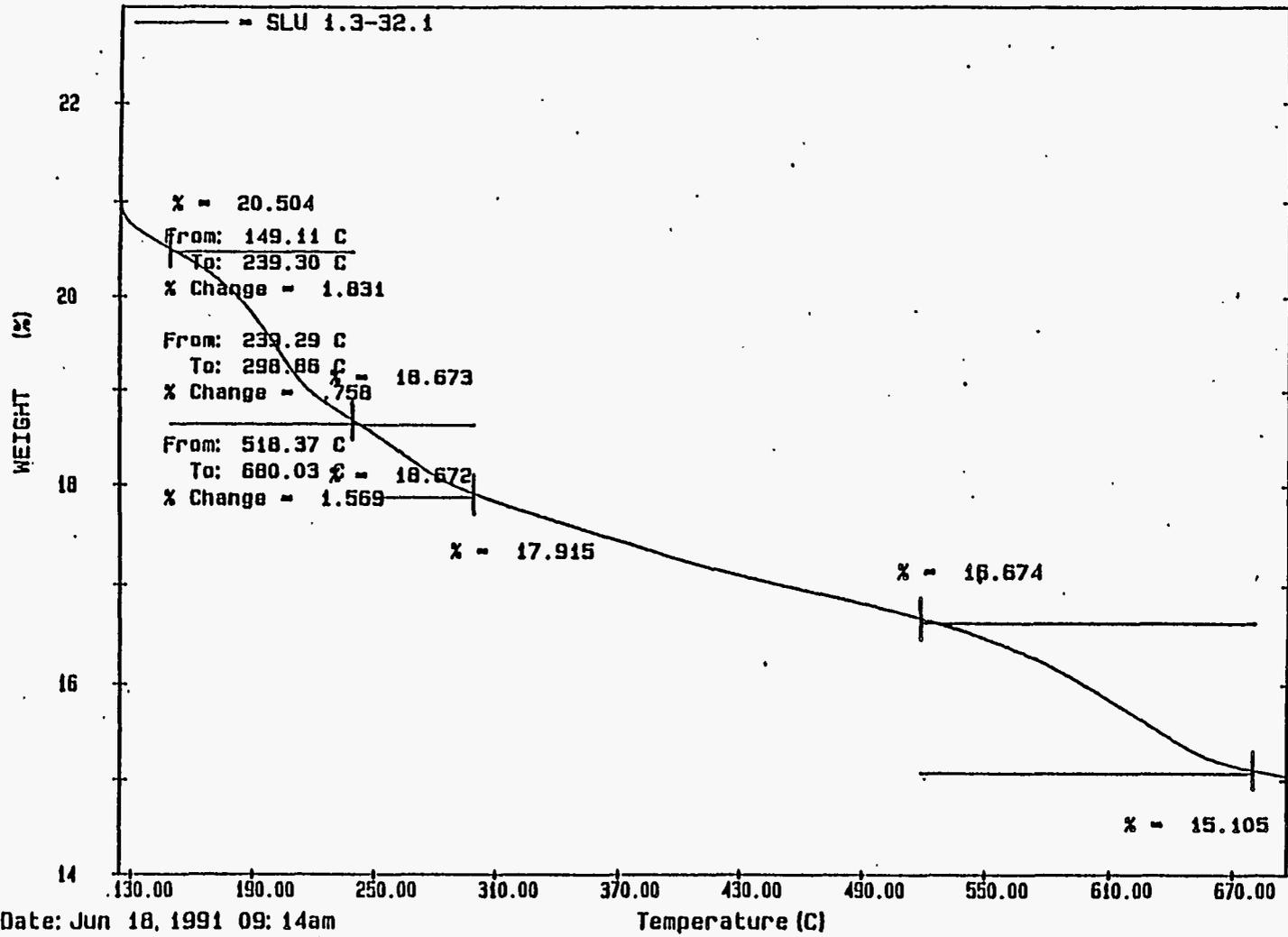


Figure G.8. Weight Loss from 40 to 700°C of Test 1.3 (Mid-Amount of Formic Acid Added) *Formated* NCAW Simulant Measured by Thermogravimetric Analysis (Same as Figure G7, but Different Scale)

