**Evaluation of HWVP Feed Preparation
Chemistry for an NCAW Simulant—
Fiscal Year 1993: Effect of Noble
Metals Concentration on Offgas
Generation and Ammonia Formation**

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March 1995

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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Summary

The High-Level Waste Vitrification Program is developing technology for the Department of Energy to immobilize high-level and transuranic wastes as glass for permanent disposal. Pacific Northwest Laboratory (PNL) is conducting laboratory-scale melter feed preparation studies using a HWVP simulated waste slurry, Neutralized Current Acid Waste (NCAW). A FY 1993 laboratory-scale study focused on the effects of noble metals (Pd, Rh, and Ru) on feed preparation offgas generation and NH_3 production. The noble metals catalyze H_2 and NH_3 production, which leads to safety concerns. The information gained from this study is intended to be used for technology development in pilot scale testing and design of the Hanford High-Level Waste Vitrification Facility. The work performed during FY 1993 was initiated under the Hanford Waste Vitrification Program (HWVP).

Six laboratory-scale feed preparation tests were performed as part of the FY 1993 testing activities using nonradioactive NCAW simulant. Tests were performed with 10%, 25%, 50% of nominal noble metals content and nominal noble metals content. Also tested were 25% of the nominal Rh and a repeat of 25% nominal noble metals.

The following summarizes the results of the test activities:

Offgas profiles exhibited three reaction stages: I, CO_3^{2-} decomposition, II, NO_2^- destruction, and III, H_2 plus NH_3 formation. Hydrogen is formed during reaction stage III as a product of noble metals catalyzed HCOOH decomposition. The peak H_2 generation rate and total H_2 measured increased with noble metal concentration until a maximum level was reached at 25%-50% nominal noble metals concentration. The maximum derivative of the H_2 generation rate showed an almost linear increase as a function of noble metals concentration.

The observed relationship between noble metals concentration and the H_2 generation rate may be coupled to a higher NO_2^- concentration at the initiation of the H_2 peak in the 10% nominal noble metals test compared to the 25%, 50%, and nominal tests. Higher NO_2^- would be expected to reduce the H_2 generation rate (Smith 1993).

A test performed with only 25% Rh showed significantly different behavior than the 25% nominal noble metals test; therefore, it was concluded that the other noble metals (Pd and Ru) contributed catalytic activity to H_2 production. This conclusion does not agree with the work of King at the University of Georgia (King and Bhattacharyya 1993). A replicate of this test should be performed to verify the results.

Ammonia is also formed during stage III as a product of a reaction between HCOOH and NO_3^- . The amount of NH_3 measured in the slurry following stage III increased as the noble metals concentration increased. Ammonia production is speculated to be related to H_2 production because H_2 is an intermediate reactant in the NH_3 reaction. Therefore, as the total H_2 measured increases as a function of noble metals concentration, NH_3 generation increases as well.

Formation of a black residue in the nominal noble metals concentration test indicated the presence of reduced noble metals. The residue was not observed at lower concentrations, however, the slurry

appeared darker in the 50% test which may indicate the presence of reduced noble metals. King^(a) found that supported rhodium metal catalysts favor NH_3 production. The reduced noble metals, therefore, may have a significant effect on NH_3 production because of the change to the metallic state, or because they are behaving as supported catalysts. Supported catalysts favor NH_3 production, while soluble catalysts favor HCOOH decomposition. Further work is needed to study the effect of the reduced noble metals on NH_3 production.

Carbon dioxide formed during all three reaction stages. In stage I, CO_2 formed primarily from CO_3^{2-} decomposition. The reduction of MnO_2 also contributes to the CO_2 generation during stage I. The amount of CO_2 formed was approximately the same for each test, since the CO_3^{2-} and MnO_2 concentrations in the simulant were the same for all tests. Therefore, the noble metals concentration does not affect CO_3^{2-} decomposition. The onset of the stage I peak was related to pH and the amount of HCOOH added. The peak occurred at a pH of approximately 7, which corresponded to 16-18 g of HCOOH . The maximum CO_2 generation rate during stage I decreased with noble metals concentration to 50% nominal noble metals, then increased with the nominal concentration. Currently, no explanation is available for this trend.

During stage II, CO_2 was generated from reactions of HNO_2 with NaCOOH , which also produced NO and N_2O . The peak CO_2 generation rate increased with increasing noble metals concentration. The 10% nominal noble metals and 25% nominal Rh test lacked a well defined peak. The amount of CO_2 formed during this stage did not vary significantly, although a slight increase with noble metals concentration was noted.

During stage III, CO_2 formed from HCOOH decomposition and also as a product of the NH_3 formation reaction. The peak generation rate did not vary significantly during this stage. However, the amount of CO_2 that formed increased linearly as a function of noble metals concentration.

During stage II, NO_x formed by disproportionation and destruction of HNO_2 . The peak NO_x generation rate increased slightly with increased noble metals concentration. The NO_2^- chemistry is complex, with at least three known potential reaction pathways dependent on noble metal catalytic activity and pH. Changes in the amount of NO_x measured as a function of noble metals concentration were not significant enough to derive correlations. Additional tests may help to establish a better correlation.

During stage II, NO_2^- reduction by HCOOH produced N_2O . The N_2O peak generation rate and the amount of N_2O measured increased as a function of noble metals concentration. The reaction, therefore, must be catalyzed by noble metals. Carbon dioxide is also a product of this reaction and behaves in a similar manner (ie., the peak CO_2 generation rate and total CO_2 measured increased with noble metals concentration). It should be noted however, that CO_2 is produced by other reactions during stage II.

Mass balances performed for C showed that either too much or too little C was accounted for. The error is due mainly to analytical uncertainty. Future test should use a different technique such as a total carbon measurement the mass balance. This technique was available only in hot cells, but cold laboratory equipment for this measurement recently became available. The N mass balance also contained some

^(a) King, R. B., and N. K. Bhattacharyya. 1994. *Hanford Waste Vittrification Plant Hydrogen Generation Study: Formation of Ammonia From Nitrate and Nitrite in Hydrogen Generating Systems*. PVTD C94-03.02Y. University of Georgia, Athens, Georgia.

error, but it was better than the C mass balance in that the numbers were within 13% of full accountability, except for one measurement that was easily explainable by equipment malfunction.

Acronyms

ATC	Automatic Temperature Compensation
DIW	Deionized Water
DOE	Department of Energy
FY	Fiscal Year
GC	Gas Chromatograph
gWO/L	Gram Waste Oxide per Liter
HWVP	Hanford Waste Vitrification Plant
IC	Ion Chromatography
L	Liter
MFC	Mass Flow Controller
n/a	Not Available
NCAW	Neutralized Current Acid Waste
NM	Noble Metals
PHTD	PNL HWVP Technology Development
PNL	Pacific Northwest Laboratory
PUREX	Plutonium/Uranium Extraction Process
PVTD	PNL Vitrification Technology Development
sccpm	Standard Cubic Centimeter per Minute
sLpm	Standard Liter per Minute
SRTC	Savannah River Technology Center
TC	Thermocouple
WHC	Westinghouse Hanford Company
Wt %	Weight Percent

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1.0 Introduction

Vitrification technology is being developed for the Hanford High-Level Waste Vitrification Program sponsored by the U.S. Department of Energy (DOE) to immobilize high-level and transuranic wastes as glass for permanent disposal. Pacific Northwest Laboratory (PNL)^(a) is supporting the High-Level Waste Vitrification Program by conducting laboratory-scale studies of the vitrification feed preparation chemistry. These studies were performed on simulated (nonradioactive) pretreated neutralized current acid waste (NCAW). This high-level waste originating from the plutonium/uranium extraction (PUREX) plant has been partially denitrated with sugar and neutralized with NaOH; it is stored in double-shell tanks (Peterson, Scheele, and Tingey 1989). The nonradioactive simulated waste (simulant) used for the present study included the same components found in the waste, with the exception of surrogates used for selected radioactive, toxic, or costly compounds. The simulant preparation reproduced the chemical processing characteristics of the actual waste. The noble metals (Pd, Ru, and Rh) are present in the waste as uranium fission products and are included in the simulant. Noble metals catalyze the decomposition of HCOOH into H₂ and CO₂, as well as the production of NH₃ from HCOOH and NO₃⁻. Hydrogen generation can lead to safety issues because of the possibility of producing flammable gas mixtures. Ammonia generation can also result in safety issues through the production of NH₄NO₃, which is an unstable, strong oxidizer, particularly in the presence of organic compounds.

The potential for generating H₂ and NH₃ during treatment of HLW with HCOOH was identified by Wiemers(1988). Work performed at PNL during FY 1990^(b), FY 1991^(c), FY 1992^(d), and FY 1993 (Smith 1993) further documented the generation of H₂ and NH₃ in NCAW slurries treated with HCOOH. Studies at the University of Georgia under contract with Savannah River Technology Center (SRTC) (King et al. 1993) (King, Bhattacharyya 1994) and PNL verified the catalytic role of noble metals in generating H₂ and NH₃. Laboratory-scale and pilot-scale studies at SRTC have documented the H₂ and NH₃ generation phenomena (Ritter, Zamecnik, and Hsu 1992).

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- (a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.
 - (b) Wiemers, K. D. 1990. *The Effect of HWVP Feed Nitrate and Carbonate Content on Glass Redox Adjustment*. Technical Report HWVP-90-1.2.2.03.03A. Pacific Northwest Laboratory, Richland, Washington.
 - (c) Wiemers, K. D., M. H. Langowski, M. R. Powell, and D. E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant-Fiscal Year 1991: Evaluation of Off-gas Generation, Reductant Requirements and Thermal Stability*. Technical Report PHTD-C92-03.02A. Pacific Northwest Laboratory, Richland, Washington.
 - (d) Smith, H. D., K. D. Wiemers, M. H. Langowski, M. R. Powell, and D. E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant-Fiscal Year 1992: Evaluation of Offgas Generation and Ammonia Formation*. Technical Report PHTD-C93-03.02. Pacific Northwest Laboratory, Richland, Washington.

An objective of the FY 1993 laboratory testing was to determine the effect of noble metals concentration in the waste on H_2 and NH_3 production during the batch preparation of melter feed. This information would serve several purposes: to determine if noble metal additions could be limited in pilot scale batches, to provide information for design of a H_2 mitigation system, and to predict the impact of waste compositions with varying noble metals content on the process requirements.

In FY 1993, six tests were performed with different noble metal content: 10% of nominal, 25% of nominal, 50% of nominal, nominal concentration, 25% of nominal Rh, and a repeat of 25% of nominal. During these tests, offgas measurements were taken for H_2 , CO_2 , N_2O , and NO_x during formic acid addition and digestion, and analytical measurements were taken for NH_4^+ , $COOH^-$, NO_3^- , and NO_2^- in the slurry and condensate before formic acid addition, after formic acid addition but before digestion, and after digestion.

Offgas profiles were compiled based on the offgas measurements. The offgas profiles occur in three stages: CO_3^{2-} decomposition, NO_2^- destruction, and H_2 plus NH_3 formation (Smith 1993). Changes in the profiles are explained in terms of the concentration of catalytically active noble metals (Pd, Rh, and Ru). Emphasis is placed on the assessment of H_2 generation rate, the cumulative amount of NH_3 produced, and the derivative of the H_2 generation rate as it relates to plant operation response time requirements. Generation of CO_2 , NO_x , and N_2O are compared between tests. Mass balances for N and C were calculated. An extensive appendix summarizes laboratory process data for each run, covering the offgas and analytical chemistry data as well as test observations.

This work was conducted in accordance with the planning document, *Addendum to Test Plan PHTD C92-03.02B; Part A: Effect of Noble Metal Concentration in an NCAW Simulant on H_2 Generation Rate and NH_3 Production During Treatment of the Simulant with Formic Acid.*^(a) The addendum was based on the FY 1993 Project Work Plan for Applied Technology Development in Support of the HWVP Project,^(b) the need to establish correlations between noble metals and H_2 and NH_3 production, and the new information needs communicated to PNL by Westinghouse Hanford Company (WHC). This draft report satisfies contractor milestone C94-03.02F as described in the *FY 1994 Pacific Northwest Laboratory Vittrification Technology Development (PVTD) Project Work Plan.*^(c) The work was performed under Impact Level II quality assurance requirements.

-
- (a) Smith, H. D., and K. D. Wiemers. 1993. *Addendum to Test Plan PHTD C92-03.02B. Evaluation of Pretreated Neutralized Current Acid Waste (NCAW): Reductant Requirements, Offgas Productivity and Feed Preparation Reactions. Part A: Effect of Noble Metal Concentration in an NCAW Simulant on H_2 Generation Rate and NH_3 Production During Treatment of the Simulant with Formic Acid.* Test Plan PHTD-C93-03.02P, Pacific Northwest Laboratory, Richland, Washington.
 - (b) *FY 1993 Pacific Northwest Laboratory Hanford Waste Vittrification Plant Technology Development (PHTD) Project Work Plan.* PHTD-93-002 Rev 0. Pacific Northwest Laboratory, Richland, Washington.
 - (c) *FY 1994 Pacific Northwest Laboratory Vittrification Technology Development (PVTD) Project Work Plan: Volume I - HLW Vittrification.* PVTD-94-001, Vol I, Rev. 0.

2.0 Conclusions and Recommendations

These tests performed at PNL during FY 1993 focused on the behavior of the feed preparation process chemistry of an NCAW simulant as noble metals concentration decreases from the nominal concentration. Safety concerns directed primary attention to the behavior of H_2 and NH_3 . The conclusions were made from a limited amount of data, which was not replicated. The data trends need confirmation at additional noble metals concentrations and performing replication of critical tests, such as the 10% nominal noble metals test. Experience from just one replicate test indicates significant variability due to the sensitivity of the variables to changes in test parameters^(a).

2.1 H_2 and NH_3

Offgas profiles exhibited three reaction stages: I, CO_3^{2-} decomposition, II, NO_2^- destruction, and III, H_2 plus NH_3 formation. Hydrogen is formed during reaction stage III as a product of noble metals catalyzed $HCOOH$ decomposition. The peak H_2 generation rate and total H_2 measured increased with noble metals concentration to a maximum level of 25%-50% nominal noble metals concentration. The maximum derivative of the H_2 generation rate showed an almost linear increase as a function of noble metals concentration.

The observed relationship between noble metals concentration and the H_2 generation rate may be coupled to a higher NO_2^- concentration at the initiation of the H_2 peak in the 10% nominal noble metals test than in the 25%, 50%, and nominal tests. Higher NO_2^- would be expected to decrease the H_2 generation rate (Smith 1993).

A test with 25% Rh showed significantly different behavior than the 25% nominal noble metals test; therefore, it was concluded that the other noble metals (Pd and Ru) contributed catalytic activity to H_2 production. This conclusion does not agree with the work of King at the University of Georgia (King and Bhattacharyya 1993). A replicate of this test should be performed to verify the results.

Ammonia is also formed during stage III as a product of a reaction between $HCOOH$ and NO_3^- . The amount of NH_3 measured in the slurry following stage III increased with the noble metals concentration. Ammonia production is speculated to be related to H_2 production because H_2 participates in an intermediate reaction in the NH_3 reaction sequence. Therefore, as the total H_2 measured increases as a function of noble metals concentration, NH_3 generation increases as well.

At the nominal noble metals concentration, a black residue indicated the presence of reduced noble metals. The residue was not seen at lower concentrations; however, the slurry appeared darker in

(a) Langowski, M.H., E.V. Morrey, J.M. Tingey, and M.R. Beckett. 1993. *Offgas Characterization from the Radioactive NCAW Core Samples (102-AZ-C1) and Simulant During HWVP Feed Preparation Testing*. PHTD-C93-03.08A, Pacific Northwest Laboratory, Richland, Washington.

the 50% test which may indicate the presence of reduced noble metals. King^(a) found that supported rhodium metal catalysts favor NH_3 production. The reduced noble metals, therefore, may have a significant effect on NH_3 production because of the change to the metallic state, or because they are behaving as supported catalysts. Supported catalysts favor NH_3 production while soluble catalysts favor HCOOH decomposition. The effect of the reduced noble metals on NH_3 production further work.

2.2 CO_2 , NO_x , and N_2O

Carbon dioxide formed during all three reaction stages. In stage I, CO_2 formed primarily from CO_3^{-2} decomposition, and from MnO_2 reduction. The amount of CO_2 formed was approximately the same for each test, since the CO_3^{-2} and MnO_2 concentrations of the simulant were the same for all tests. Therefore, it was concluded that the noble metals concentration does not affect CO_3^{-2} decomposition. The onset of the stage I peak was found to be related to pH and the amount of HCOOH added. The peak occurred at approximately a pH 7, which corresponded to 16-18 g of HCOOH . The maximum CO_2 generation rate during stage I decreased with noble metals concentration to 50% nominal noble metals, then increased with the nominal concentration. This trend remains unexplained.