G.9

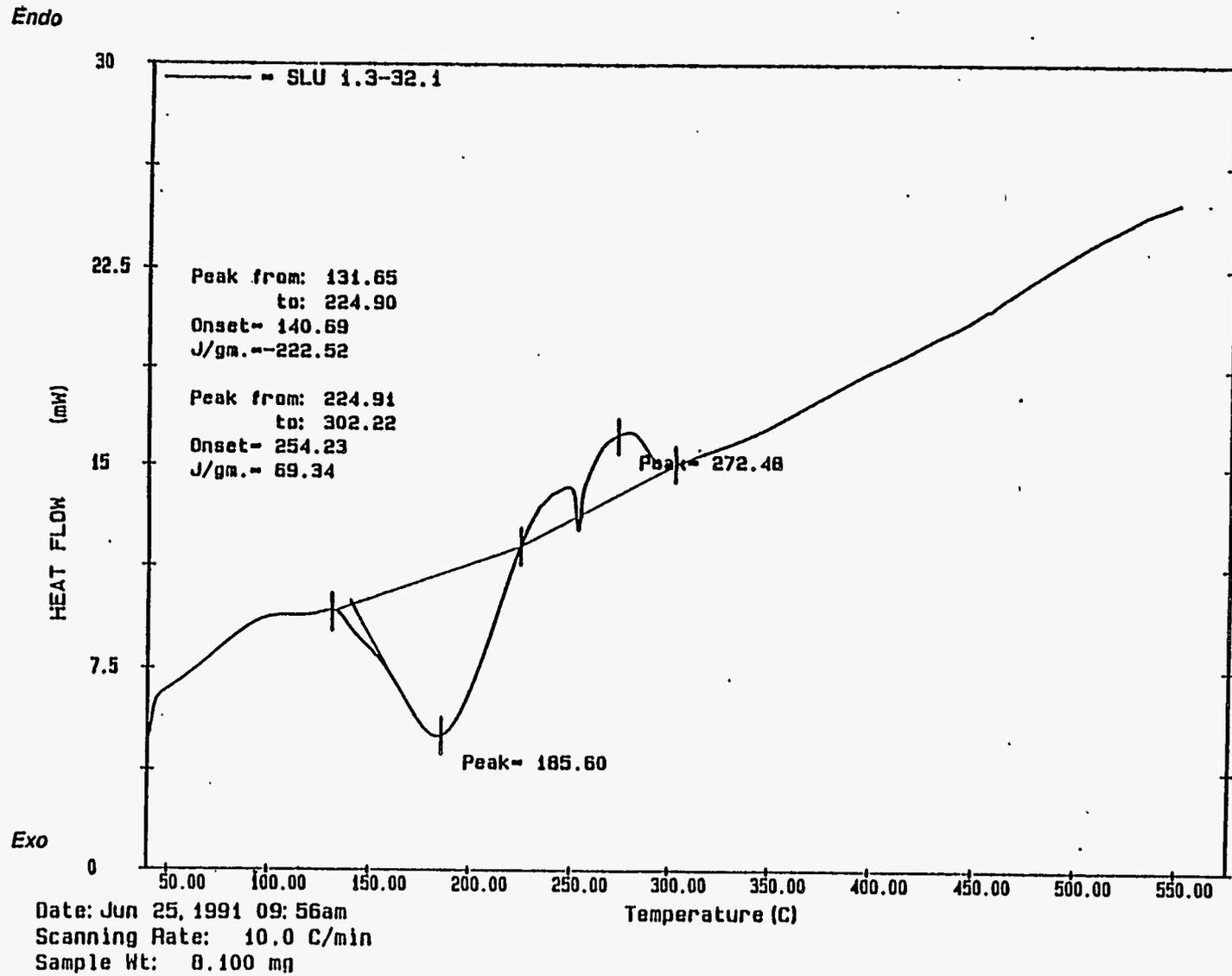


Figure G.9. Heat Flow from 40 to 550°C of Test 1.3 (Mid Amount of Formic Acid Added) *Formatted* NCAW Simulant Measured by Differential Scanning Calorimetry