During stage II, reactions of HNO_2 with NaCOOH generated CO_2 , NO , and N_2O . The peak CO_2 generation rate during this stage increased with noble metals concentration. The 10% nominal noble metals and 25% nominal Rh tests lacked a well defined peak. The amount of CO_2 formed during this stage did not vary significantly, though a slight increase with noble metals concentration was noted.

During stage III, CO_2 formed from HCOOH decomposition and during the NH_3 formation reaction. The peak generation rate did not vary significantly during this stage; however, formation of CO_2 increased linearly as a function of noble metals concentration.

During stage II, NO_x formed by disproportionation and destruction of HNO_2 . The peak NO_x gas generation rate increased slightly with noble metals concentration. The NO_2^- chemistry is complex with at least three known potential reaction pathways dependent on noble metals catalytic activity and pH. Changes in the amount of NO_x measured as a function of noble metals concentration were not significant enough to derive correlations; additional tests may help to establish a better correlation.

Nitrous oxide also formed during stage II as a result of NO_2^- reduction by HCOOH . The N_2O peak generation rate and the amount of N_2O measured increased as a function of noble metals concentration. This reaction is therefore sensitive to the amount of noble metals present. This also contributes to the stage II behavior of CO_2 , which is another product of the reaction producing N_2O . The peak CO_2 generation rate and total CO_2 measured increased with noble metals concentration. It should be noted however, that CO_2 is produced by other reactions during stage II.

Mass balances performed for C showed that either too much or too little C was accounted for. The

(a) King, R. B., and N. K. Bhattacharyya. 1994. *Hanford Waste Vittrification Plant Hydrogen Generation Study: Formation of Ammonia From Nitrate and Nitrite in Hydrogen Generating Systems*. PVTD C94-03.02Y. University of Georgia, Athens, Georgia.

error is due mainly to analytical uncertainty. For the future, a different technique, such as a total carbon measurement, should be used for the mass balance. This technique was available only in hot cells, but cold laboratory equipment for this measurement recently became available. The N mass balance also contained some error, but the numbers were within 13% of full accountability, except for one measurement, which was easily explainable by equipment malfunction.

3.0 Approach

This section discusses the approach to performing the laboratory-scale tests of the vitrification feed chemistry. The discussion includes descriptions of the feed simulant, preparation method, test methods, and equipment.

3.1 Description of the Simulant

The reference NCAW target composition was given by Smith (1991)^(a) and is shown in Table 3.1. The simulant was prepared on a laboratory-scale with large-scale preparation procedures^{(b)(c)} and the same batch materials.

The stock simulant was prepared by first coprecipitating a hydroxide slurry containing the major waste oxide elements (Fe, Ni, Zr, Al, and Mn). Added to the hydroxide slurry was another slurry prepared by precipitating cationic species from soluble nitrates with insoluble components (oxides, fluorides). Excess nitrate and sodium were removed by washing. The third slurry added solubles/slightly solubles containing a variety of salts (halides, hydroxides, nitrates, nitrites, sulphates, borates, phosphates, oxides, and oxalate). The washed feed was analyzed for sodium and nitrate, which had been added in various amounts with other elements, and appropriate additions were made to bring these components to nominal levels.

A noble metals slurry was prepared for the purpose of adjusting the noble metals concentration in the simulant. The slurry was prepared with a HNO₃ solution of the three noble metals (Pd, Rh, Ru) nitrates at known concentrations and in the desired proportions. This nitrate solution was titrated with 10 M NaOH to pH 7.5. A precipitate began to form before pH 6 was attained. Once the NaOH addition was completed, the solution was boiled for 10 to 15 min to complete precipitation of the Ru. The slurry was then washed with deionized water to remove nitrate and sodium. The wash water was allowed to separate as a supernate over 12 to 24 h and was decanted. Several wash/decant cycles were completed. Noble metals concentrations on the order of 20 to 30 ppm in the decanted supernates, indicated that the hydroxide slurry retained 99.7% of the noble metals. The nominal noble metals concentration in the NCAW is given in Table 3.1. Table 3.2 shows the noble metals concentration for each of the six FY 1993 tests.

-
- (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. #915051.
 - (b) Procedure for the Preparation of Simulated HWVP NCAW Feed, TP92-SIPT-100, October 30, 1992.
 - (c) Test Instructions for Slurry-Integrated Performance Testing-Weigh Out of Chemicals and Preparation of NCAW Simulant, TI92-SIPT-100, Rev. 0, October 15, 1992.

Table 3.1. Reference and Simulant Target Compositions

FY 1991 Pretreated Reference NCAW Feed Composition ^(a)				NCAW Simulant Target Composition ^(b)	
Oxide	Feed Oxides (wt %)	Moles Element/ L Feed (125 gWO/L)	Substitute/ Delete	Feed Oxides (wt %)	Moles Element/ L Feed (125 gWO/L)
Ag ₂ O	1.20E-01	1.29E-03	—	1.22E-01	1.32E-03
Al ₂ O ₃	9.04E+00	2.22E-01	—	9.25E+00	2.27E-01
Am ₂ O ₃	7.22E-02	5.38E-07	Del ^(c)	—	—
As ₂ O ₃	4.25E-05	3.41E-04	Del ^(d)	—	—
B ₂ O ₃	5.75E-03	2.06E-04	—	5.86E-03	2.10E-04
BaO	1.76E-01	1.43E-03	—	1.79E-01	1.46E-03
BeO	1.01E-01	5.04E-03	Sub Mg ^(d)	—	—
Br	—	—	N/A ^(e)	—	—
CaO	7.91E-01	1.76E-02	—	8.06E-01	1.80E-02
CdO	3.02E+00	2.94E-02	—	3.08E+00	3.00E-02
CeO ₂	6.05E-01	4.39E-03	—	6.56E-01	4.77E-03
Co ₂ O ₃	—	—	To be determined ^(e)	—	—
Cr ₂ O ₃	2.62E-01	4.30E-03	—	2.67E-01	4.39E-03
Cs ₂ O	6.05E-01	5.32E-03	—	6.12E-01	5.43E-03
CuO	2.45E-01	3.85E-03	—	2.50E-01	3.93E-03
Dy ₂ O ₃	1.04E-04	6.98E-07	Sub Nd ^(f)	—	—
Er ₂ O ₃	3.08E-06	2.02E-08	Sub Nd ^(f)	—	—
Eu ₂ O ₃	2.02E-02	1.42E-04	Sub Nd ^(f)	—	—
F	9.70E-02	6.38E-03	—	9.90E-02	6.52E-03
Fe ₂ O ₃	2.82E+01	4.42E-01	—	2.88E+01	4.51E-01
Gd ₂ O ₃	3.70E-03	2.57E-05	Sub Nd ^(f)	—	—
GeO ₂	1.57E-04	1.82E-06	—	1.56E-04	1.86E-06
HgO	—	—	N/A ^(e)	—	—
Ho ₂ O ₃	5.32E-06	3.52E-08	Sub Nd ^(f)	—	—
I	4.50E-06	4.36E-08	— ^(g)	4.60E-06	4.53E-08
In ₂ O ₃	—	—	N/A ^(e)	—	—
K ₂ O	1.96E-01	5.21E-03	—	2.00E-01	5.32E-03
La ₂ O ₃	6.53E-01	5.01E-03	—	6.67E-01	5.12E-03
Li ₂ O	1.84E-04	5.92E-06	—	7.23E-05	6.05E-06
MgO	2.02E-01	6.25E-03	—	3.72E-01	1.15E-02
MnO ₂	2.14E+00	3.08E-02	—	2.19E+00	3.15E-02
MoO ₃	5.59E-01	4.85E-03	—	5.70E-01	4.95E-03
Na ₂ O	2.14E+01	8.64E-01	—	2.19E+01	8.82E-01
Nb ₂ O ₃	1.01E-02	1.08E-04	—	1.03E-02	1.10E-04
Nd ₂ O ₃	5.78E-01	4.29E-03	—	3.56E+00	2.64E-02
NiO	2.30E+00	3.85E-02	—	2.35E+00	3.93E-02
NpO ₂	—	—	N/A ^(e)	—	—
P ₂ O ₅	8.72E-01	1.53E-02	—	8.87E-01	1.56E-02
PbO ₂	7.00E-01	3.66E-03	—	7.15E-01	3.74E-03
PdO	1.20E-01	1.23E-03	—	1.23E-01	1.26E-03
Pm ₂ O ₃	4.60E-02	3.32E-04	Sub Nd ^(f)	—	—
Pr ₂ O ₃	1.53E-01	1.16E-03	—	1.56E-01	1.18E-03
PuO ₂	6.00E-02	2.77E-04	Sub Ce ^(c)	—	—
Rb ₂ O ₃	5.75E-02	6.56E-04	—	5.87E-02	6.70E-04
Rh ₂ O ₃	1.04E-01	1.02E-03	—	1.06E-01	1.04E-03
Ru ₂ O ₃	3.80E-01	3.77E-03	—	3.87E-01	3.85E-03
SO ₃	6.55E-01	1.02E-02	—	6.69E-01	1.04E-02
Sb ₂ O ₃	5.88E-03	5.00E-05	—	5.95E-03	5.11E-05
SeO ₂	1.59E-02	1.78E-04	—	1.61E-02	1.82E-04

Table 3.1. (contd)

FY 1991 Pretreated Reference NCAW Feed Composition ^(a)				NCAW Simulant Target Composition ^(b)	
Oxide	Feed Oxides (wt%)	Moles Element/L Feed (125 gWO/L)	Substitute/Delete	Feed Oxides (wt%)	Moles Element/L Feed (125 gWO/L)
SiO ₂	4.03E+00	8.38E-02	--	4.11E+00	8.56E-02
Sm ₂ O ₃	7.50E-02	5.42E-04	— ^(c)	7.72E-02	5.54E-04
SnO	1.08E-02	9.78E-05	--	1.08E-02	9.99E-05
SrO	1.19E-01	1.43E-03	--	1.21E-01	1.46E-03
Ta ₂ O ₅	3.33E-03	1.88E-05	--	3.39E-03	1.92E-05
Tb ₂ O ₃	2.26E-04	1.54E-06	Sub Nd ^(f)	--	--
Tc ₂ O ₇	1.52E-01	1.23E-03	--	--	--
TeO ₂	1.07E-01	7.77E-04	--	1.01E-01	7.94E-04
ThO ₂	--	--	Sub Zr ^(c)	--	--
TiO ₂	6.52E-01	1.02E-02	--	6.66E-01	1.04E-02
Tm ₂ O ₃	1.68E-10	1.09E-12	Sub Nd ^(f)	--	--
U ₃ O ₈	4.74E+00	2.11E-02	Sub Nd ^(c)	--	--
Y ₂ O ₃	7.99E-02	8.85E-04	--	8.17E-02	9.04E-04
ZnO	3.34E-01	5.13E-03	— ^(d)	3.41E-01	5.24E-03
ZrO ₂	1.51E+01	1.53E-01	— ^(f)	1.54E+01	1.56E-01
Sum	1.00E+02	2.02E+00	--	1.00E+02	2.06E+00

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

(a) NCAW target composition supplied by WHC for FY 91 testing.

(b) Adjusted target composition based on (a).

(c) Radioactive.

(d) Toxic.

(e) None in reference feed composition.

(f) Expensive.

(g) Addition of 0.25 g I/L of feed is necessary to meet gas chromatograph's detection limit for the analysis of volatilized iodine.

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

Table 3.2. Noble Metals Concentrations for FY 1993 Tests

Test Identification	Noble Metals Concentration
T93-NM-1	10% of Nominal Concentration
T93-NM-2	25% of Nominal Concentration
T93-NM-3	Nominal Concentration
T93-NM-4	50% of Nominal Concentration
T93-NM-5	25% of Nominal Rh Concentration
T93-NM-6	25% of Nominal Concentration (Repeat of T93-NM-2 test)

3.2 Equipment and Test Methods

Equipment and test methods used during FY 1993 were essentially identical to those used during FY 1991^(a) and FY 1992.^(b) Figures 3.1 and 3.2 are schematics of the instrumented reaction vessel and the offgas measurement system, respectively.

The instrumented reaction vessel shown in Figure 3.1 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 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, with the addition rate controlled by a peristaltic pump. The sweep gas, Ar with a He tracer, carried offgases from the reaction vessel plenum, through the condensers, to the offgas measuring system.

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- (a) Wiemers, K. D., M. H. Langowski, M. R. Powell, and D. E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant-Fiscal Year 1991: Evaluation of Off-gas Generation, Reductant Requirements and Thermal Stability*. Technical Report PHTD-C92-03.02A. Pacific Northwest Laboratory, Richland, Washington.
- (b) Smith, H. D., K.D. Wiemers, M. H. Langowski, M. R. Powell, and D. E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant -- Fiscal Year 1992: Evaluation of Offgas Generation and Ammonia Formation*. Technical Report PHTD-C93-03.02B. Pacific Northwest Laboratory, Richland, Washington.

Figure 3.1. Schematic of the Laboratory-Scale Reaction Vessel for FY 1993 Hanford Waste Vitrification Plant Neutralized Current Acid Waste Simulant Feed Preparation Process Tests

Figure 3.2. Schematic of the Laboratory-Scale Offgas Equipment Configuration for FY 1993 Hanford Waste Vitrification Plant Neutralized Current Acid Waste Simulant Feed Preparation Process Tests

Figure 3.2 includes a schematic of the offgas measuring equipment configuration. Because of the dynamic nature of the feed process chemistry and resultant gas generation, real-time monitoring was used to characterize the generation rates of the major gaseous reaction products. The emission rate behaviors of H_2 , CO_2 , and N_2O were monitored by a gas chromatograph (GC). A chemiluminescent NO/NO_x analyzer measured NO_x . The nominal sampling rates were approximately 80 s and 60 s for the GC and the NO_x analyzer, respectively.

Typical tests steps are described in the following sections. Table 3.3 provides a summary table giving specific information for each test.

3.2.1 Preparations for HCOOH Addition

The following steps were taken to prepare for HCOOH addition:

1. A given weight of slurry simulant with known gram oxide waste loading and specific gravity was placed into the cleaned reaction vessel.
2. Noble metals slurry, shim chemicals ($NaNO_3$, $NaNO_2$, and Na_2CO_3), and antifoam were added.
3. The reaction vessel lid, which had been modified for the instrumentation, agitation, sampling, and offgas collection, was clamped in place.
4. The slurry was heated to boiling, with vigorous agitation, for 10 min to 1 h and cooled to 95°C. Air was used as the sweep gas during this stage.
5. Slurry and condensate were sampled.

3.2.2 Formic Acid Addition

The following steps were taken to add formic acid:

1. The sweep gas (99.99% Ar) flow rate was established.
2. Formic acid was added at a predetermined rate until the addition was complete. The amount of formic acid added in excess of the amount needed to generate significant H_2 . The amount was determined based on previous test experience.
3. The temperature was maintained within $\pm 1^\circ C$ (except during sampling and condensate replacement).
4. The temperature, pH, and offgas generation rate were measured as a function of process time. The pH was measured at process temperature.

5. Slurry and condensate were sampled. Condensate was removed until a target gram waste oxide loading of 150 gWO/L was reached.

3.2.3 Digestion Period (4 h)

The following steps were followed during the digestion period:

1. The slurry temperature was raised to boiling.
2. Temperature, pH, and offgas measurements were continued.
3. Slurry and condensate were sampled. Condensate was periodically replaced with deionized water.

During the tests, condensate and slurry samples were taken. Primary condensate was collected from the first condenser and secondary condensate from the second condenser. Primary condensate volume was always 100 to 1,000 times greater than secondary. The condensate samples were collected over a period of time. Slurry samples, on the other hand, were collected at specific times, generally before and after HCOOH addition and after digestion. Slurry samples destined for chemical analysis were refrigerated. Nitrate, NO_2^- , NH_3 , COOH^- content, and pH at room temperature were measured for the slurry and condensate samples.

A technical data log was maintained during the tests. The primary function of the log was to record observations of slurry color and behavior. The log was also used to record slurry temperature and pH as a backup to the data acquisition system and to record the beginning and ending of the various test stages. Most slurry observations were about the degree of foaming and the actions taken to control the foam. Other observations included the appearance of secondary phases (in the form of films or scums on the slurry surface) or about the slurry color, which appeared to change from an initial chocolate red-brown to a brown or dark gray-brown when the slurry was extensively formed.

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

Table 3.3. Summary Table of Test Variables and Test Conditions for the FY 1994 Noble Metals Testing

Test No.	Initial Slurry Volume (L)	Initial Slurry Density (g/mL)	Initial Slurry Concentration (g WO/L)	Target Final Slurry Concentration (g WO/L)	Carrier Gas
All Tests	1.5	1.12	127	150	Ar/He

Test No.	Target Composition Initial Nitrate in Slurry			Target Composition Initial Nitrite in Slurry			Target Composition Initial Carbonate in Slurry		
	(mol)	(mol/L)	(g/L)	(mol)	(mol/L)	(g/L)	(mol)	(mol/L)	(g/L)
All Tests	0.174	0.116	7.19	0.653	0.435	20.01	0.188	0.125	7.5

Test No.	Noble Metals	Noble Metals Target Concentration			Formic Acid Addition (Formic acid was added as a 90.6 wt% solution)			HCOOH Addition Rate
	Percent of Nominal	Pd (mol/L)	Rh (mol/L)	Ru (mol/L)	HCOOH (g of 90.6 wt% soln)	HCOOH (g)	HCOOH (mol)	Target/Actual (g/min)
T93-NM-1	10%	1.26E-04	1.04E-04	3.85E-04	136.0	123.2	2.677	0.6/0.63
T93-NM-2	25%	3.15E-04	2.60E-04	9.63E-04	135.6	122.9	2.670	0.6/0.63
T93-NM-3	100%	1.26E-03	1.04E-03	3.85E-03	131.9	119.5	2.596	0.6/0.57
T93-NM-4	50%	6.30E-04	5.20E-04	1.93E-03	137.3	124.4	2.703	0.6/0.57
T93-NM-5	25% Rh	0.0	2.60E-04	0.0	139.5	126.4	2746	0.6/0.59
T93-NM-6	25%	3.15E-04	2.60E-04	9.63E-04	140.0	126.8	2.755	0.6/0.69

4.0 Results and Discussion

4.1 Offgas Profiles

The offgas profiles for the six tests performed by PNL in FY 1993 are shown in Figures 4.1 through 4.6. The profiles show gas generation rates versus test time for four gases (H_2 , CO_2 , N_2O , and NO_x). Individual profiles for each gas are given in Appendix A. During test T93-NM-2 (25 % nominal noble metals), an equipment malfunction delayed NO_x gas measurement and resulted in the loss of NO_x data at the beginning of the test. During test T93-NM-6 (repeat test for 25 % nominal noble metals), a malfunction of the GC data collection system resulted in the loss of H_2 and CO_2 data during peak H_2 generation. The gas generation profile was estimated from manually recorded data. In almost all of the profiles, sudden drops occurred in the H_2 and CO_2 gas generation rates which were caused by sampling and condensate replacement. During these operations, the system was opened and thus gas was released. Condensate replacement also caused a simultaneous drop in temperature, which contributed to the drop in H_2 and CO_2 gas generation rates.

The offgas profiles show gas generation rate versus time and can be divided into three reaction stages which occur during the course of $HCOOH$ addition and digestion; these stages have been fully described by Smith (1993). During stage I, carbonate decomposition and MnO_2 reduction result in the generation of CO_2 . Nitrous acid destruction and disproportionation during stage II generate CO_2 , N_2O , and NO_x . During stage III, H_2 , from $HCOOH$ decomposition, and NH_3 , from a net reaction between $HCOOH$ and NO_3^- , are generated. The behavior of each gas will be discussed individually in more detail in the subsequent subsections. Tables 4.1 through 4.4 provide summaries of peak generation rates and total gas measured during each stage for the six tests.

4.2 H_2 Behavior

Figures 4.7 and 4.8 show the H_2 profiles of the six tests. Figure 4.7 compares the 10%, 25%, 50%, and 100% nominal noble metals tests, and Figure 4.8 compares the 25% nominal noble metals test (T93-NM-2 and T93-NM-6) and the 25% nominal Rh test. The peak H_2 generation rate, peak derivative of the H_2 generation rate, and total H_2 measured are compared with respect to noble metals concentration in Figures 4.9 through 4.11.

The noble metals concentration causes only a slight difference in the start times of H_2 generation relative to the start of $HCOOH$ addition (Figure 4.7). All the start times occur between 180 and 200 min, where a small peak corresponds to the end of stage II. This peak may be useful as an indicator of the subsequent major H_2 generation peak. The time of the major H_2 generation peak varies slightly among the 25%, 50%, and nominal tests. The peak for the 10% test lags approximately 60 min behind the others.

Figure 4.1. Offgas Profile for Test T93-NM-1 Containing 10% of the Nominal Noble Metals

Figure 4.2. Offgas Profile for Test T93-NM-2 Containing 25% of the Nominal Noble Metals

Figure 4.4. Offgas Profile for Test T93-NM-3 Containing the Nominal Noble Metal Content

Figure 4.5. Offgas Profile for Test T93-NM-5 Containing 25% of the Nominal Rh

Figure 4.6. Offgas Profile for Test T93-NM-6 Containing 25% Nominal Noble Metals

Table 4.1. Peak Generation Rates for All Gases

Test	Description	H ₂		CO ₂ Stage I		CO ₂ Stage II		CO ₂ Stage III	
		Time (min)	H ₂ Peak (mmole/min)	Time (min)	CO ₂ Peak (mmole/min)	Time (min)	CO ₂ Peak (mmole/min)	Time (min)	CO ₂ Peak (mmole/min)
T93-NM-1	10% NM	318	0.523	21	7.877	155	2.313	318	1.036
T93-NM-2	25% NM	258	1.895	25	7.418	185	3.922	258	2.908
T93-NM-3	100% NM	245	1.757	34	6.803	182	7.527	245	2.893
T93-NM-4	50% NM	262	1.924	30	5.813	194	6.370	259	2.707
T93-NM-5	25% Rh	279	0.812	31	6.493	175	2.073	278	1.722
T93-NM-6	25% NM	253	1.438	31	7.191	181	3.030	246	2.582

Test	Description	N ₂ O		NO _x	
		Time (min)	N ₂ O Peak (mmole/min)	Time (min)	NO _x Peak (mmole/min)
T93-NM-1	10% NM	93	0.166	99	4.431
T93-NM-2	25% NM	186	0.363	166	4.691
T93-NM-3	100% NM	182	1.657	180	6.328
T93-NM-4	50% NM	194	0.840	194	5.126
T93-NM-5	25% Rh	112	0.121	112	3.768
T93-NM-6	25% NM	181	0.152	97	4.500

Table 4.2. Gas Measured During Noble Metals Tests
(Time Interval of 0 to Completion of Test.)

Test	Description	Ending Time (min)	H ₂ Stage I (mmoles)	H ₂ Stage II (mmoles)	H ₂ Stage III (mmoles)	H ₂ Total (mmoles)	CO ₂ Stage I (mmoles)	CO ₂ Stage II (mmoles)	CO ₂ Stage III (mmoles)	CO ₂ Total (mmoles)	NO _x Stage I (mmoles)	NO _x Stage II (mmoles)	NO _x Stage III (mmoles)	NO _x Total (mmoles)	N ₂ O Stage I (mmoles)	N ₂ O Stage II (mmoles)	N ₂ O Stage III (mmoles)	N ₂ O Total (mmoles)
T93-NM-1	10% Nominal	444	0.00	0.32	34.34	34.34	212.65	266.18	84.18	563.00	26.79	472.01	1.02	499.83	0.86	15.03	0.60	16.49
T93-NM-2	25% Nominal	479	0.00	0.38	119.24	119.62	237.34	301.81	246.86	786.01	0.00	341.04	1.98	343.02	1.69	20.40	1.49	23.58
T93-NM-4	50% Nominal	531	0.00	1.00	193.37	194.37	229.86	302.81	413.75	946.41	37.48	420.72	1.22	459.42	1.85	22.81	3.43	28.09
T93-NM-3	100% Nominal	498	0.00	2.56	168.17	170.73	223.44	429.09	533.40	1185.93	28.59	509.58	0.87	539.04	2.48	51.98	3.70	58.17
T93-NM-5	25% Nominal Rh	505	0.00	0.21	46.70	46.91	228.51	246.08	164.48	639.07	38.32	429.61	1.54	469.47	1.33	11.64	1.64	14.61
T93-NM-6	25% Nominal	337	0.00	0.75	56.43	57.17	234.03	271.29	119.14	624.46	46.23	128.86	300.25	475.35	2.16	16.57	0.97	19.70

Table 4.3. Gas Measured During Noble Metals Tests
(Time Interval of 0 to 444 Minutes)

Test	Description	Ending Time (min)	H ₂ Stage I (mmoles)	H ₂ Stage II (mmoles)	H ₂ Stage III (mmoles)	H ₂ Total (mmoles)	CO ₂ Stage I (mmoles)	CO ₂ Stage II (mmoles)	CO ₂ Stage III (mmoles)	CO ₂ Total (mmoles)	NO _x Stage I (mmoles)	NO _x Stage II (mmoles)	NO _x Stage III (mmoles)	NO _x Total (mmoles)	N ₂ O Stage I (mmoles)	N ₂ O Stage II (mmoles)	N ₂ O Stage III (mmoles)	N ₂ O Total (mmoles)
T93-NM-1	10% Nominal	444	0.00	0.32	34.01	34.34	212.65	266.18	84.18	563.00	26.79	472.01	1.02	499.83	0.86	15.03	0.60	16.49
T93-NM-2	25% Nominal	444	0.00	0.38	104.38	104.76	237.34	301.81	217.68	756.83	0.00	341.04	1.78	342.82	1.69	20.40	1.46	23.55
T93-NM-4	50% Nominal	444	0.00	1.00	172.79	173.79	229.86	302.81	361.86	894.53	37.48	420.72	0.92	459.12	1.85	22.81	2.46	27.12
T93-NM-3	100% Nominal	444	0.00	2.56	159.34	161.90	223.44	429.09	498.07	1150.61	28.59	509.58	0.86	539.03	2.48	51.98	3.61	58.07
T93-NM-5	25% Nominal Rh	444	0.00	0.21	45.04	45.25	228.51	246.08	152.23	626.82	38.32	429.61	1.22	469.47	1.33	11.64	1.22	14.19

Table 4.4. Gas Measured During 25 % Nominal Noble Metals and 25% Nominal Rh Tests
(Time Interval of 0 to 337)

Test	Description	Ending Time (min)	H ₂ Stage I (mmoles)	H ₂ Stage II (mmoles)	H ₂ Stage III (mmoles)	H ₂ Total (mmoles)	CO ₂ Stage I (mmoles)	CO ₂ Stage II (mmoles)	CO ₂ Stage III (mmoles)	CO ₂ Total (mmoles)	NO _x Stage I (mmoles)	NO _x Stage II (mmoles)	NO _x Stage III (mmoles)	NO _x Total (mmoles)	N ₂ O Stage I (mmoles)	N ₂ O Stage II (mmoles)	N ₂ O Stage III (mmoles)	N ₂ O Total (mmoles)
T93-NM-2	25% Nominal	337	0.00	0.38	78.35	78.73	237.34	301.81	144.01	683.16	0.00	341.04	1.38	342.42	1.69	20.40	1.45	23.54
T93-NM-6	25% Nominal	337	0.00	0.75	56.43	57.17	234.03	271.29	119.14	624.46	46.23	128.86	300.25	475.35	2.16	16.57	0.97	19.70
T93-NM-5	25% Nominal Rh	337	0.00	0.21	39.34	39.55	228.51	246.08	104.26	578.85	38.32	429.61	0.71	468.64	1.33	11.64	0.68	13.65

Figure 4.7. The H_2 Offgas Profiles for 10%, 25%, 50%, and 100% Nominal Noble Metals

Figure 4.8. The H_2 Offgas Profiles for 25% Nominal Noble Metals and 25% Nominal Rh

Figure 4.9. Peak H₂ Generation Rate as a Function of Noble Metals Content

Based on the six tests, the peak H₂ generation rate increases with increasing noble metals concentration until a maximum rate is reached near 25% nominal noble metals concentration (Figure 4.9). The data are normalized with respect to the digestion slurry volume, which varied from 1.1 to 1.3 L among the tests. Repeat tests were not performed, and therefore scatter in the data was not evaluated. Test T93-NM-6 was intended as a repeat of the 25% nominal noble metals test; however, a malfunction occurred in the GC data collection system during H₂ peaking and the results from this test contain a great deal of uncertainty because the true peak may not have been found. During the malfunction, the data were recorded manually approximately every 10 min. The data from Test T93-NM-6 are shown for completeness.

The maximum derivative of the H₂ generation rate peak increases with increasing noble metals concentration (Figure 4.10). The existence of a linear trend is difficult to determine because of the scatter in the data at 25% nominal noble metals concentration. The scatter may result from the sensitivity of the derivative to test parameters. The derivative signifies the rate of increase in the H₂ generation rate; these data are important for determining minimum response time needed to detect and mitigate H₂ gas in the batch HLW vitrification plant process.

The total H₂ measured in each test is shown in Figure 4.11. This value was calculated using the area under the generation rate curve over a time interval that started at 0 min and ended at 444 min.

Figure 4.10. Maximum Derivative of H₂ Generation Rate as a Function of Noble Metals Content

Figure 4.11. Hydrogen Measured During the Time Interval 0 to 444 Minutes Except for Test T93-NM-6 (repeat of 25% nominal noble metals), Which Ended at 337 Minutes

For test T93-NM-6 (repeat of 25% nominal noble metals), the ending time was 337 min. The ending time was selected based on the shortest run time among the first four tests. Three of the tests ran longer than 444 min and would have resulted in inflated H_2 values if the area had been calculated over the entire test. The data were also normalized with respect to slurry volume. Figure 4.11 shows that the amount of H_2 produced increases with increasing noble metals concentration and, like the peak generation rate, reaches a saturation level. A possible explanation of this behavior may be that at low noble metals concentrations, $HCOOH$ decomposition is limited by the amount of catalyst (noble metals) present. As the amount of catalyst increases, the reaction reaches a point where it becomes reaction rate limited. Increasing the catalyst at this point will no longer increase the reaction rate. The amount of $HCOOH$ was in excess and therefore not a limiting factor. Another contributing factor was the fact that in the nominal test, the noble metals were reduced and formed a black residue. This change of state may have decreased the effectiveness of the catalyst and contributed to the H_2 behavior.

Experiments performed by King et al. (1993, 1994) demonstrated that H_2 increased linearly with respect to Rh concentration. An increase in measured H_2 with respect to noble metals concentration was also noted by PNL researchers performing studies on radioactive NCAW simulant^(a).

During the FY 1993 testing, it was observed that the behavior of the 10% nominal noble metals test was very different than the other tests. The offgas profile shapes were similar in the 25%, 50%, and nominal tests for all the gases measured, while the offgas profile shapes in the 10% test were different. Specifically, the H_2 peak was significantly smaller, broader, and lagged behind the peaks of the other gases. This behavior may have resulted from the decrease in noble metals concentration and a higher NO_2^- concentration (Table 4.5) before H_2 evolution. The catalytic behavior of the noble metals is sensitive to the NO_2^- concentration. At high and low concentrations of NO_2^- , the catalyst is inhibited (Smith 1993). The initial NO_2^- concentrations of slurries were the same for all the tests. However, the NO_2^- consumption in the 10% nominal noble metals test was less than in the other tests. A repeat of the 10% test is necessary because of the emphasis placed on this point in identifying data trends.

In Figure 4.8, H_2 gas profiles using 25% nominal noble metals and 25% nominal Rh are compared. The profile of 25% nominal Rh is very different from the other test containing 25% nominal noble metals. The 25% nominal Rh test has a smaller peak generation rate, broader peak, lags behind the 25% nominal noble metals H_2 peak and produces less H_2 . Based on these results, Pd and Ru appear to modify the H_2 generation behavior. This is different from work performed by King and Bhattacharyya (1994) who performed experiments using individual noble metals as well as mixtures of noble metals in his simulants. King concluded that Rh was responsible for H_2 generation, Pd reduced NO to N_2O , and Ru did not contribute to gas generation. King's experiments were performed using a slurry made of only major components, and he used a static reaction system, while the system used at PNL for the FY 1993 testing was a dynamic system. Also, King used chlorides as the source for noble metals, while nitrates were used

(a) Langowski, M.H., E.V. Morrey, J.M. Tingey, and M.R. Beckett. 1993. *Offgas Characterization from the Radioactive NCAW Core Samples (102-AZ-C1) and Simulant During HWVP Feed Preparation Testing*. PHTD-C93-03.08A, Pacific Northwest Laboratory, Richland, Washington.

Table 4.5. Slurry NO₂⁻ Concentration Measured During Tests

Noble Metals Concentration (% of Nominal)	Initial NO ₂ ⁻ Concentration (g/L)	Post forming NO ₂ ⁻ Concentration (g/L)	Post digestion NO ₂ ⁻ Concentration (g/L)
10%	25.3	10.3	< 0.2
25%	23.2	0.63	< 0.2
50%	23.1	< 0.2	< 0.2
100%	21.1	< 0.2	< 0.2

at PNL. These differences may contribute to the difference in results.