G.10

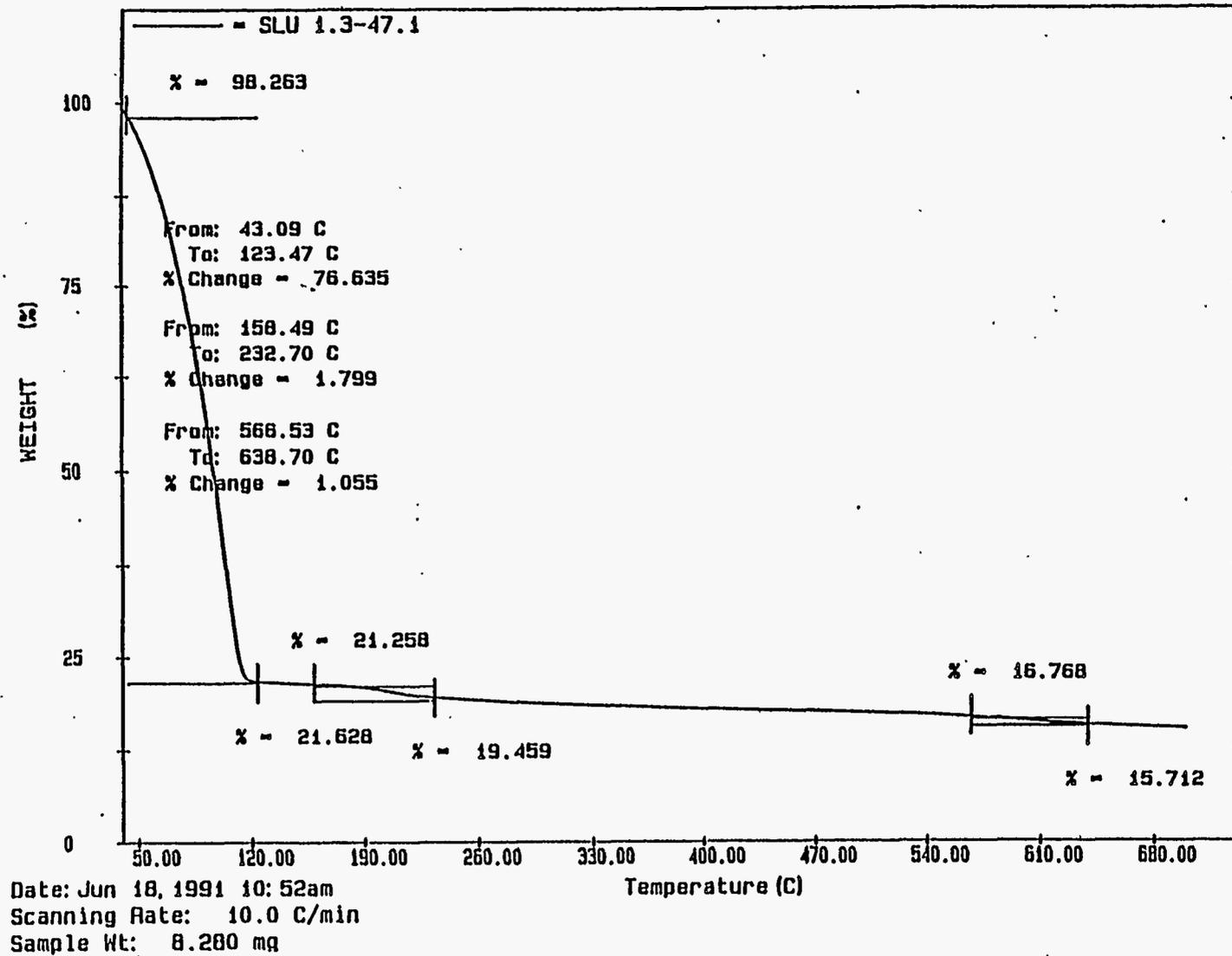


Figure G.10. Weight Loss from 40 to 700°C of Test 1.3 (Mid-Amount of Formic Acid Added) *Formatted* NCAW Simulant *Plus* *Recycle* Simulant Measured by Thermogravimetric Analysis