4.3 CO₂ Behavior

Figures 4.12 and 4.13 show the CO₂ profiles of the six tests. Figure 4.12 compares the 10%, 25%, 50%, and nominal noble metals tests, and Figure 4.13 compares the 25% nominal noble metals tests (T93-NM-2 and T93-NM-6) and the 25% nominal Rh test. The peak CO₂ generation rates and the total CO₂ measured for three reaction stages as a function of noble metals concentration are compared in Figures 4.14 and 4.15. The reactions producing CO₂ in the three stages have been proposed and discussed in detail in work performed during FY 1992^(a).

4.3.1 Stage I

During reaction stage I, CO₃⁻² (as carbonic acid) in the slurry decomposes into CO₂ and H₂O.

The reaction causes the initial CO₂ peak in the offgas profile. The time at which the first CO₂ generation rate peak occurs coincidentally increases as noble metals concentration increases. The peak time is not a function of noble metals concentration, but rather a function of how swiftly the pH decreases during HCOOH addition (Figure 4.16), which is related to HCOOH addition rate and buffering capacity. Figure 4.17 shows HCOOH addition as a function of time during the first 50 min. Variability in the HCOOH

(a) Smith, H.D., K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal Year 1992: Evaluation of Off gas Generation and Ammonia Production*. PHTD-C93-03.02, Pacific Northwest Laboratory, Richland, Washington.

Figure 4.12. The CO₂ Offgas Profiles for 10%, 25%, 50%, and 100% Nominal Noble Metals

Figure 4.13. The CO₂ Offgas Profiles for 25% Nominal Noble Metals and 25% Nominal Rh

Figure 4.14. Peak CO₂ Generation Rate as a Function of Noble Metals Content

Figure 4.15. Carbon Dioxide Measured During the Time Interval 0 to 444 Minutes

Figure 4.16. pH Measured During First 50 Minutes

Figure 4.17. Amount of HCOOH Added During First 50 Minutes

Table 4.6. Carbon Dioxide Mass Balance During Stage I

Test	Initial CO ₃ ⁻² (moles)	Initial MnO ₂ (moles)	Calculated CO ₂ produced from CO ₃ ⁻² and MnO ₂ (moles)	Measured CO ₂ during Stage I (moles)	Percent Difference (%)
10% NM	0.183	0.0469	0.230	0.213	7.4
25% NM	0.188	0.0473	0.235	0.237	0.9
50% NM	0.188	0.0475	0.236	0.229	3.0
100% NM	0.188	0.0465	0.235	0.223	5.1
25% NM (Repeat)	0.188	.0475	0.236	0.234	0.8
25% Rh	0.187	0.0475	0.235	0.229	2.6

addition is caused by adjustments made by test operators during the first 50 min to achieve a rate of 0.6 g HCOOH/min. The CO₂ peaks for each test occur approximately at pH 7 and after 16-18 g of HCOOH has been added. The pH of the 10% nominal noble metals falls more rapidly than the other tests and reaches a pH of 7 before the 25%, 50%, and nominal noble metals tests.

The stage I peak heights decrease with noble metals concentration except in the 100% nominal noble metals test. The deviation in peak height may be within experimental error, leading to the conclusion that the peak heights are the same. The amount of CO₂ measured during stage I is approximately the same for all tests, including the 25% nominal Rh test. This is expected since the CO₃⁻² and MnO₂ concentration were the same for all the tests, and reaction 1 is not catalyzed by noble metals. Table 4.6 shows the amount of CO₂ calculated to form from CO₃⁻² and MnO₂ and the amount of CO₂ measured during stage I. The difference between the two values is less than 8% in all cases. The calculated value is the higher value in all but one case. This can be explained by incomplete MnO₂ reduction. Some NO_x is formed during stage I which is attributed to HNO₂ disproportionation instead of HNO₂ destruction, which would produce additional CO₂.

4.3.2 Stage II

Reactions occurring during Stage II are shown in Reactions 2 through 4.

Reaction 2 represents HNO_2 disproportionation, and Reactions 3 and 4 represent HNO_2 destruction. It is HNO_2 destruction which is responsible for CO_2 production during stage II. Sharp peaks in the CO_2 offgas profiles (Figures 4.12 and 4.13) are observed for only four of the tests. The lack of a definite peak in the 10% nominal noble metals test and the 25% nominal Rh test may be related to the low concentration of noble metals in these tests. The behavior of the peak gas generation rate supports this, since the rate increases with increasing noble metals concentration. The total amount of CO_2 measured during stage II does change significantly until the nominal noble metals concentration is reached.

4.3.3 Stage III

During stage III, CO_2 is generated by HCOOH decomposition (Reaction 5) and by reaction of NO_3^- with HCOOH (Reaction 6), which also produces NH_3 .

The CO_2 peak generation rate during stage III follows a trend similar to the peak H_2 generation rate. There is an initial increase in CO_2 production with increasing noble metals concentration until a maximum level is reached (Figures 4.9 and 4.14). The total CO_2 measured follows a different trend (Figures 4.11 and 4.15); the CO_2 measured increases with increasing noble metals concentration. This does not follow the behavior of the total H_2 measured as a function of noble metals concentration because CO_2 is generated by two reactions (Reactions 5 and 6) while H_2 is generated by only the HCOOH decomposition reaction (Reaction 5).

4.4 NO_x Behavior

Figures 4.18 and 4.19 show the NO_x profiles of the six tests. Figure 4.18 compares the 10%, 25%, 50%, and nominal noble metals tests, and Figure 4.19 compares the 25% nominal noble metals test (T93-NM-2 and T93-NM-6) and the 25% nominal Rh test. The peak NO_x generation rates and the total NO_x measured as a function of noble metals concentration are compared in Figures 4.20 and 4.21.

Essentially all the NO_x is generated during stage II and consists of NO gas. Noble metals concentration has a slight effect on the behavior of the NO_x peak generation rate and amount of NO_x generated. Sharp peaks in the NO_x generation rate are only observed in the 50% and 100% nominal noble metals test. A peak is not observed in the initial 25% nominal noble metals test but is observed in the repeat test. The NO_x data in the initial 25% test contain a great deal of uncertainty because an equipment malfunction during the test caused a loss of NO_x data from 0 to 111 min. The repeat test, in this case, has more reliable data. The lack of well defined peak in the 10% nominal noble metals test and the 25% Rh test may be related to noble metals concentration. This behavior follows that of the CO_2 during stage II. The value of the peak NO_x generation rate shows a slight increase with increasing noble metals concentration.

Figure 4.18. The NO_x Offgas Profiles for 10%, 25%, 50%, and 100% Nominal Noble Metals

Figure 4.19. The NO_x Offgas Profiles for 25% Nominal Noble Metals and 25% Nominal Rh

Figure 4.20. Peak NO_x Generation Rate as a Function of Noble Metals Content

Figure 4.21. The NO_x Measured During the Time Interval 0 to 444 Minutes

The total amount of NO_x gas measured initially decreases with noble metals concentration and then increases. This observation is based on the nominal noble metals test. Since this test was not repeated, it is difficult to determine whether this is a true trend. It is interesting to note that the amount of NO_x measured during the 25 % Rh test agrees very well with the 25 % nominal noble metals test despite the fact that the peak generation rates and the profile shapes do not agree well.

A small peak was noted on all the NO_x profiles. The peak occurred within the initial rise of NO_x generation rate and corresponded well to the last CO_2 peak that occurred during stage I. No explanation for this feature is available at this time.

4.5 N_2O Behavior

Figures 4.22 and 4.23 show the N_2O profiles of the six tests. Figure 4.22 compares the 10 %, 25 %, 50 %, and nominal noble metals tests, and Figure 4.23 compares the 25 % nominal noble metals test (T93-NM-2 and T93-NM-6) and the 25 % nominal Rh test. The peak N_2O generation rates and the total N_2O measured as a function of noble metals concentration are compared in Figures 4.24 and 4.25.

Nitrous oxide is a product of HNO_2 destruction during stage II according to Reaction 3, which was presented earlier. The shape of the N_2O profile is consistent for all runs. The profiles show a broad initial peak followed by a sharper peak near the end of N_2O generation. The N_2O peak generation rate increases approximately linearly with respect to noble metals concentration. The total N_2O measured demonstrates a similar trend. Based on this evidence, HNO_2 destruction by Reaction 3 is dependent on noble metals concentration. The 25 % nominal Rh provides evidence that Rh is the catalyst that most affects this reaction because the value of peak generation rate and total N_2O measured are within experimental error of the 25 % nominal noble metals test.

4.6 NH_3 Behavior

Ammonia evolves during stage III from a reaction of formic acid with NO_3^- (Reaction 6). The ammonia exists primarily as NH_4^+ in the slurry, based on the low pH of the stage III slurry (ph 3-5). Higher pHs cause evolution of NH_3 into the condensate. The amount of NH_3 found in the condensate was negligible. The digestion period corresponds approximately to stage III; however, some tests ran longer than others, which might have resulted in high ammonia values for those tests. This error might not be significant since most of the ammonia was probably generated during the same time as the H_2 peak. It has been proposed that H_2 is involved as an intermediate reactant for NH_3 generation (Reaction 7, 8).

Figure 4.22. The N_2O Offgas Profiles for 10%, 25%, 50%, and 100% Nominal Noble Metals

Figure 4.23. The N_2O Offgas Profiles for 25% Nominal Noble Metals and 25% Nominal Rh

Figure 4.24. Peak N_2O Generation Rate as a Function of Noble Metals Content

Figure 4.25. The N_2O Measured During the Time Interval 0 to 444 Minutes

Figure 4.26. Ammonia Measured Following Stage III

Other researchers^{(a), (b)} have shown that an increase in H₂ increases NH₃ generation.

Figure 4.26 shows the amount of NH₃ measured in the slurry following stage III as a function of noble metals concentration. The data indicate that NH₃ increases linearly with noble metals concentration. These data follow a similar trend as the stage III CO₂ data. It is interesting to note that total H₂ measured reaches a saturation level, while both CO₂ and NH₃ increase linearly with noble metals concentration.

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- (a) Wiemers, K.D., M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements and Thermal Stability*. PHTD-93-K899, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.
- (b) Smith, H.D., K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal Year 1992: Evaluation of Off gas Generation and Ammonia Production*. PHTD-C93-03.02, Pacific Northwest Laboratory, Richland, Washington.

King^(a) has found that HCOOH decomposition is better catalyzed by soluble Rh catalysts, while NH₃ generation is better catalyzed by a Rh metals supported catalyst. During the nominal noble metals test, a black residue was observed that has been attributed to reduced noble metals precipitated from solution.^(b) These precipitated noble metals may act as a supported Rh catalyst though there is no direct evidence of this behavior. Further tests are required for verification. Close agreement of the 25 % nominal Rh test and both 25 % nominal noble metals tests shows that NH₃ generation is primarily catalyzed by Rh.

A comparison was made between the amount of NH₃ measured during stage III and the amount of CO₂ that was measured. According to Reaction 6, four moles of CO₂ are generated for every mole of NH₃. The amount of CO₂ produced by Reaction 6 can be calculated by subtracting the amount of CO₂ formed by HCOOH decomposition (Reaction 5) from the total amount of CO₂ formed during stage III. Table 4.7 gives the numbers used for the comparison.

There is a great deal of difference between the calculated CO₂ based on offgas data (column 4) and the calculated CO₂ based on NH₃ measurement (column 6). The difference can not be explained by

Table 4.7. Comparison of CO₂ and NH₃ Measured During Stage III

Test	Total CO ₂ Measured During Stage III (moles)	CO ₂ Produced from Reaction 5 based on H ₂ Measurement (moles)	Calculated CO ₂ Produced by Reaction 6 (moles)	Total NH ₃ Measured During Stage III (moles)	Calculated CO ₂ Produced by Reaction 6 Based on NH ₃ Measurement (moles)	Difference Between Column 4 and 6 (moles)
10% NM	0.0842	.0343	0.0499	0.0002	0.0008	0.0491
25% NM	0.247	0.119	0.128	0.002	0.008	0.120
50% NM	0.414	0.193	0.221	0.0132	0.0528	0.168
100% NM	0.533	0.168	0.365	0.0257	0.103	0.262
25% Rh	0.164	0.0467	0.117	0.0029	.0116	0.105
25% NM (Repeat)	0.119	0.0564	.0626	0.0013	.0052	0.0574

- (a) King, R. B. and N. K. Bhattacharyya. 1994. *Hanford Waste Vitrification Plant Hydrogen Generation Study: Formation of Ammonia From Nitrate and Nitrite in Hydrogen Generating Systems*. PVTD C94-03.02Y. University of Georgia, Athens, Georgia.
- (b) Smith, H.D., K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal Year 1992: Evaluation of Off gas Generation and Ammonia Production*. PHTD-C93-03.02, Pacific Northwest Laboratory, Richland, Washington.

measurement error alone. Possible explanations are that the all NH_3 produced may not have been detected, or CO_2 is being produced by another unidentified reaction. King found similar results when comparing CO_2 and NH_3 data.^(a) King proposed that partial Fe reduction is responsible for producing additional CO_2 (Reaction 9).

Work performed in FY 1991^(b) documented that Fe^{+2} becomes more soluble as H_2 is generated during stage III. This provides evidence that Fe reduction is occurring. Additional work is needed for verification of Fe reduction.

4.7 Carbon and Nitrogen Mass Balances

Tables 4.8 and 4.9 contain mass balances for carbon and nitrogen for the six tests. The error in the analysis is random and can not be attributed to a systemic cause. The majority of the error is caused by uncertainty in aqueous chemistry analytical measurements. It is recommended that total carbon be measured for the purpose of a carbon mass balance. This would provide an independent measure of carbon content, and would measure the carbon from all species in solution. If carbon was present in other species besides the formate ion, it would cause the percentage of carbon accounted for to be low.

The nitrogen mass balance (Table 4.9) is more successful than the carbon balance. Error is still introduced by analytical error. The 25% noble metals test mass balance contains a great deal of uncertainty because of equipment malfunction. Nitrogen oxide data was lost during the beginning of the test which explains why only 60% of the nitrogen accounted for by mass balance.

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- (a) King, R. B. and N. K. Bhattacharyya. 1994. *Hanford Waste Vitrification Plant Hydrogen Generation Study: Formation of Ammonia From Nitrate and Nitrite in Hydrogen Generating Systems*. PVTD C94-03.02Y. University of Georgia, Athens, Georgia.
- (b) Wiemers, K.D., M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. *Evaluation of HWVP Feed Preparation Chemistry for an NCAW Simulant--Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements and Thermal Stability*. PHTD-93-K899, Rev. 0, Pacific Northwest Laboratory, Richland, Washington.

Table 4.8. Carbon Mass Balance for FY 1993 Tests

Test	Initial Carbon from CO_3^{2-} and TOC (moles)	Added Carbon from HCOOH (moles)	Carbon Released as CO_2 gas (moles)	Amount of Carbon Removed by Sampling (moles)	Measured Amount of Carbon Remaining as COOH^- (moles)	Percent Carbon Accounted For by Mass Balance*
10% NM	0.208	2.677	0.563	0.155	$2.848 \pm 10\%$	123.6
25% NM	0.208	2.669	0.786	0.108	$2.512 \pm 10\%$	126.6
50% NM	0.208	2.702	0.946	0.040	$1.904 \pm 10\%$	99.3
100% NM	0.208	2.596	1.186	0.039	$1.739 \pm 10\%$	105.7
25% Rh	0.208	2.746	0.639	0.070	$2.149 \pm 10\%$	96.7
25% NM (Repeat)	0.208	2.756	0.624	0.056	$1.942 \pm 10\%$	88.5

*Column 7 = $100 \times (\text{Column 4} + \text{Column 5} + \text{Column 6}) / (\text{Column 2} + \text{Column 3})$

Table 4.9. Nitrogen Mass Balances for FY 1993 Tests

Test	Initial Nitrogen from NO_3^- and NO_2^- (moles)	Nitrogen Released as NO_x and N_2O Gas (moles)	Amount of Nitrogen Removed by Sampling (moles)	Measured Amount of Nitrogen Remaining as NO_3^- , NO_2^- , and NH_3 (moles)	Percent Nitrogen Accounted for by Mass Balance*
10% NM	0.827	0.532	0.037	$0.260 \pm 10\%$	100.3
25% NM	0.827	0.390	0.022	$0.248 \pm 10\%$	79.9
50% NM	0.827	0.515	0.024	$0.262 \pm 10\%$	96.9
100% NM	0.827	0.655	0.018	$0.174 \pm 10\%$	102.5
25% Rh	0.827	0.498	0.022	$0.299 \pm 10\%$	99.1
25% NM (Repeat)	0.827	0.514	0.019	$0.259 \pm 10\%$	95.9

*Column 6 = $100 \times (\text{Column 3} + \text{Column 4} + \text{Column 5}) / (\text{Column 2})$

5.0 References

King, R.B., A.D. King, N.K. Bhattacharyya, C.M. King, and L.F. Landon. 1993. "Noble Metal Fission Products as Catalysts for Hydrogen Evolution from Formic Acid Used in Nuclear Waste Treatment." Presented at the Washington American Chemical Society meeting 1993, to be published in *Chemical Pretreatment of Nuclear Waste for Disposal*, W.W. Schulz and E. P. Horwitz, eds., 1993.