G.11

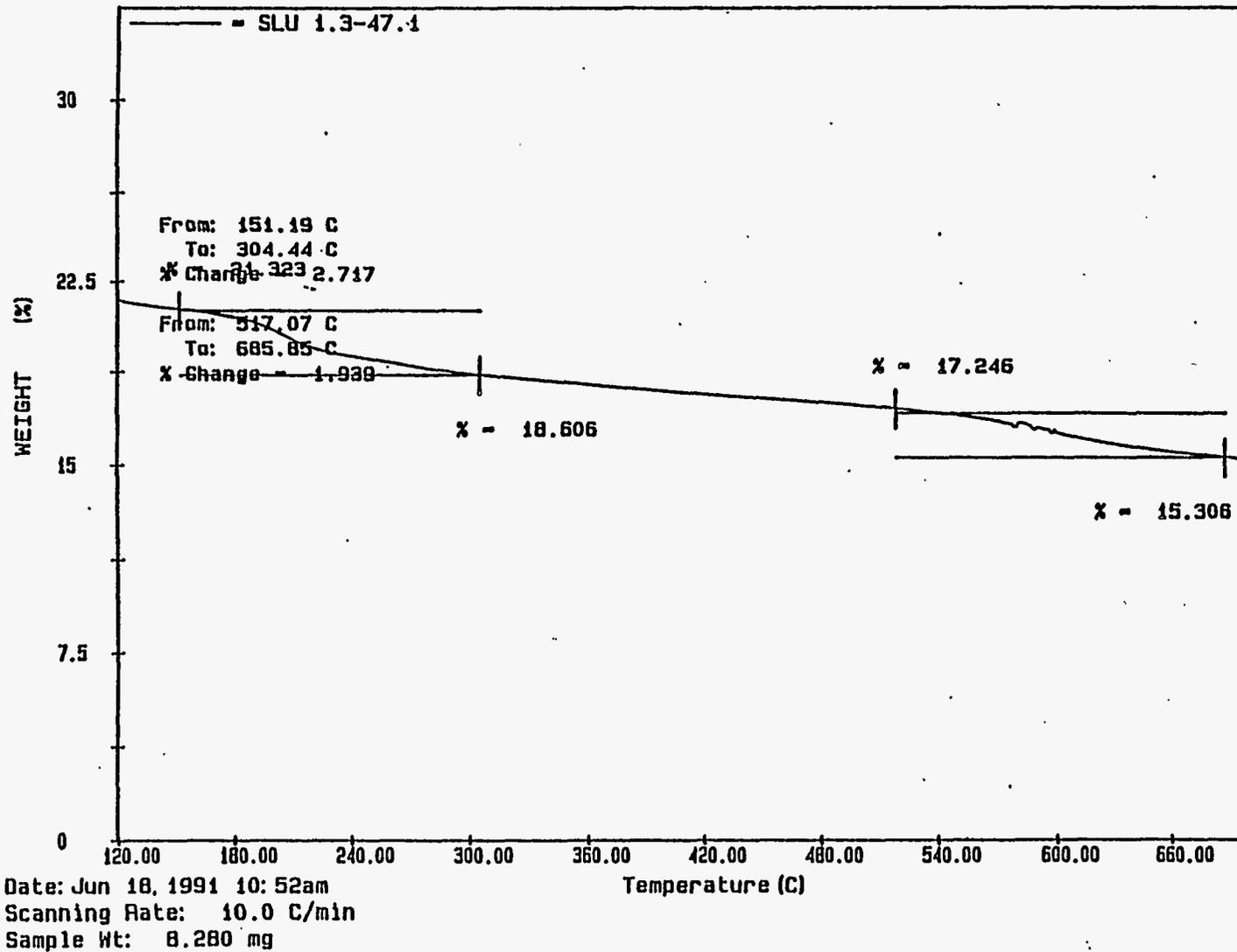


Figure G.11. Weight Loss from 120 to 700°C of Test 1.3 (Mid-Amount of Formic Acid Added) *Formated* NCAW Simulant Plus Recycle Simulant Measured by Thermogravimetric Analysis (Same as Figure G10, but Different Scale)