King, R.B. and N.K. Bhattacharyya. 1994. *Noble Metal Catalyzed Hydrogen Generation From Formic Acid in Nitrite-Containing Simulated Nuclear Waste Media*. Submitted for publication to *Journal of Molecular Catalysis*, 1994.

Peterson, M.E., R.D. Scheele, and J.M. Tingey. 1989. "Characterization of the First Core Sample of Neutralized Current Acid Waste From Double-Shell Tank 101-AZ." PNL-7758, Pacific Northwest Laboratory, Richland, Washington.

Ritter, J.A., J.R. Zamecnik, and C.W Hsu. 1992. "Hydrogen Generation During Treatment of Simulated High-Level Radioactive Waste with Formic Acid (U)." In Proceedings of the Third International Conference on High-Level Radioactive Waste Management. Las Vegas, Nevada, April 12-16 1992.

Smith, H.S., K.D. Wiemers, M.H. Langowski, M.R. Powell, and D.E. Larson. 1993. "Reaction Sequences in Simulated Neutralized Current Acid Waste Slurry During Processing with Formic Acid." A paper presented at the Materials Research Society Fall Meeting, Boston, Massachusetts (November 29 - December 3, 1993). Proceedings to be published by Materials Research Society.

Wiemers, K.D. 1988. "Evaluation of Process Off Gases Released During the Formating of Simulated HWVP Feed." A paper presented at the American Institute of Chemical Engineers National Meeting, Denver, Colorado (August 21-24, 1988).

APPENDIX

TEST SUMMARIES

Appendix A

Test Summaries

This test summary is designed to provide the test information in more detail than provided in the text of the report. For each of the six tests, the following are provided:

- Offgas profiles for each gas individually
- Test activity log
- Formic acid addition log
- Gram waste oxide tracking sheet
- Analytical Data Measurements

In addition, a graph of pHs for each test, and a graph of HCOOH additions are provided.

Test T93-NM-1: 10% Nominal Noble Metals

Figure A.1. Offgas Profile for Test T93-NM-1 Containing 10% of the Nominal Noble Metals

Figure A.2. Hydrogen Offgas Profile for Test T93-NM-1 Containing 10% of the Nominal Noble Metals

Figure A.3. Carbon Dioxide Offgas Profile for Test T93-NM-1 Containing 10% of the Nominal Noble Metals

Figure A.5. Nitrous Oxide Offgas Profile for Test T93-NM-1 Containing 10% of the Nominal Noble Metals

Table A.1. Activity Log - Test T93-NM-1

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
5/20/93						
09:00	11.27	22	22	22	23	Established air flow over vessel at 1.950 L/min.
09:10	--	39	28	22	22	Set temperature to 50°C. Removed pH probe.
09:15	--	48	37	23	22	Set temperature to 90°C.
09:25	--	65	53	22	21	--
09:30	--	78	68	22	21	--
09:35	--	82	73	22	21	--
09:40	--	85	77	23	22	Set temperature to 101°C.
09:45	--	94	86	23	22	--
09:50	--	96	89	23	22	--
09:55	--	97	90	22	21	--
10:00	--	98	91	22	22	--
10:05	--	100	93	22	22	Took primary condenser sample.
10:10	9.5	101	92	22	23	Boiling.
10:15	--	100	92	21	22	--
10:20	--	101	92	21	23	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
10:25	--	101	92	22	23	Took primary condenser sample. Set temperature to 95°C.
11:18	--	94	--	--	--	Compared measuring TC with another calibrated TC (#01551). They compared within 1°C. Thermister reading 3°C higher.
11:33	9.35	94	--	--	--	--
11:39	9.27	95	--	--	--	--
11:45	9.13	95	66	21	22	--
11:50	8.26	95	--	--	--	--
11:55	7.43	95	--	--	--	Smooth surface.
11:56	7.22	95	--	--	--	Surface foam. HCOOH addition rate 0.6 g/min.
12:05	6.81	97	--	--	--	--
12:09	6.50	97	--	--	--	HCOOH addition rate 0.6 g/min.
12:11	6.33	97	--	--	--	Surface foam.
12:14	6.22	97	--	--	--	--
12:18	6.00	97	77	20	21	--
12:21	5.87	97	--	--	--	Large bubble foam.
12:25	5.73	97	--	--	--	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
12:27	5.66	97.8	--	--	--	Large bubble foam. HCOOH addition rate 0.64 g/min.
12:30	5.52	98.3	--	--	--	--
12:33	5.29	95.3	--	--	--	Foam to top of vessel.
12:36	5.15	97.6	--	--	--	Note that foam began building up at a pH > 7, and was actively breaking up when the pH reached 5.15. The foam level was at the base of the flair on the reaction vessel when at its highest.
12:43	4.81	95	--	--	--	--
12:46	4.73	94	--	--	--	--
12:49	4.66	95	--	--	--	--
12:54	4.60	96	--	--	--	--
13:00	4.55	96	--	--	--	--
13:13	4.47	96	--	--	--	--
13:19	4.39	96	--	--	--	--
13:26	4.40	96	--	--	--	Thin layer of foam.
13:30	4.39	96	--	--	--	Slurry color unchanged.
13:37	4.34	96	--	--	--	--
12:43	4.32	96	--	--	--	--
13:55	4.24	96	--	--	--	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
14:03	4.21	96	--	--	--	--
14:10	4.17	96	--	--	--	--
14:14	4.13	96	--	--	--	--
14:18	4.05	96	--	--	--	--
14:27	4.05	96	--	--	--	--
14:33	3.96	96	--	--	--	--
14:34	--	--	--	--	--	HCOOH addition vessel refilled. Weight went from 540.4 to 557.2 g.
14:35	--	--	--	--	--	--
14:44	3.84	95	--	--	--	--
14:52	3.79	95	--	--	--	--
14:57	3.75	95	--	--	--	--
15:04	3.69	94	--	--	--	--
15:20	3.70	--	--	--	--	Completed forming.
15:30	3.75	95	90	22	21	--
15:38	3.78	96	--	--	--	--
16:00	3.82	100	--	--	--	Start digestion.
16:15	3.83	101	94	20	23	--
16:20	3.84	101	93	17	22	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
16:30	3.85	101	--	--	--	Smooth surface.
16:35	3.87	101	--	--	--	--
16:40	3.87	101	94	17	22	--
16:45	3.89	102	--	--	--	--
16:50	3.90	102	93	17	21	Surface foam.
16:58	3.84	--	--	--	--	Condensate replacement (132.73 g DIW).
17:01	3.89	98	90	21	22	Smooth surface.
17:11	3.96	102	--	--	--	--
17:20	3.95	100	93	19	21	Surface foam.
17:25	3.97	100	93	17	22	--
17:30	3.99	100	--	--	--	--
17:40	4.00	100	--	--	--	--
17:45	4.01	100	94	18	21	--
17:50	4.03	100	94	18	22	--
18:00	--	--	--	--	--	Condensate replacement (165.30 g DIW).
18:05	4.07	97	91	21	22	--
18:12	4.09	100	94	22	22	--
18:20	4.08	100	--	--	--	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
18:24	4.10	100	94	19	23	--
18:30	4.11	100	--	--	--	--
18:36	4.11	100	--	--	--	--
18:40	4.11	100	94	20	22	--
18:45	4.10	100	--	--	--	--
18:51	4.10	100	--	--	--	--
18:55	4.10	100	94	20	22	Set temperature to 0°.
19:00	4.10	100	--	--	--	Turned off air to vessel.
19:14	5.55	80	--	--	--	Stopped agitation.

Table A.2 HCOOH Addition - Test T93-NM-1

Time	Minutes Relative to Start of HCOOH Addition (min)	Weight of 90.6 Wt % HCOOH Added (g)
11:38	0	0
11:45	7	6.6
12:02	24	20.0
12:05	27	21.9
12:09	31	24.4
12:11	33	26.2
12:14	36	27.9
12:18	40	30.2
12:21	43	32.1
12:25	47	34.3
12:27	49	35.8
12:30	52	37.7
12:33	55	39.7
12:36	58	41.7
12:43	65	45.7
12:46	68	47.6
12:49	71	49.4
12:54	76	52.9
13:00	82	56.4
13:13	95	64.7
13:19	101	68.5
13:26	108	72.8
13:30	112	75.5
13:37	119	79.9
13:43	125	83.7
13:55	137	91.4
14:03	145	96.7
14:10	152	101.1
14:14	156	103.8
14:18	160	106.5
14:27	169	112.1
14:33	175	115.9
14:44	186	122.4
14:52	194	127.9
14:57	199	131.3
15:04	206	135.8
15:20	222	136.0
Total HCOOH Added:		136.0

Table A.3. Gram Waste Oxide Tracking Log - Test T93-NM-1

Sample/Action	Sample Type	Sample Weight (g)	Calc. Sample Volume (mL)	Slurry Weight (g)	Slurry Volume (mL)	Oxide Loading (gWO/L)	Total Oxide Weight (g)	Calc. Density (g/mL)
Initial slurry	N/A	N/A	N/A	1680	1500	127	190.5	1.120
Noble Metals slurry addition	N/A	4.58	4.58	1685	1505	127	190.5	1.120
T93-NM-1-1-1, plus spillage	Slurry	43.85	39.16	1641	1465	127	185.5	1.120
Antifoam	N/A	10.00	10.00	1651	1475	126	185.4	1.119
T93-NM-1-2-1	Primary Condensate (Replaced)	81.30	81.30	1651	1475	126	185.4	1.119
T93-NM-1-2-2	Primary Condensate	238.95	238.95	1412	1236	150	185.4	1.143
T93-NM-1-2-2s	Secondary Condensate	1.00	1.00	1411	1235	150	185.4	1.143
T93-NM-1-1-2	Slurry	23.00	20.13	1388	1214	150	182.4	1.143
T93-NM-1-2-3	Primary Condensate (Replaced)	316.40	316.40	1388	1214	150	182.3	1.143
T93-NM-1-2-3s	Secondary Condensate (Replaced)	164.21	164.21	1388	1214	150	182.3	1.143
T93-NM-1-1-3	Slurry	19.30	16.88	1368	1197	150	179.8	1.143
Final Measured Slurry Weight				1303.0				

Table A.4. Analytical Laboratory Results - Test T93-NM-1

Sample ID	Time	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH @ RT	NH ₃ (g/L)	HCOO ⁻ (g/L)	NO ₂ ⁻ (g/L)	NO ₃ ⁻ (g/L)
SLURRY												
T93-NM-1-1-1	*	Initial	37.85	1641	1465	127	1.120	11.50	0.0011	<0.5	25.3	8.9
T93-NM-1-1-2	*	Formating	23.00	1388	1214	150	1.143	5.16	0.00054	56.7	10.3	13.5
T93-NM-1-1-3	*	Digestion	19.30	1368	1197	150	1.143	4.03	0.0028	100	<0.2	13.5
CONDENSATE (Sample Weight indicates entire condensate collected during time period.)												
T93-NM-1-2-1	10:05-10:20	Initial	81.30	1614	1475	126	1.094	6.88	0.0030	<0.0050	<0.05	0.00063
T93-NM-1-2-2	12:05:15:20	Formating	238.95	1375	1236	150	1.113	2.06	0.00026	4.6	<0.05	1.0
T93-NM-1-2-2s	16:00	Formating	1.00	1374	1235	150	1.113	n/a	0.034	0.51	<0.05	27.4
T93-NM-1-2-3	16:25-18:53	Digestion	316.40	1351	1214	150	1.113	2.32	<0.00010	10.5	<0.005	<0.05
T93-NM-1-2-3s	16:37-19:01	Digestion	164.21	1351	1214	150	1.113	2.30	0.00012	8.7	<0.05	0.006
Drierite			120.48						4.15	μgNH ₃ /	g drierite	
* Time was not recorded.												

Test T93-NM-2: 25% Nominal Noble Metals

Figure A.6. Offgas Profile for Test T93-NM-2 Containing 25% of the Nominal Noble Metals

Figure A.7. Hydrogen Offgas Profile for Test T93-NM-2 Containing 25% of the Nominal Noble Metals

Figure A.8. Carbon Dioxide Offgas Profile for Test T93-NM-2 Containing 25% of the Nominal Noble Metals

Figure A.9. Nitrogen Oxide Offgas Profile for Test T93-NM-2 Containing 25% of the Nominal Noble Metals

Figure A.10. Nitrous Oxide Offgas Profile for Test T93-NM-2 Containing 25% of the Nominal Noble Metals

Table A.5 Activity Log - Test T93-NM-2

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
<u>5/25/93</u>						
08:20	--	--	--	--	--	Set temperature to 50°C. Set agitator to 6. Set air flow to 1.950 sL/min.
09:45	--	50	40.4	21.9	21.4	Set temperature to 90°C.
10:00	--	72	60.8	20.7	20.8	--
10:05	--	84	75.1	20.4	20.7	Set temperature to 102°C.
10:10	--	92	84.8	21.9	21.8	--
10:15	--	98	90.3	22.4	21.4	--
10:30	--	98	90.9	22.6	21.0	--
10:35	--	100	92.0	--	--	--
10:45	--	101	96.5	--	--	Boiling.
10:50	8.50	101	94.3	22.4	21.1	Set temperature to 95°C. Added 113.4 g DIW.
11:15	--	95	--	--	--	Calibrated NO/NOx analyzer.
11:50	8.61	95	--	--	--	Calibrated instruments.
12:15	8.65	94	87.1	22.9	21.1	Began purging system prior to forming.
12:31	8.65	95	87.1	--	--	--
12:36	8.65	94	87.0	25.4	21.4	Began forming.

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
12:39	8.62	95	86.9	25.2	21.3	--
12:42	8.56	95	87.1	25.2	21.2	0.62g HCOOH/min addition rate over 5 minutes.
12:45	8.47	95	87.2	24.8	21.0	--
12:48	8.34	95	--	--	--	--
12:50	8.20	95	87.4	25.7	21.7	--
12:56	7.41	95	87.6	26.1	22.1	0.60 g/min addition rate. Foaming.
13:01	6.82	96	81.8	26.2	21.4	--
13:05	6.50	96	81.2	25.5	21.2	--
13:08	6.23	96	80.9	25.3	21.1	--
13:12	5.93	96	80.5	24.9	21.0	Foaming.
13:15	5.68	96	80.7	24.7	21.4	0.61 g/min addition rate.
13:17	5.48	96	80.4	24.7	21.7	--
13:21	5.24	96	80.3	25.0	21.9	Foaming.
13:29	4.92	96	79.2	24.2	21.3	--
13:40	4.39	95	81.6	24.8	22.2	Small amount (1/4") foam.
13:50	3.89	95	85.6	25.6	21.8	No foam.
14:00	3.62	95	84.4	26.2	21.2	--
14:10	3.63	95	78.3	25.5	21.2	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
14:14	3.46	97	78.2	25.1	21.8	--
14:21	3.17	96	78.8	24.7	21.6	0.63 g/min addition rate.
14:27	2.69	96	80.5	24.6	21.2	--
14:36	2.83	95	82.5	25.5	20.9	--
14:40	2.86	95	82.8	25.6	21.3	--
14:46	2.87	95	83.2	25.7	21.8	--
14:51	3.02	95	83.4	25.9	21.3	--
15:00	3.23	95	84.1	25.8	21.1	--
15:06	3.26	95	85.2	--	--	No foam.
15:10	3.23	95	85.4	26.1	21.9	--
15:16	3.05	95	85.4	26.4	21.8	--
15:21	3.17	95	85.4	26.2	21.3	--
15:24	3.21	95	85.6	26.1	21.3	--
15:36	3.26	95	85.1	25.9	20.9	No foam.
15:43	3.30	95	84.5	26.3	21.3	--
15:52	3.10	95	86.4	26.1	21.9	0.64 g/min H ₂ in gas.
15:56	3.08	94	87.4	26.1	21.6	--
16:03	3.07	94	88.1	25.9	21.3	--
16:08	3.05	94	88.1	26.0	21.2	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
16:10	3.06	--	--	--	--	Formating completed.
16:45	2.93	95	86.8	--	--	Set temperature to 100°C.
16:50	2.86	98	89.6	26.3	21.7	--
16:56	2.58	100	89.5	--	--	Suspected pH meter malfunction. ATC probe reads 87°C and dropping.
17:00	--	100	89.7	--	--	--
17:12	2.87	99	90.3	26.4	21.2	New pH meter w/o ATC.
17:30	3.01	102	90.8	26.8	21.3	Started digestion. Creamy dark brown foam on surface.
17:44	3.01	101	89.3	--	--	--
17:52	3.03	101	89.6	27.1	22.1	--
17:56	3.03	100	90.3	--	--	--
18:01	3.03	101	90.3	26.6	21.4	Dark brown foam around center shaft only.
18:07	3.03	101	90.9	26.6	21.3	--
18:11	3.04	101	90.9	--	--	--
18:22	3.03	101	90.8	26.9	22.0	--
18:26	3.05	94	87.5	26.2	21.7	Replaced condensate.
18:34	3.07	101	90.3	26.2	21.2	--
18:39	3.05	102	91.0	26.6	21.3	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
18:47	3.05	101	91.3	27.1	22.3	No foam.
18:53	3.05	101	91.3	--	--	--
19:01	3.06	102	90.6	26.5	21.3	--
19:11	3.08	102	90.1	27.2	21.9	--
19:23	3.09	102	89.8	--	--	--
19:24	--	--	--	--	--	Added 126.7 g DIW.
19:30	3.11	101	88.9	26.2	21.3	--
19:39	3.08	102	90.6	27.7	22.1	~ 1" foam.
19:46	2.98	102	90.1	27.7	21.6	--
19:52	2.88	101	88.9	26.8	21.2	No foam.
20:00	2.77	102	90.1	26.8	21.7	--
20:11	--	101	--	--	--	Foam ~ 1" high. Foam even with top of heater.
20:20	2.780	102	89.4	27.1	21.4	Large bubble foam.
20:26	2.842	102	89.4	27.4	22.0	Foam to top of heater. Set temperature to 0°C. Added 131.3 g DIW.
20:40	--	85	--	--	--	Stopped stirrer and argon flow.

Table A.6. HCOOH Addition Log - Test T93-NM-2

Time	Minutes from Start of HCOOH Addition (min)	Weight of 90.6 Wt % HCOOH Added (g)
12:37	0	0.0
12:39	2	4.8
12:42	5	6.7
12:45	8	8.6
12:48	11	10.0
12:50	13	11.7
12:56	19	15.7
13:01	24	18.5
13:05	28	20.8
13:08	31	22.7
13:12	35	24.7
13:15	38	26.7
13:17	40	28.2
13:21	44	30.4
13:29	52	35.5
13:40	63	41.8
13:50	73	48.2
14:00	83	54.4
14:10	93	60.5
14:14	97	63.8
14:21	104	67.7
14:27	110	72.0
14:36	119	77.3
14:40	123	79.4
14:46	129	83.8
14:51	134	86.8
15:00	143	91.8
15:06	149	95.8
15:10	153	98.7
15:16	159	102.6
15:21	164	105.8
15:24	167	107.3
15:36	179	115.0
15:43	186	119.1
15:52	195	125.3
15:56	199	128.1
16:03	206	132.2
16:08	211	135.6
Total HCOOH Added:		135.6

Table A.7. Gram Waste Oxide Tracking Log - Test T93-NM-2

Sample/Action	Sample Type	Sample Weight (g)	Calc. Sample Volume (mL)	Slurry Weight (g)	Slurry Volume (mL)	Oxide Loading (gWO/L)	Total Oxide Weight (g)	Calc. Density (g/mL)
Initial slurry	N/A	N/A	N/A	1680	1500	127	190.5	1.120
Noble Metals slurry addition	N/A	11.46	11.00	1691	1511	126	190.5	1.119
T93-NM-2-2-1	Primary Condensate (Replaced)	113.40	113.40	1691	1511	126	190.5	1.119
Antifoam	N/A	10.00	10.00	1701	1521	125	190.5	1.119
T93-NM-2-1-1	Slurry	20.30	18.15	1681	1503	125	188.2	1.119
T93-NM-2-2-2	Primary Condensate	307.79	307.79	1373	1195	157	188.2	1.149
T93-NM-2-2-2s	Secondary Condensate	12.24	12.24	1361	1183	159	188.2	1.151
T93-NM-2-1-2	Slurry	15.90	13.82	1345	1169	159	186.0	1.151
T93-NM-2-2-3	Primary Condensate (Replaced)	372.40	372.40	1345	1168	159	185.9	1.152
T93-NM-2-2-3s	Secondary Condensate (Replaced)	10.90	10.90	1345	1168	159	185.9	1.152
T93-NM-2-1-3	Slurry	16.46	14.29	1329	1154	159	183.6	1.152
Final Measured Slurry Weight				1287.6				

Table A.8. Analytical Laboratory Results - Test T93-NM-2

Sample ID	Time	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH @ RT	NH ₃ (g/L)	HCOO ⁻ (g/L)	NO ₂ ⁻ (g/L)	NO ₃ ⁻ (g/L)
SLURRY												
T93-NM-2-1-1		Initial	20.30	1618	1502	125	1.119	11.46	0.0014	<0.5	23.2	7.5
T93-NM-2-1-2	16:40	Formating	15.90	1345	1168	159	1.151	4.00	0.00070	103	0.63	13.5
T93-NM-2-1-3	20:40	Digestion	16.46	1329	1154	159	1.152	4.85	0.030	98	<0.2	13.2
CONDENSATE (Sample Weight indicates entire condensate collected during time period.)												
T93-NM-2-2-1	10:25-10:50	Initial	113.40	1691	1511	126	1.119	6.48	0.0044	0.032	<0.050	<0.050
T93-NM-2-2-2	13:00-16:15	Formating	307.79	1373	1195	158	1.149	2.03	0.00020	5.1	<0.050	1.2
T93-NM-2-2-2s	13:00-16:15	Formating	12.24	1361	1182	159	1.151	1.15	0.0051	4.0	<0.050	8.5
T93-NM-2-2-3	18:00-20:22	Digestion	372.40	1345	1168	159	1.152	2.31	<0.0001	4.6	<0.050	<0.050
T93-NM-2-2-3s	18:00-20:22	Digestion	10.90	1345	1168	159	1.152	1.87	0.0004	8.8	<0.050	0.90
Drierite			113.40						0.97 µgNH ₃ / g drierite			

Test T93-NM-3: 100% Nominal Noble Metals

Figure A.11. Offgas Profile for Test T93-NM-3 Containing the Nominal Noble Metal Content

Figure A.12. Hydrogen Offgas Profile for Test T93-NM-3 Containing the Nominal Noble Metal Content

Figure A.13. Carbon Dioxide Offgas Profile for Test T93-NM-3 Containing the Nominal Noble Metal Content

Figure A.14. Nitrogen Oxide Offgas Profile for Test T93-NM-3 Containing the Nominal Noble Metal Content

Figure A.15. Nitrous Oxide Offgas Profile for Test T93-NM-3 Containing the Nominal Noble Metal Content

Table A.9. Activity Log - Test T93-NM-3

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
10:00	--	24	20.7	21.5	20.4	Set temperature to 100°C.
10:06	--	38	22.6	21.4	20.7	--
10:15	--	55	26.1	21.4	20.7	--
10:19	--	69	30.4	21.6	20.6	--
10:25	--	78	38.6	--	--	--
10:30	--	88	56.2	22.4	20.6	--
10:35	--	95	75.7	24.4	21.5	--
10:48	--	97	77.1	25.7	21.8	--
10:55	--	97	77.6	25.7	21.2	Set point to 102°C.
11:00	--	99	80.7	26.1	21.4	--
11:15	--	99	72.0	25.5	20.1	--
11:25	--	99	80.2	26.0	21.3	--
11:30	--	99	79.7	26.2	21.3	--
11:40	--	99	78.1	--	--	--
11:47	--	100	62.3	26.6	20.8	--
11:55	--	101	63.4	27.1	21.3	Boiling.
12:00	--	101	70.5	28.1	21.4	--
12:05	--	101	71.2	27.8	20.9	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
12:10	--	101	72.0	28.3	20.9	Set point to 95 °C. Added 226.39 DIW.
12:30	--	95	--	--	--	Recalibrated offgas system.
13:30	--	95	--	--	--	Recalibrated offgas system.
14:00	--	95	26.7	22.6	21.4	--
14:14	--	95	28.2	--	--	Began forming.
14:20	9.231	93	47.7	--	--	--
14:25	9.238	93	47.6	25.1	20.7	--
14:30	9.241	93	51.2	--	--	--
14:35	9.241	93	51.8	25.7	21.9	--
14:42	8.989	94	51.4	--	--	--
14:48	8.782	94	--	--	--	--
14:53	8.392	94	51.5	26.4	21.2	0.56 g HCOOH/min addition rate.
14:59	7.986	94	52.2	--	--	0.61 g/min addition rate.
15:05	6.967	94	46.3	26.7	21.2	--
15:10	6.808	94	43.1	--	--	0.62 g/min addition rate.
15:15	6.479	95	42.3	25.9	20.6	--
15:19	6.220	95	43.7	--	--	Foaming ~ 1".
15:25	5.950	95	43.2	25.7	20.8	Foaming. 0.55 g/min addition rate.

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
15:30	5.239	95	43.2	25.6	21.7	Some foam ~ 1/2". 0.54 g/min addition rate.
15:40	5.426	95	40.8	24.8	20.4	Some foam. 0.57 g/min addition rate.
15:50	5.094	95	40.9	24.8	21.3	Some foam. 0.55 g/min addition rate.
15:55	5.012	95	41.6	25.2	21.6	Surface foam around center shaft.
16:00	4.251	95	41.3	25.3	21.3	--
16:10	4.559	95	39.8	24.5	20.6	--
16:20	4.489	96	41.4	25.2	21.4	Surface foam. 0.56 g/min addition rate.
16:30	4.444	96	39.2	24.7	20.7	--
16:40	4.400	96	40.3	24.8	20.7	0.59 g/min addition rate.
16:50	4.377	96	40.7	25.3	21.4	--
17:03	4.384	95	40.7	25.0	20.4	--
17:10	4.391	95	41.2	25.6	21.2	--
17:20	4.390	95	39.7	25.4	21.0	--
17:30	4.540	96	38.8	25.0	20.2	--
17:40	4.785	96	39.6	25.4	21.6	--
17:50	4.550	95	41.3	25.2	20.9	--
18:00	4.370	95	43.4	25.6	21.1	--
18:10	4.224	95	45.3	25.7	21.6	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
18:15	4.151	95	45.7	26.1	21.1	--
18:20	4.111	95	45.4	26.2	20.6	--
18:25	4.070	95	45.2	26.3	20.9	--
18:30	4.049	95	45.7	26.6	21.4	--
18:31	4.049	--	--	--	--	Formating completed.
18:39	4.131	95	--	--	--	--
18:41	--	--	--	--	--	Took slurry sample.
18:47	4.174	95	42.9	--	--	--
18:56	4.214	95	45.1	--	--	Black residue noted on baffle.
19:02	4.312	98	47.2	--	--	--
19:06:45	4.384	99	48.4	--	--	Set point to 101 °C.
19:15	4.454	100	--	--	--	Black residue in foam. Boiling. Digestion started.
19:17	4.573	101	50.8	26.8	20.8	~1" foam.
19:18	4.601	101	50.8	--	--	--
19:19	4.607	101	50.4	--	--	--
19:20	4.609	101	50.4	27.2	21.0	--
19:21	4.606	101	50.1	--	--	--
19:22	4.598	101	--	--	--	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
19:24	4.493	101	44.6	27.2	21.5	Foam to top of heater. Set point to 100°C.
19:29	4.430	100	36.6	--	--	Long bubble foam to top of vessel.
19:32	4.489	100	33.9	24.3	21.4	--
19:34	4.574	101	--	--	--	Large bubble foam to vessel lid interface.
19:39	4.697	101	33.6	22.8	20.7	Bubbles slowly receding. Condensate forming slowly.
19:47	4.750	100	33.6	--	--	--
19:51	4.721	100	32.6	22.8	21.7	Dark foam to top of heater.
19:56	4.693	100	--	--	--	Foam to top of vessel.
20:02	4.683	101	30.8	22.0	20.7	--
20:07	4.676	101	30.2	--	--	--
20:10	4.734	101	30.1	21.8	21.0	--
20:17	5.008	101	30.8	--	--	--
20:24	5.210	101	29.3	21.7	20.9	Foam to bottom of vessel lid interface.
20:28	5.125	101	28.5	--	--	--
20:33	5.352	101	29.0	21.2	20.7	Set temperature to 99°C in attempt to break foam block on surface.
20:42	5.381	100	29.0	--	--	--
20:50	5.398	99	28.4	--	--	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
20:55	5.391	100	29.8	21.2	20.6	--
21:02	5.387	100	31.1	21.9	21.6	--
21:14	5.321	100	31.5	21.8	20.3	Dark, thick looking foam on surface.
21:21	5.346	100	34.3	--	--	--
21:30	5.267	99	36.8	23.7	21.6	--
21:36	5.255	100	39.2	24.1	20.7	Slurry seems to be getting darker.
21:44	5.149	100	42.2	24.8	20.6	--
21:54	5.698	100	43.2	25.9	21.7	--
22:02	5.470	100	42.7	25.6	20.6	Reset temperature at 102 °C.
22:08	5.325	100	51.0	26.4	20.7	
22:16	5.464	101	54.5	27.3	21.8	Temperature set at 0 °C. Added back 126.6 g DIW. Removed pH probe. Slurry coloration dark brownish green.
23:00	--	--	--	--	--	Shut off agitator and flow.
6/4/94						
7:30	--	--	--	--	--	After removing lid from vessel/color-dark olive green with reddish scum on top-consistency of oatmeal. Propeller blades oxidized black.

Table A.10. HCOOH Addition Log - Test T93-NM-3

Time	Minutes Following Start of HCOOH Addition (min)	Weight of 90.6 Wt % HCOOH Added (g)
14:35	0	0.0
14:42	7	2.8
14:48	13	5.7
14:53	18	8.0
14:59	24	11.4
15:05	30	15.2
15:10	35	17.9
15:15	40	20.8
15:19	44	23.5
15:25	50	26.2
15:30	55	28.9
15:40	65	34.6
15:50	75	40.1
15:55	80	43.8
16:00	85	45.8
16:10	95	52.1
16:20	105	57.7
16:30	115	63.3
16:40	125	69.0
16:50	135	74.6
17:03	148	82.6
17:10	155	85.9
17:20	165	91.5
17:30	175	97.2
17:40	185	102.7
17:50	195	108.5
18:00	205	114.0
18:10	215	119.7
18:15	220	123.1
18:20	225	125.4
18:25	230	128.4
18:30	235	131.2
18:31	236	131.9
Total HCOOH Added:		131.9

Table A.11. Gram Waste Oxide Tracking Log - Test T93-NM-3

Sample/Action	Sample Type	Sample Weight (g)	Calc. Sample Volume (mL)	Slurry Weight (g)	Slurry Volume (mL)	Oxide Loading (gWO/L)	Total Oxide Weight (g)	Calc. Density (g/mL)
Initial slurry	N/A	N/A	N/A	1680	1500	127	190.5	1.120
Noble Metals slurry addition	N/A	45.80	46.00	1726	1546	123	190.5	1.116
T93-NM-3-2-1	Primary Condensate (Replaced)	222.59	222.59	1726	1546	123	190.5	1.116
T93-NM-3-2-1s	Secondary Condensate (Replaced)	3.73	3.73	1726	1546	123	190.5	1.116
T93-NM-3-1-1	Slurry	16.27	14.58	1710	1531	123	188.7	1.116
Antifoam	N/A	10.00	10.00	1720	1541	122	188.7	1.116
T93-NM-3-2-2	Primary Condensate	290.9	290.9	1429	1251	151	188.7	1.142
T93-NM-3-2-2s	Secondary Condensate	11.23	11.23	1417	1239	152	188.7	1.144
T93-NM-3-1-2	Slurry	17.70	15.48	1400	1224	152	186.4	1.144
T93-NM-3-2-3	Primary Condensate (Replaced)	118.40	118.40	1400	1224	152	186.4	1.144
T93-NM-3-2-3s	Secondary Condensate (Replaced)	8.20	8.20	1400	1224	152	186.4	1.144
T93-NM-3-1-3	Slurry	19.2	16.79	1381	1207	152	183.8	1.144
Final Measured Slurry Weight				1367.2				