G.12

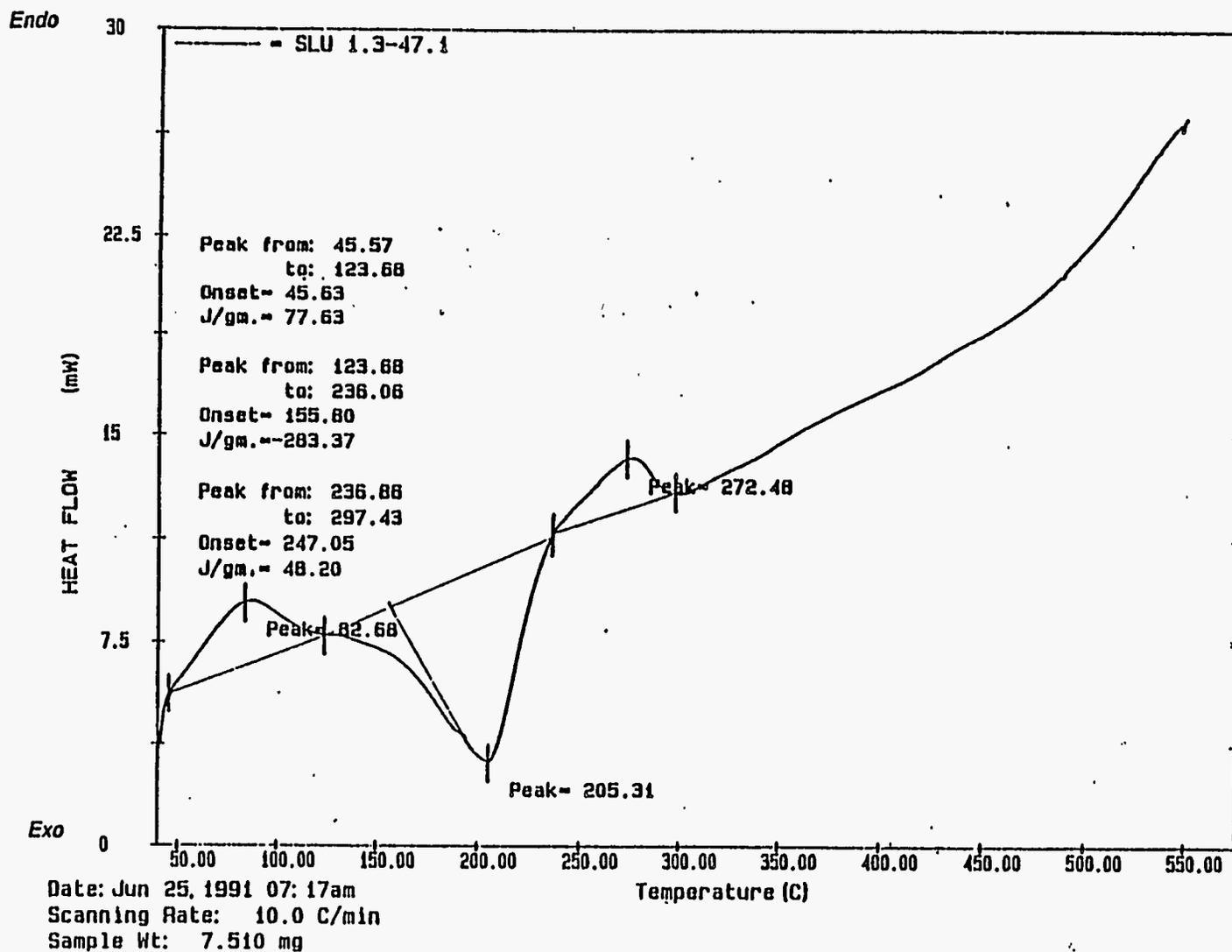


Figure G.12. Heat Flow from 40 to 550°C of Test 1.3 (Mid-Amount of Formic Acid Added) *Formated* NCAW Simulant *Plus* *Recycle Simulant* Measured by Differential Scanning Calorimetry

Appendix H

**Total Amount of NH_4^+ in NCAW Slurry Simulant as a
Function of Process Time for FY 1991
Laboratory-Scale Feed Preparation Tests**

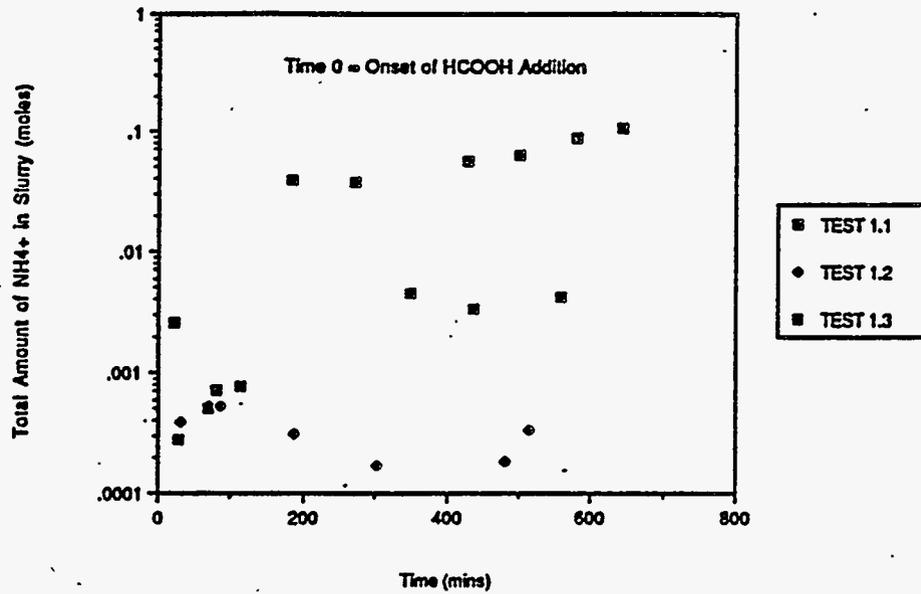


Figure H.1. Total Amount of Ammonium Ion in Slurry as a Function of Process Time for NCAW Slurry Test Set 1: Maximum Amount of Formic Acid Added (Includes Tests 1.1, 1.2, and 1.3)

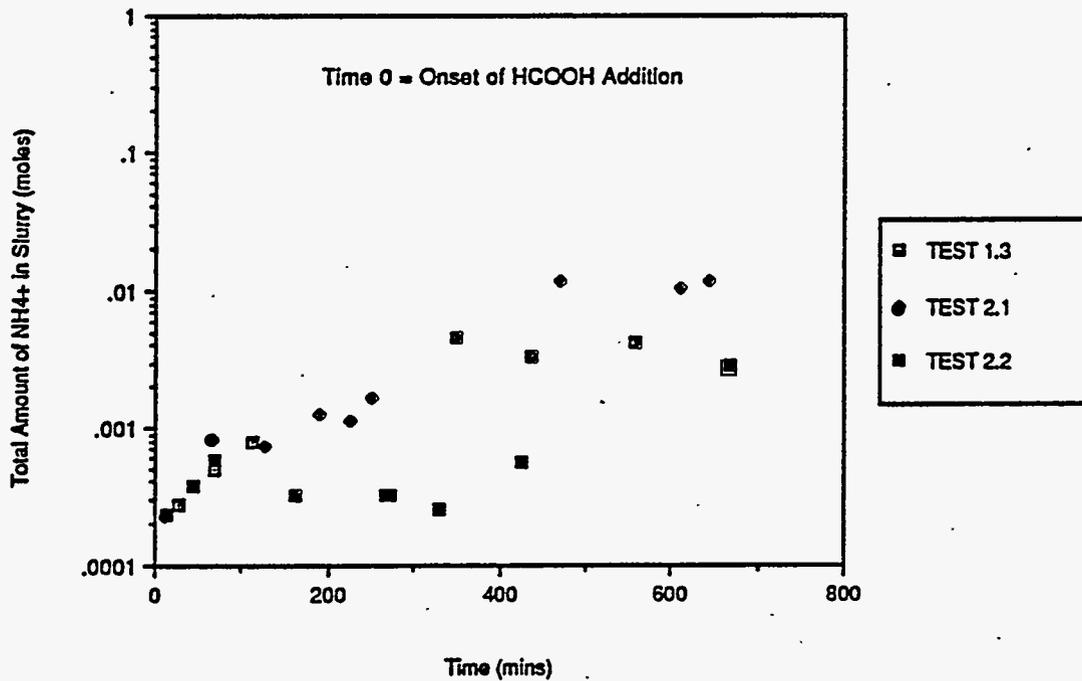


Figure H.2. Total Amount of Ammonium Ion in Slurry as a Function of Process Time for NCAW Slurry Test Set 2: Rate of Formic Acid Addition (Includes Tests 1.3, 2.1, and 2.2)

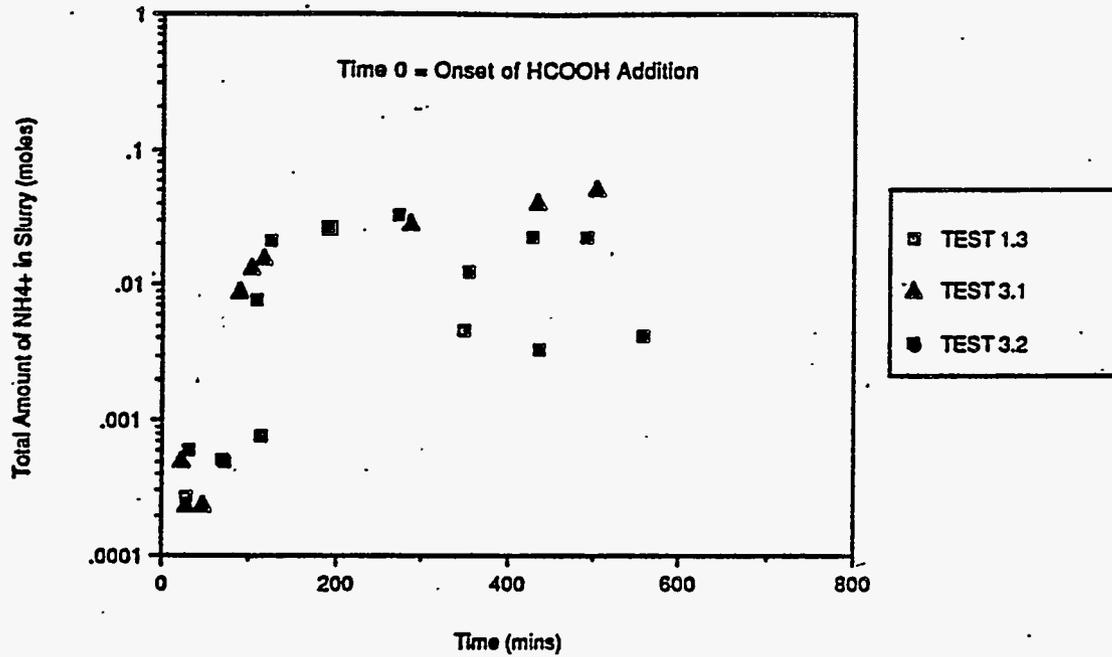


Figure H.3. Total Amount of Ammonium Ion in Slurry as a Function of Process Time for NCAW Slurry Test Set 3: Nitrite Addition (Includes Tests 1.3, 3.1, and 3.2)