Table A.12. Analytical Laboratory Results - Test T93-NM-3

Sample ID	Time	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH @ RT	NH ₃ (g/L)	HCOO ⁻ (g/L)	NO ₂ ⁻ (g/L)	NO ₃ ⁻ (g/L)
SLURRY												
T93-NM-3-1-1	12:40	Initial	16.27	1710	1531	123	1.116	11.29	0.00027	<0.5	21.1	7.4
T93-NM-3-1-2	18:42	Formating	17.70	1400	1224	152	1.144	4.38	0.0028	91	<0.2	11.3
T93-NM-3-1-3	22:27	Digestion	19.20	1381	1207	152	1.144	6.28	0.33	64.8	<0.2	7.6
CONDENSATE (Slurry Weight indicates entire condensate collected during time period.)												
T93-NM-3-2-1	10:51-12:17	Initial	222.59	1726	1546	123	1.116	9.27	0.0058	0.00083	0.0013	0.00046
T93-NM-3-2-1s	10:51-12:17	Initial	3.73	1726	1546	123	1.116	n/a	0.030	0.052	0.0090	0.084
T93-NM-3-2-2	14:40-18:35	Formating	290.9	1429	1251	151	1.142	2.15	0.0020	0.89	0.0058	0.74
T93-NM-3-2-2s	14:40-18:35	Formating	11.23	1417	1239	152	1.144	1.52	0.011	0.79	< .0050	4.9
T93-NM-3-2-3	19:49-22:10	Digestion	118.40	1400	1224	152	1.144	8.22	0.30	0.46	< .0050	0.0039
T93-NM-3-2-3s	19:49-22:13	Digestion	8.20	1400	1224	152	1.144	4.43	0.59	2.1	< .0050	0.014
Drierite			118.16	148.1 µg NH ₃ / g drierite								

Test T93-NM-4: 50% Nominal Noble Metals

Figure A.16. Offgas Profile for Test T93-NM-4 Containing 50% of the Nominal Noble Metals

Figure A.17. Hydrogen Offgas Profile for Test T93-NM-4 Containing 50% of the Nominal Noble Metals

Figure A.18. Carbon Dioxide Offgas Profile for Test T93-NM-4 Containing 50% of the Nominal Noble Metals

Figure A.20. Nitrous Oxide Offgas Profile for Test T93-NM-4 Containing 50% of the Nominal Noble Metals

Table A.13. Activity Log - T93-NM-4

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
6/29/93						
11:20	11.294	--	--	--	--	Agitation set at 6.
11:50	11.422	24	21.8	21.6	20.8	Argon flow started through vessel.
12:50	10.956	88	35.4	22.2	20.3	Set temperature to 90 °C. Set point to 102°C.
15:51	--	99	--	--	--	Because test was late getting started it was decided to shut down until 6/30/93.
6/30/93						
6:30	--	29	--	--	--	Set point to 102°C.
6:38	10.786	33	22.6	21.9	21.3	--
6:47	10.176	51	23.6	21.7	21.0	--
6:57	10.124	79	29.2	--	--	--
7:09	8.991	95	40.6	22.7	21.2	--
7:18	8.992	97	42.3	22.3	20.4	--
7:24	8.975	98	44.8	--	--	--
7:46	9.008	97	43.9	22.5	20.6	--
7:53	9.028	99	46.1	23.1	21.4	--
7:57	9.024	100	47.6	23.4	21.7	--
8:03	8.985	101	48.3	22.8	21.1	Boiling.

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
8:08	8.975	101	47.8	22.6	20.4	--
8:13	8.967	101	48.9	22.9	21.0	--
8:20	8.966	101	49.7	23.5	21.8	--
8:24	8.943	101	49.9	23.6	21.9	--
8:27	8.921	101	--	--	--	Set point to 95°C.
9:01	8.914	92	73.1	22.3	20.6	Started HCOOH addition.
9:07	9.129	92	72.8	--	--	--
9:11	9.102	92	73.4	23.1	21.9	--
9:15	9.005	93	73.6	23.4	22.1	--
9:20	8.839	93	72.2	22.9	21.6	--
9:25	8.527	93	70.3	22.4	20.8	--
9:30	8.107	93	71.1	22.8	21.2	--
9:35	7.333	93	72.4	23.2	21.9	--
9:42	6.831	94	62.1	23.3	21.9	--
9:50	6.349	94	60.4	22.4	20.6	Surface foam.
9:56	5.905	94	58.7	22.8	21.2	--
10:05	5.716	94	60.5	23.3	22.1	--
10:10	5.218	94	61.1	23.4	22.2	--
10:17	4.991	94	65.2	22.6	21.0	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
10:24	4.646	94	68.1	22.9	21.1	Surface foam.
10:30	4.555	94	69.8	23.3	22.0	--
10:37	4.271	94	71.2	23.7	22.3	--
10:42	4.216	94	68.7	23.1	21.3	--
10:46	4.158	94	68.6	22.8	20.9	No foam. Condensate becoming more yellow.
10:53	4.102	94	67.9	23.3	21.5	--
10:59	4.041	94	66.8	23.8	22.1	No foam.
11:04	4.003	95	65.6	23.4	21.7	--
11:10	3.967	95	62.5	22.5	20.4	--
11:15	3.955	95	62.1	23.0	20.9	--
11:19	3.945	95	63.4	23.1	21.3	No foam.
11:29	3.927	95	61.6	23.0	21.0	--
11:34	3.912	95	60.4	22.6	20.4	Small bubble foam.
11:40	3.896	95	60.4	23.1	20.9	--
11:45	3.873	95	58.3	23.2	21.4	--
11:50	3.857	95	57.8	23.2	21.6	--
11:55	3.843	95	38.9	22.8	20.7	--
12:00	3.843	95	38.7	22.7	20.4	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
12:05	3.841	95	39.3	23.0	20.9	Small bubble surface foam.
12:10	3.842	95	39.3	23.3	21.3	--
12:15	3.858	95	38.6	23.1	21.2	--
12:20	3.885	95	37.7	22.7	20.4	--
12:25	3.944	96	38.3	22.8	20.6	--
12:30	3.896	94	41.1	22.9	21.0	--
12:37	3.733	94	41.8	23.2	21.5	--
12:42	3.671	94	41.1	22.8	20.9	--
12:46	3.616	94	40.9	22.6	20.3	--
12:54	3.550	94	41.4	23.1	21.1	--
13:00	3.468	95	41.4	23.4	21.6	--
13:05	3.496	95	40.2	23.1	21.4	Foam around shaft.
13:08	3.496	95	39.7	22.8	20.9	Formating complete.
13:24	3.552	90	36.7	22.9	21.5	Added 150 g Deionized Water (DIW). Set point to 102°C.
13:34	3.694	98	42.6	22.6	20.0	Took slurry sample.
13:43	3.775	98	43.9	--	--	--
13:48	3.814	99	44.9	--	--	Began digestion. Small surface bubbles.
13:53	3.852	100	45.4	23.1	21.4	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
13:58	3.874	100	44.9	22.8	21.1	Small bubble surface foam.
14:00	3.891	100	46.0	22.7	20.7	--
14:12	3.917	99	46.6	23.1	21.3	--
14:17	3.907	98	44.8	23.2	21.4	--
14:25	3.823	98	43.3	22.6	20.8	--
14:35	3.862	100	45.4	23.0	21.2	--
14:40	4.159	96	--	--	--	Added 78.26 g DIW.
14:45	4.290	99	43.7	22.9	21.1	--
14:50	4.381	101	43.8	22.8	20.7	Surface foam.
14:55	4.419	102	41.3	22.6	20.4	~0.5" foam.
15:00	4.579	102	41.1	22.6	20.9	--
15:05	4.695	101	41.2	22.8	21.3	--
15:10	4.685	101	40.9	22.9	21.3	--
15:15	4.683	97	--	--	--	Added 68.53 g DIW.
15:22	4.690	99	39.8	22.4	20.0	Color seems to be getting darker. Surface foam.
15:27	4.772	101	40.6	22.8	20.9	--
15:32	4.858	102	40.6	22.9	21.4	Foam to top of mantel.
15:37	4.842	102	40.5	22.9	21.4	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
15:43	4.970	102	39.4	22.8	21.0	~0.5" of foam.
15:48	4.911	100	40.7	22.7	20.9	--
15:53	4.871	101	41.1	22.8	20.9	Medium size dark brown bubbles around shaft. Added 71.21 g DIW.
15:59	4.931	98	--	--	--	--
16:00	4.914	100	40.1	22.8	21.4	--
16:11	4.872	101	39.6	22.6	21.1	--
16:16	4.843	103	39.9	22.4	20.9	Large bubble foam to top of mantle.
16:22	4.774	102	41.1	22.8	21.3	--
16:32	4.774	102	35.5	22.7	21.3	--
16:38	4.464	102	34.4	22.4	21.1	--
16:42	4.416	103	35.1	22.3	21.0	--
16:47	4.388	102	34.8	22.0	20.7	--
16:52	4.318	100	--	--	--	--
17:01	4.251	98	41.4	23.0	21.6	Added 36.84 g DIW.
17:06	4.442	100	42.5	23.0	21.2	Dark smooth surface.
17:10	4.393	103	--	--	--	Boil over into condenser.
17:17	--	99	37.6	22.4	20.7	Set point to 99°C.
17:23	4.51	99	40.1	23.2	21.5	Set point to 100°C.

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
17:31	4.435	100	41.3	23.3	21.6	Small bubbles around shaft.
17:36	4.612	100	39.6	23.0	21.3	--
17:48	4.276	102	34.8	22.6	20.8	Foam to top of vessel, set point to 99°C.
17:45	4.475	103	31.6	22.4	20.7	--
17:50	4.461	102	30.3	22.6	21.1	Foam to top of mantel.
17:57	4.657	101	29.7	22.8	21.7	--
18:00	4.619	100	30.9	22.7	21.6	Set point to 0°C.
18:11	--	83	--	--	--	Air flow off, agitator off.

Table A.14. HCOOH Addition Log - T93-NM-4

Time	Minutes Following HCOOH Start of Addition (min)	Weight of 90.6 Wt % HCOOH Added (g)
9:10	0	0.0
9:11	1	1.9
9:15	5	3.8
9:20	10	7.2
9:25	15	9.6
9:30	20	10.9
9:35	25	14.6
9:42	32	19.4
9:50	40	23.3
9:56	46	25.4
10:05	55	30.9
10:10	60	34.0
10:17	67	38.9
10:24	74	41.5
10:30	80	45.4
10:37	87	49.5
10:42	92	53.1
10:46	96	55.4
10:59	109	59.5
11:04	114	63.1
11:10	120	66.7
11:15	125	69.2
11:19	129	71.4
11:29	139	77.7
11:34	144	80.5
11:40	150	84.5
11:45	155	87.0
11:50	160	89.9
11:55	165	92.9
12:00	170	96.0
12:05	175	98.9
12:10	180	101.9
12:15	185	105.0
12:20	190	108.0
12:25	195	111.2
12:30	200	113.9
12:37	207	118.8
12:42	212	121.2
12:46	216	123.9
12:54	224	128.7
13:00	230	132.8
13:05	235	135.5
13:08	238	137.3
Total HCOOH Added:		137.3

Table A.15. Gram Waste Oxide Tracking Log - Test T93-NM-4

Sample/Action	Sample Type	Sample Weight (g)	Calc. Sample Volume (mL)	Slurry Weight (g)	Slurry Volume (mL)	Oxide Loading (gWO/L)	Total Oxide Weight (g)	Calc. Density (g/mL)
Initial slurry	N/A	N/A	N/A	1680	1500	127	190.5	1.120
Noble Metals slurry addition	N/A	23.00	23.00	1703	1523	125	190.5	1.118
T93-NM-4-2-1	Primary Condensate (Replaced)	219.70	219.70	1703	1523	125	190.5	1.118
T93-NM-4-2-1s	Secondary Condensate (Replaced)	5.50	5.50	1703	1523	125	190.5	1.118
T93-NM-4-1-1	Slurry	18.00	16.10	1685	1507	125	188.5	1.118
Antifoam	N/A	10.00	10.00	1695	1517	124	188.5	1.117
T93-NM-4-2-2	Primary Condensate	339.93	339.93	1355	1177	160	188.5	1.151
T93-NM-4-2-2s	Secondary Condensate	11.51	11.51	1344	1165	162	188.5	1.153
Added DI H2O	N/A	150.00	150.00	1494	1315	143	188.5	1.135
T93-NM-4-1-2	Slurry	17.40	15.33	1476	1300	143	186.3	1.135
T93-NM-4-2-3	Primary Condensate (Replaced)	254.90	254.90	1476	1300	143	186.3	1.135
T93-NM-4-2-3s	Secondary Condensate (Replaced)	10.04	10.04	1476	1300	143	186.3	1.135
T93-NM-4-1-3	Slurry	17.56	15.47	1459	1285	143	184.1	1.135
Final Measured Slurry Weight				1344.8				

Table A.16. Analytical Laboratory Results - Test T93-NM-4

Test T93-NM-5: 25% Nominal Rh

Figure A.21. Offgas Profile for Test T93-NM-5 Containing 25% of the Nominal Rh

Figure A.22. Hydrogen Offgas Profile for Test T93-NM-5 Containing 25% of the Nominal Rh

Figure A.23. Carbon Dioxide Offgas Profile for Test T93-NM-5 Containing 25% of the Nominal Rh

Figure A.25. Nitrous Oxide Offgas Profile for Test T93-NM-5 Containing 25% of the Nominal Rh

Table A.17. Activity Log - T93-NM-5

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
<u>7/7/93</u>						
9:44	11.277	23	23.1	23.3	16.7	Set point to 104 °C.
10:07	10.596	72	42.8	22.4	21.4	--
10:12	9.144	83	56.4	23.2	22.2	--
10:20	--	96	78.6	23.1	21.8	--
10:26	8.730	99	81.6	23.8	21.5	--
10:32	8.716	100	82.7	23.6	21.3	--
10:35	8.705	101	83.8	23.4	21.2	Boiling.
10:40	--	101	85.0	23.5	22.2	--
10:45	--	101	84.9	23.6	22.6	--
10:50	8.661	101	85.5	23.3	21.8	--
10:52	8.709	101	84.6	23.2	21.6	Set point to 95°C.
11:33	8.699	94	74.5	22.7	20.9	Began forming.
11:38	8.834	94	75.8	23.1	21.3	--
11:42	8.793	94	77.1	23.5	21.8	--
11:46	8.729	94	76.7	23.6	22.0	Smooth surface.
11:51	8.630	94	76.4	23.3	21.5	--
11:54	8.445	94	76.3	23.1	21.3	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
11:58	8.403	94	76.4	22.9	21.2	--
12:03	7.625	94	76.3	22.9	20.8	--
12:00	7.097	94	75.2	22.8	20.9	Surface foam.
12:15	6.998	96	69.5	23.7	21.8	--
12:20	6.326	95	69.4	23.4	21.6	--
12:25	5.978	95	67.6	22.9	21.2	--
12:30	5.652	95	68.7	22.9	20.8	--
12:35	5.366	95	68.1	22.8	20.6	--
12:40	5.164	95	67.6	22.6	20.7	--
12:45	4.876	95	66.6	23.2	21.2	Surface foam.
12:50	4.816	95	71.1	23.6	21.9	--
12:55	4.498	95	70.2	23.4	21.5	--
13:03	4.455	95	71.9	23.3	21.0	--
13:05	4.444	95	70.7	23.3	21.0	--
13:10	4.630	95	72.1	23.2	20.9	--
13:15	4.400	95	70.3	23.1	20.7	--
13:20	4.241	95	69.5	23.3	20.6	--
13:25	4.333	95	68.9	23.8	21.3	--
13:30	4.259	95	54.4	24.0	22.0	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
13:40	4.080	95	53.7	24.2	21.1	--
13:53	4.061	95	54.0	23.4	20.9	--
13:58	3.999	95	55.4	23.4	21.0	--
14:03	3.843	95	54.0	23.4	21.0	--
14:10	4.095	95	55.1	24.1	21.7	--
14:17	3.980	95	49.3	23.9	21.8	--
14:25	3.930	95	49.2	23.8	21.2	--
14:30	3.846	95	48.2	23.6	20.9	--
14:43	3.661	95	47.7	23.7	21.1	--
14:47	3.637	95	48.5	24.6	21.6	--
14:51	3.626	95	47.9	24.2	21.9	--
14:55	3.536	95	47.3	23.9	21.7	--
15:00	3.528	95	46.8	26.6	21.6	--
15:05	3.483	95	46.8	23.6	21.0	--
15:10	3.448	95	47.6	23.5	20.9	--
15:18	3.219	95	46.2	23.2	20.6	--
15:25	3.388	95	48.4	23.9	21.6	--
15:30	3.297	95	48.6	24.0	21.9	--
15:33	2.968	95	--	--	--	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
15:35	3.114	95	48.5	23.7	21.6	Formating completed.
15:55	3.425	98	64.9	22.8	21.2	--
16:01	3.425	100	56.7	23.1	21.3	Boiling-small patches surface foam.
16:05	3.436	100	57.6	23.4	21.9	--
16:10	3.409	101	57.7	23.6	22.2	--
16:15	3.355	102	55.6	23.3	21.7	Creamy surface foam.
16:33	3.566	99	51.7	22.8	21.3	--
16:38	3.613	101	54.1	23.4	21.9	--
16:43	3.648	102	55.1	23.7	22.2	--
16:50	3.647	102	53.9	23.3	21.9	--
16:55	3.636	101	55.2	23.1	21.7	--
16:58	5.597	96	--	--	--	--
17:05	3.605	100	53.5	23.1	21.1	Added 79.50 g DIW.
17:10	3.667	101	56.3	23.9	21.7	Few surface bubbles.
17:14	3.528	102	56.6	24.2	22.1	--
17:20	3.676	101	54.7	23.9	22.3	--
17:26	3.648	101	54.8	23.6	21.7	--
17:31	3.616	97	50.7	--	--	Added 78.82 g DIW.
17:40	3.531	99	54.8	23.3	21.3	--