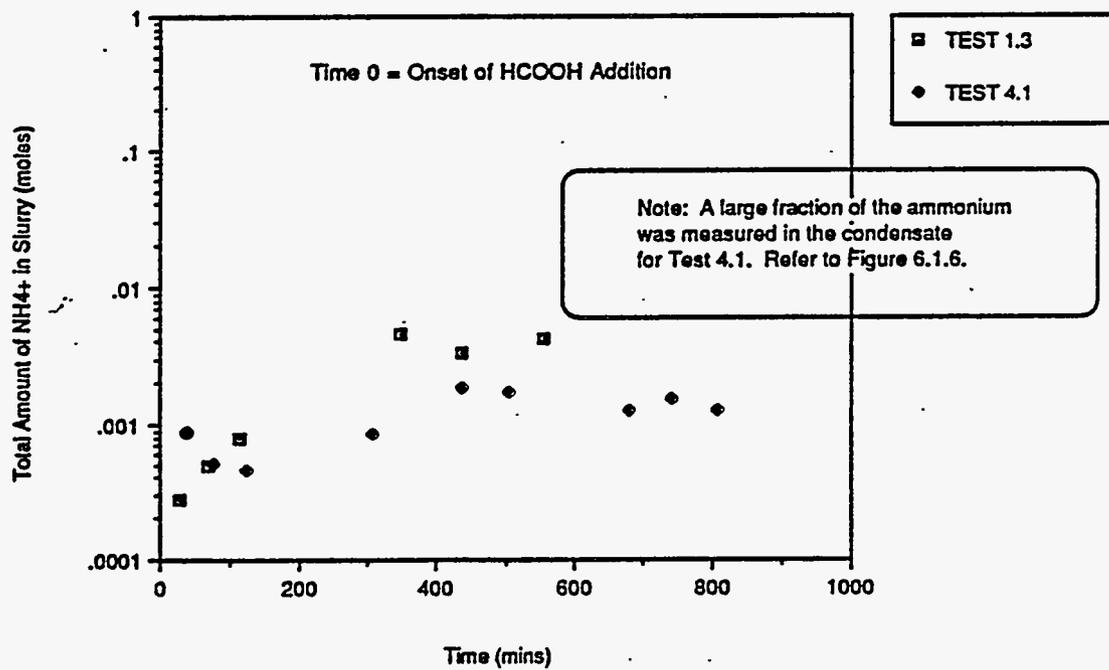


Figure H.4. Total Amount of Ammonium Ion in Slurry as a Function of Process Time for NCAW Slurry Test Set 4: Extended Digestion Period (Includes Tests 1.3 and 4.1)

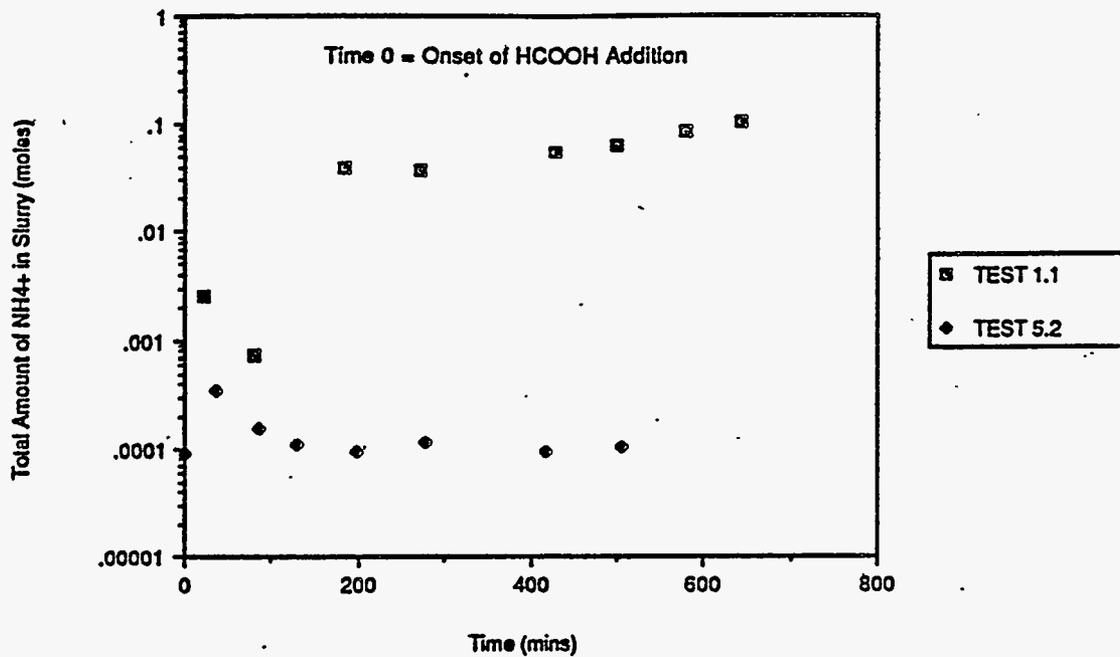


Figure H.5. Total Amount of Ammonium Ion in Slurry as a Function of Process Time for NCAW Slurry Test Set 5: Noble Metal Concentration. (Includes Tests 1.1 and 5.2)