Date/Time	pH	Slurry	Temperatures (°C)			Activity/Observations
			Condenser			
			#1	#2	#3	
17:47	3.654	101	54.1	23.9	21.8	Few surface bubbles.
17:52	3.670	102	54.8	24.1	22.4	--
17:56	3.544	102	53.7	23.9	22.4	--
18:00	--	97	--	--	--	Added 78.18 g DIW.
18:19	3.662	100	50.3	23.2	21.3	--
18:26	3.738	103	51.1	23.9	22.4	Creamy surface foam.
18:31	3.747	102	49.6	23.8	22.1	--
18:35	3.411	98	--	--	--	Added 38.83 g DIW.
18:44	3.706	101	49.7	23.1	21.4	--
18:48	3.717	101	50.2	23.0	21.3	--
18:56	3.819	101	51.0	23.5	21.9	--
19:01	3.825	101	51.6	23.8	22.5	--
19:10	3.466	101	51.0	23.3	21.8	--
19:13	3.427	96	--	--	--	Added 79.83 g DIW.
19:24	3.527	102	52.5	23.6	21.6	--
19:29	3.507	101	53.7	23.4	21.6	--
19:34	3.496	101	54.0	23.8	21.5	--
19:43	3.462	101	54.8	24.0	21.5	--
19:47	3.665	101	54.8	29.3	21.7	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
19:55	3.612	101	54.5	24.3	22.3	--
20:03	3.522	101	55.0	24.2	22.3	Set point to 0°C. Added 91.65 g DIW.
20:15	3.890	85	39.5	23.4	21.8	Stirrer off. Air flow off.

Table A.18. HCOOH Addition - Test T93-NM-5

Time	Minutes Relative to Start of HCOOH Addition (min)	Weight of 90.6 Wt % HCOOH Added (g)
11:39	0	0.0
11:42	3	3.3
11:46	7	5.2
11:51	12	8.1
11:54	15	9.9
11:58	19	12.3
12:03	24	15.1
12:06	27	17.2
12:15	36	22.4
12:20	41	25.3
12:25	46	28.1
12:30	51	31.0
12:35	56	34.0
12:40	61	37.1
12:45	66	40.2
12:50	71	43.3
12:55	76	46.3
13:05	86	53.0
13:10	91	55.4
13:15	96	58.4
13:20	101	61.3
13:25	106	64.1
13:30	111	67.0
13:40	121	72.5
13:53	134	78.0
13:58	139	82.9
14:03	144	85.8
14:10	151	89.9
14:17	158	93.9
14:25	166	98.5
14:30	171	101.4
14:43	184	109.3
14:34	175	250.4
14:47	188	111.4
14:51	192	113.7
14:55	196	116.0
15:00	201	119.1
15:05	206	121.9
15:10	211	124.8
15:18	219	129.9
15:25	226	133.7
15:30	231	136.6
15:33	234	138.3
15:35	236	139.5
Total HCOOH Added:		139.5

Table A.19. Gram Waste Oxide Tracking Log - Test T93-NM-5

Sample/Action	Sample Type	Sample Weight (g)	Calc. Sample Volume (mL)	Slurry Weight (g)	Slurry Volume (mL)	Oxide Loading (gWO/L)	Total Oxide Weight (g)	Calc. Density (g/mL)
Initial slurry	N/A	N/A	N/A	1680	1500	127	190.5	1.120
Rh Metals slurry addition	N/A	19.52	19.52	1700	1520	125	190.5	1.118
T93-NM-5-2-1	Primary Condensate (Replaced)	77.40	77.40	1700	1520	125	190.5	1.118
T93-NM-5-2-1s	Secondary Condensate (Replaced)	1.58	1.58	1700	1520	125	190.5	1.118
T93-NM-5-1-1	Slurry	14.12	12.62	1685	1507	125	188.9	1.118
Antifoam	N/A	10.00	10.00	1695	1517	125	188.9	1.118
T93-NM-5-2-2	Primary Condensate	340.57	340.57	1355	1176	161	188.9	1.152
T93-NM-5-2-2s	Secondary Condensate	15.44	15.44	1339	1161	163	188.9	1.154
T93-NM-5-1-2	Slurry	16.40	14.21	1323	1147	163	186.6	1.154
T93-NM-5-2-3	Primary Condensate (Replaced)	437.73	437.73	1323	1147	163	186.6	1.154
T93-NM-5-2-3s	Secondary Condensate (Replaced)	9.08	9.08	1323	1147	163	186.6	1.154
T93-NM-5-1-3	Slurry	17.82	15.45	1305	1131	163	184.1	1.154
Final Measured Slurry Weight:				1210.6				

Table A.20. Analytical Laboratory Results - Test T93-NM-5

Sample ID	Time	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH @ RT	NH ₃ (g/L)	HCOO ⁻ (g/L)	NO ₂ ⁻ (g/L)	NO ₃ ⁻ (g/L)
SLURRY												
T93-NM-5-1-1	11:05	Initial	14.12	1685	1507	125	1.118	11.14	0.00080	0.0086	22.8	7.8
T93-NM-5-1-2	15:35	Formating	16.40	1323	1147	163	1.154	5.37	0.0009	38.6	12.1	11.30
T93-NM-5-1-3	20:06	Digestion	17.82	1305	1131	163	1.154	4.70	0.044	84.60	1.3	16.2
CONDENSATE (Sample Weight indicates entire condensate collected during time period.)												
T93-NM-5-2-1	10:53	Initial	77.40	1700	1520	125	1.118	8.93	0.0056	0.0030	0.00088	0.0012
T93-NM-5-2-1s	10:54	Initial	1.58	1700	1520	125	1.118	n/a	0.0083	0.20	< 0.020	0.46
T93-NM-5-2-2	15:30	Formating	340.57	1355	1176	161	1.152	2.17	< 0.00010	4.4	< 0.020	0.99
T93-NM-5-2-2s	15:30	Formating	15.44	1339	1161	163	1.154	1.32	0.0600	1.9	0.027	9.0
T93-NM-5-2-3	16:35-19:47	Digestion	437.73	1323	1147	163	1.154	2.64	0.00025	2.3	< 0.030	< 0.030
T93-NM-5-2-3s	16:35-19:47	Digestion	9.08	1323	1147	163	1.154	2.07	0.0010	7.0	< 0.030	0.85
Drierite			123.16							10 µg NH ₃ / g drierite		

Test T93-NM-6: 25% Nominal Noble Metals

Figure A.26. Offgas Profile for Test T93-NM-6 Containing 25% Nominal Noble Metals

Figure A.27. Hydrogen Offgas Profile for Test T93-NM-6 Containing 25% Nominal Noble Metals

Figure A.28. Carbon Dioxide Offgas Profile for Test T93-NM-6 Containing 25% Nominal Noble Metals

Figure A.29. Nitrogen Oxide Offgas Profile for Test T93-NM-6 Containing 25% Nominal Noble Metals

Figure A.30. Nitrous Oxide Offgas Profile for Test T93-NM-6 Containing 25% Nominal Noble Metals

Table A.21. Activity Log - T93-NM-6

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
<u>7/23/93</u>						
9:30	11.257	22	21.7	22.0	20.7	Set point to 100°C.
9:42	10.790	43	27.9	21.3	19.9	--
9:52	10.285	69	48.2	21.2	20.0	--
10:02	9.479	90	74.1	21.3	19.9	--
10:06	9.231	96	82.1	21.4	19.9	Set point to 103°C.
10:12	9.108	99	86.4	21.7	20.0	--
10:17	9.093	100	87.4	21.9	19.9	--
10:30	9.075	101	88.7	22.2	19.9	Boiling.
10:35	9.045	101	89.0	22.2	19.9	--
10:40	9.041	102	89.3	22.4	20.1	--
10:46	9.043	101	88.3	22.2	19.9	Set point to 95°C.
11:36	9.127	94	84.1	23.5	22.7	Began HCOOH addition.
11:45	9.055	94	83.4	22.9	21.3	--
11:47	8.948	94	83.4	23.1	21.2	--
11:55	8.249	95	83.4	24.2	22.6	--
12:05	8.122	95	83.9	24.9	23.4	--
12:08	6.882	95	80.6	25.1	23.6	Surface foam.

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
12:20	6.225	96	76.2	25.2	23.8	--
12:42	5.111	96	76.4	25.3	23.8	Some foam. 0.7 g HCOOH/min addition rate.
12:54	4.595	95	81.3	25.6	23.9	0.70 g/min addition rate.
13:04	4.399	96	79.7	25.6	23.8	--
13:13	4.323	96	77.4	25.6	23.9	--
13:19	4.311	96	76.9	25.6	24.0	--
13:24	4.310	96	77.0	25.6	24.0	--
13:30	4.307	96	77.7	25.0	23.0	--
13:36	4.273	95	79.3	23.6	21.2	--
13:41	4.242	95	80.3	23.3	20.8	--
13:46	4.208	95	81.4	23.1	20.6	--
13:51	4.196	95	81.7	22.8	20.5	--
13:55	4.167	95	81.8	22.7	20.4	--
14:00	4.155	95	82.0	22.7	20.3	--
14:12	4.113	95	82.1	22.3	20.2	--
14:20	4.081	95	82.1	22.4	20.1	--
14:25	4.067	95	82.2	22.2	20.1	--
14:33	4.024	95	82.3	22.2	20.1	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
14:40	4.004	95	82.6	22.1	20.1	--
14:45	4.001	95	82.5	22.1	20.1	--
14:52	3.959	95	84.2	22.0	20.2	--
14:56	3.904	94	84.7	22.1	20.2	--
15:01	3.857	95	84.9	22.1	20.4	GC computer malfunction.
15:16	3.900	95	84.9	22.0	20.0	Formating completed. Temperature to 100°C.
15:30	3.971	100	88.1	22.2	20.2	--
15:38	3.976	100	87.7	23.3	19.9	--
15:43	4.027	101	87.7	22.5	20.0	Surface foam.
15:47	4.034	101	88.3	22.3	19.9	--
15:57	4.013	101	87.6	22.6	19.9	--
16:09	4.027	100	88.3	22.6	20.9	Added 89.8 g Deionized Water (DIW).
16:13	4.021	97	86.8	22.5	19.9	--
16:19	4.061	100	88.9	22.6	19.9	--
16:26	4.067	101	89.4	22.6	19.9	--
16:32	4.104	101	89.6	22.7	20.1	--
16:36	4.105	100	89.7	22.6	20.1	--
16:43	4.104	100	89.2	22.6	20.1	--

Date/Time	pH	Temperatures (°C)				Activity/Observations
		Slurry	Condenser			
			#1	#2	#3	
16:49	4.084	101	90.3	22.7	19.9	--
16:54	4.057	101	90.1	22.8	19.9	--
16:58	4.053	101	90.2	22.8	20.2	--
17:03	4.045	101	90.3	22.8	19.9	--
17:10	4.030	101	90.2	22.7	20.1	--
17:14	4.034	101	90.1	22.7	20.0	--
17:15	4.034	101	90.0	22.8	19.9	Temperature to 0°C. Added 96.8 g DIW.
17:33	--	86	--	--	--	Shut off gas flow and stirrer.

Table A.22. HCOOH Addition - Test T93-NM-6

Time	Minutes Relative to Start of HCOOH Addition (min)	Weight of 90.6 Wt % HCOOH Added (g)
11:44	0	0.0
11:47	3	8.0
11:55	11	13.5
12:05	21	18.8
12:20	36	28.1
12:42	58	43.6
12:54	70	52.0
13:04	80	59.0
13:13	89	65.3
13:19	95	69.4
13:24	100	72.9
13:30	106	77.1
13:36	112	81.3
13:41	117	84.8
13:46	122	88.1
13:51	127	91.6
13:55	131	94.9
14:00	136	97.7
14:12	148	106.3
14:20	156	111.7
14:25	161	115.2
14:33	169	120.8
14:40	176	126.0
14:45	181	129.0
14:52	188	133.9
14:56	192	136.6
15:01	197	140.0
Total HCOOH Added:		140.0

Table A.23. Gram Waste Oxide Tracking Log - Test T93-NM-6

Sample/Action	Sample Type	Sample Weight (g)	Calc. Sample Volume (mL)	Slurry Weight (g)	Slurry Volume (mL)	Oxide Loading (gWO/L)	Total Oxide Weight (g)	Calc. Density (g/mL)
Initial slurry	N/A	N/A	N/A	1680	1500	127	190.5	1.120
Noble Metals slurry addition	N/A	12.00	12.00	1692	1512	126	190.5	1.119
T93-NM-6-2-1	Primary Condensate (Replaced)	102.00	102.00	1692	1512	126	190.5	1.119
T93-NM-6-2-1s	Secondary Condensate (Replaced)	1.00	1.00	1692	1512	126	190.5	1.119
T93-NM-6-1-1	Slurry	17.80	15.91	1674	1496	126	188.5	1.119
Antifoam	N/A	10.00	10.00	1684	1506	125	188.5	1.118
T93-NM-6-2-2	Primary Condensate	225.30	225.30	1459	1281	147	188.5	1.139
T93-NM-6-2-2s	Secondary Condensate	11.70	11.70	1447	1269	149	188.5	1.140
T93-NM-6-1-2	Slurry	12.84	11.26	1434	1258	149	186.8	1.140
T93-NM-6-2-3	Primary Condensate (Replaced)	265.30	265.30	1434	1258	149	186.8	1.140
T93-NM-6-2-3s	Secondary Condensate (Replaced)	6.90	6.90	1434	1258	149	186.8	1.140
T93-NM-6-1-3	Slurry	15.8	13.86	1419	1244	149	184.8	1.140
Final Measured Slurry Weight:				1470.7				

Table A.24. Analytical Laboratory Results - Test T93-NM-6

Sample ID	Time	Description	Sample Weight (g)	Slurry Weight (g)	Slurry Volume (mL)	Waste Oxide Loading (gWO/L)	Slurry Density (g/mL)	pH @ RT	NH ₃ (g/L)	HCOO ⁻ (g/L)	NO ₂ ⁻ (g/L)	NO ₃ ⁻ (g/L)
SLURRY												
T93-NM-6-1-1	11:13	Initial	17.80	1674	1496	126	1.119	11.08	0.00023	0.92	23.1	7.79
T93-NM-6-1-2	15:18	Formating	12.80	1434	1258	149	1.140	3.92	0.00044	68.5	0.96	13.0
T93-NM-6-1-3	17:26	Digestion	15.80	1419	1244	149	1.140	4.20	0.017	69.2	< 0.5	12.8
CONDENSATE (Sample Weight indicates entire condensate collected during time period.)												
T93-NM-6-2-1	10:47	Initial	102.00	1692	1512	126	1.119	2.80	0.0075	0.0015	0.00116	0.196
T93-NM-6-2-1s	10:47	Initial	4.00	1692	1512	126	1.119	2.36	0.045	0.023	<0.02	0.872
T93-NM-6-2-2	15:12	Formating	225.30	1459	1281	147	1.139	2.00	0.00036	1.81	<0.02	1.20
T93-NM-6-2-2s	15:12	Formating	11.70	1447	1269	149	1.140	1.38	0.0075	1.98	<0.02	6.89
T93-NM-6-2-3	17:11	Digestion	265.30	1434	1258	149	1.140	2.45	< 0.00010	4.79	<0.02	0.069
T93-NM-6-2-3s	17:11	Digestion	6.90	1434	1258	149	1.140	1.67	0.0075	7.19	<0.02	3.00

pH and HCOOH Addition Graphs

Figure A.31. pH Measured at Process Temperature During Six Tests

Figure A.32. Formic Acid Addition During Six Tests

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