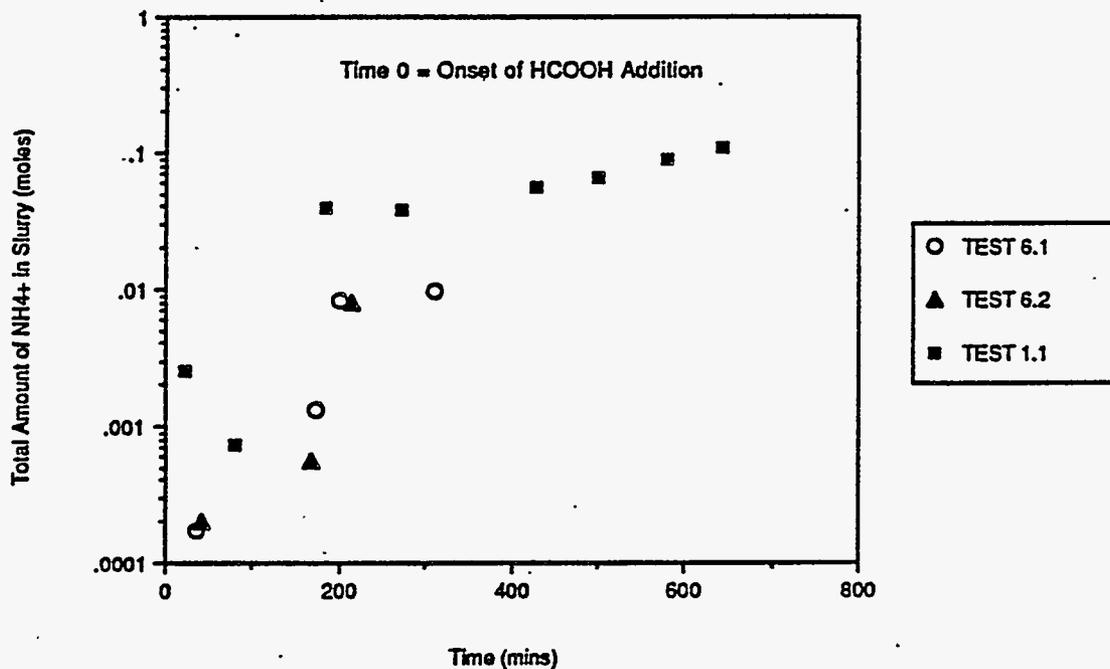


Figure H.6. Total Amount of Ammonium Ion in Slurry as a Function of Process Time for NCAW Slurry Test Set 6: Process Interrupts (Includes Tests 6.1, 6.2, and 1.1)

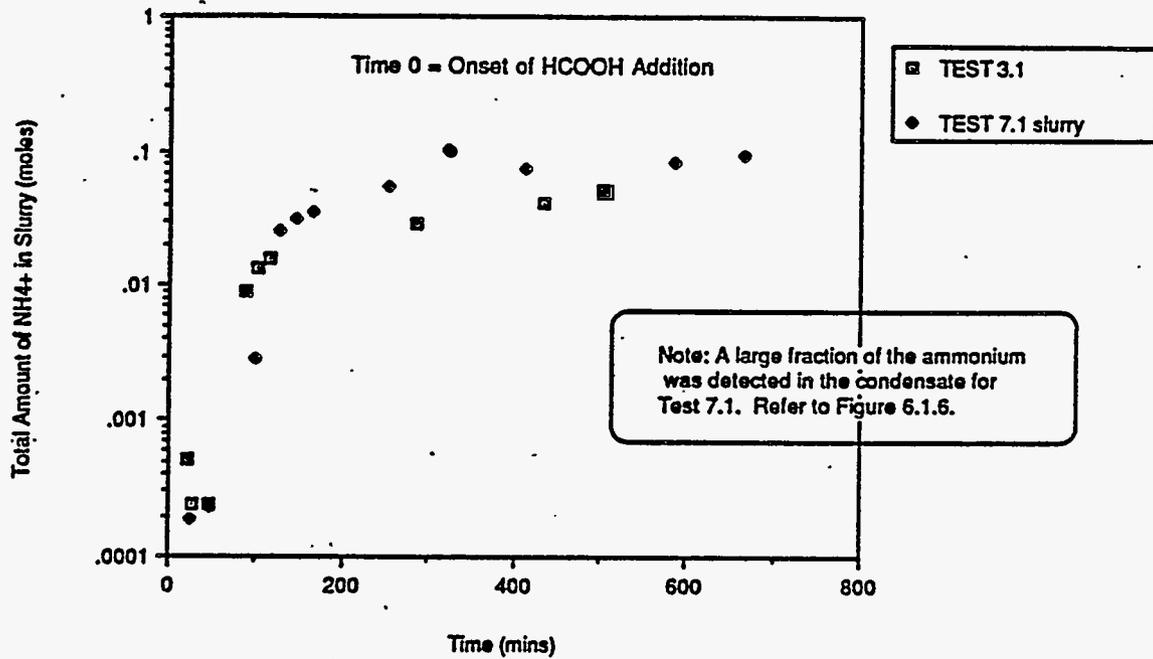


Figure H.7. Total Amount of Ammonium Ion in Slurry as a Function of Process Time for NCAW Slurry Test Set 7: Minimum Nitrite/Maximum Nitrate (Includes Tests 3.1 and 7.1 Slurry)

2

3

4