

PNNL-10983

UC-810

Project Technical Information

RECEIVED

MAR 22 1996

OSTI

**Hanford Waste Vitrification Plant
Hydrogen Generation Study:
Formation of Ammonia from Nitrate
and Nitrite in Hydrogen Generating
Systems**

**R. B. King
N. K. Bhattacharyya**

February 1996

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

**Pacific Northwest National Laboratory
Richland, Washington 99352**



MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED 35

Hanford Waste Vitrification Plant Hydrogen Generation Study: Formation of Ammonia from Nitrate and Nitrite in Hydrogen Generating Systems

R. B. King
N. K. Bhattacharyya

February 1996

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

Pacific Northwest National Laboratory
Richland, Washington 99352

DISCLAIMER

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

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC06-76RLO 1830

Printed in the United States of America

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

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



The document was printed on recycled paper.

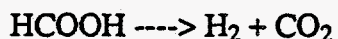
Contents

1.	Introduction.....	1
2.	Summary and Recommendations.....	2
3.	Experimental Approach	3
	3.1 Feed simulant experiments	3
	3.2 Gas analyses.....	4
	3.3 pH monitoring.....	4
	3.4 Ammonia analyses.....	5
4.	Results	5
	4.1 Ammonia analyses of previous runs.....	5
	4.2 Ammonia monitoring of runs with supported rhodium catalysts	7
	4.3 Studies with a nitrogen-free feed simulant	8
	4.4 Carbon balance studies	10
	4.5 Limited component experiments.....	12
5.	Literature References	17

1. Introduction

The Hanford Waste Vitrification Plant (HWVP) is being designed for the Department of Energy (DOE) to immobilize pretreated highly radioactive wastes in glass for permanent disposal. In the HWVP, formic acid is added to the waste before vitrification to adjust glass redox and melter feed rheology. The operation of the glass melter and durability of the glass are affected by the glass oxidation state. Formation of a conductive metallic sludge in an over-reduced melt can result in a shortened melter lifetime. An over-oxidized melt may lead to foaming and loss of ruthenium as volatile RuO_4 . Historically, foaming in the joule heated ceramic melter has been attributed to gas generation in the melt which is controlled by introduction of a reductant such as formic acid into the melter feed. Formic acid is also found to decrease the melter feed viscosity thereby facilitating pumping.

The catalytic decomposition of formic acid can lead to the unwanted generation of hydrogen by the reaction

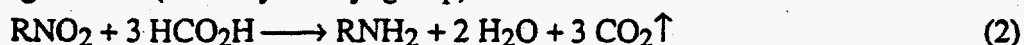


The catalytic role of the noble metals fission products, Ru, Rh, and Pd, in hydrogen generation from formic acid is discussed in previous technical reports. This technical report discusses the noble metal catalyzed formic acid reduction of nitrite and/or nitrate to ammonia, a problem of considerable concern because of the generation of a potential ammonium nitrate explosion hazard in the plant ventilation system.

2. Summary and Recommendations

The work summarized in previous technical reports^{2,3} suggests that the predominant source of hydrogen generation from the formic acid treatment of nuclear waste simulants containing nitrite and nitrate is a nitrite-promoted homogeneous rhodium-catalyzed process. A mechanism has been proposed for this process based on nitrorhodium(III) intermediates.³ In the case of ammonia generation from the formic acid treatment of the same nuclear waste feed simulants, the predominant process appears to be heterogeneous catalysis involving supported rhodium or palladium metal catalysts. Thus 5% rhodium metal supported on carbon or alumina is a considerably more active catalyst for ammonia production than soluble rhodium trichloride. Nitrate rather than nitrite appears to be the major nitrogen source for ammonia production as shown by experiments in which either nitrate or nitrite is added to a special nitrogen-free feed simulant. The following observations indicate the close similarity between the noble metal-catalyzed formic acid reduction of nitrate to ammonia on the one hand and organic hydrogenation processes^{4,5,6,7,8} on the other hand:

- (1) The supported noble metal catalysts, namely supported rhodium and palladium catalysts, are the same as those which are most active for organic hydrogenations under the mildest conditions;
- (2) Ammonia production from the noble metal-catalyzed formic acid reduction of nitrate appears to occur at the expense of hydrogen production. For example, 5% Rh/C and Rh/Al₂O₃ are good catalysts for ammonia production but poor catalysts for hydrogen production whereas RhCl₃ is a good catalyst for hydrogen production but a poor catalyst for ammonia production. Furthermore, in some of the experiments with supported palladium catalysts, some of the initially produced H₂ in the closed system is consumed as ammonia is produced.
- (3) Formic acid is known^{9,10,11} to be a transfer hydrogenation reagent for conversion of nitro compounds to amines in the presence of noble metal catalysts according to the following reaction (R = alkyl or aryl group):



Palladium on charcoal is among the most active catalysts for this reaction.⁹

These studies of ammonia production upon formic acid treatment of nitrate-containing feed simulants suggest further work in the following areas in order to obtain a greater understanding of the chemistry of reactions of formic acid with nuclear wastes:

- (1) The reaction conditions for the formic acid treatment of nitrate-containing feed simulants in the presence of supported palladium catalysts are similar to those used for the

palladium-catalyzed hydrogenation of nitrate to hydroxylamine.^{12,13,14} This suggests that reduction to hydroxylamine could be another fate of some of the nitrogen in feed simulant media upon formic acid treatment. Experiments designed to monitor the formation of hydroxylamine in feed simulant media upon treatment with formic acid are of interest. Electrochemical methods may be applicable for hydroxylamine analyses in feed simulant media based on the methodology used in the Russian work.^{12,13,14}

(2) Formation of ammonia upon treatment of nitrate- and iron-containing feed simulants appears to be accompanied by reduction of some of the iron(III) to iron(II) as indicated by the CO₂ balance as well as the color of the iron hydroxide precipitate when aliquots of the reaction mixture are made basic prior to analysis with the ammonia electrode. Use of a redox probe to monitor the redox potential of the feed simulant during formic acid titration might allow this effect to be measured.

3. Experimental Approach

3.1 Feed simulant experiments

The experimental methods were similar to those used in previous work³ with the necessary modifications to allow monitoring of ammonia production. Thus the reactions were conducted in glass reaction vessels of ~550 mL total capacity equipped with a threaded plug and O-ring adapter. A pressure gauge was attached to the system. The three side-arms of the vessel near the top were capped with rubber septa through which needles could be inserted to flush the system or to sample the gas phase. A fourth opening also capped by a rubber septum was used for the periodic withdrawal of liquid samples from the reaction mixture for ammonia analyses. The reaction vessel had two thermocouple wells. A thermocouple attached to a cycle heater was placed in one well to maintain a constant temperature. The other well was used to check the temperature of the reaction mixture independently with a second thermocouple. The reaction mixture was stirred magnetically during the course of the experiment.

In typical experiments a reaction vessel of the above type was charged with 50 mL of the feed simulant or other reaction medium, 10 mL of water, and a solid noble metal catalyst. After flushing the mixture with argon, the system was closed and the gas phase analyzed using the system described below. The solution was warmed to the desired reaction temperature (typically 90°C) and kept there using a temperature controller. Formic acid was then added below the surface of the feed simulant from a 10 mL plastic BD disposable syringe driven by a Sage Instruments Model 355 syringe pump set to deliver 0.0194 mL/min (1.164 mL/hr) corresponding to 0.448 mmoles HCO₂H/min or 26.9

mmoles $\text{HCO}_2\text{H/hr}$. The setting on the syringe pump to achieve this rate of addition was checked weekly with pure water. The pressure gauge was used to monitor the pressure buildup from the gases produced during the experiment and to assure the absence of leaks. Pressures in excess of 30 psig were frequently found to cause leakage problems and thus were avoided by limiting the amount of feed simulant used. Gas samples were withdrawn periodically at the reaction temperature using a Pressure-Lok syringe inserted into one of the rubber septa; these samples were analyzed immediately by gas chromatography as indicated below. Liquid samples were also withdrawn periodically using a 1 mL syringe and analyzed for $\text{NH}_4^+/\text{NH}_3$ using the ammonia microelectrode described below.

A summary of all of the experiments of this type is given in Appendix A.

3.2 Gas analyses

Hydrogen analyses were performed using a Varian 90P gas chromatograph. The hydrogen was eluted on an 20 cm \times 6 mm column packed with a 40/60 mesh 13 \times molecular sieve material obtained from Varian Corporation. Argon was used as the carrier gas. The column temperature was maintained at 80°C. Carbon monoxide, carbon dioxide, nitrous oxide, and nitric oxide were monitored using a Fisher Model 1200 gas partitioner. The gases were separated on the basis of their size and polarity by means of two columns, a 2m 80/100 mesh Columnpak PQ and a 3.3 m 13 \times molecular sieve column mounted in series using helium as the carrier gas. The temperatures of both columns were maintained at 50°C. Sensitivity factors were determined from known amounts of pure certified samples of the gases of interest and were rechecked every week. Nitrogen dioxide could not be determined by gas chromatography because of the $\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ equilibrium.

3.3 pH monitoring

The pH of selected reactions was monitored using an Ingold HA405-DXK-58/120 Combination Xerolyt pH electrode with a 2–14 pH range and a 0–110°C temperature range and resistant to pressures up to 16 bar at 25°C and 6 bar at 100°C without pressure compensation. Temperature compensation for the pH measurements was effected with a PT 100-S8-120 automatic temperature compensator. The pH electrode and temperature compensator were connected to an Ingold Model 2300 pH transmitter which could read both pH and temperature. Before each experiment a two-point calibration of this system was performed using standard pH 2.00 and 9.00 buffers.

3.4 Ammonia analyses

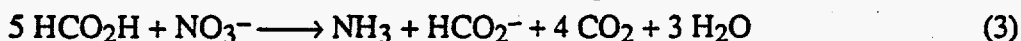
After completion of the treatment of the feed simulants with the formic acid, the resulting reaction mixture was analyzed for ammonium ion produced by nitrate or nitrite reduction. In this connection a 0.5 mL sample of the reaction mixture was diluted with 0.5 mL of distilled water and then made strongly basic with 1 to 2 drops of 10 *N* sodium hydroxide in order to convert NH_4^+ to NH_3 . The ammonia concentration was then determined using a MI-740 microammonia electrode obtained from Microelectrodes, Inc., Londonderry, New Hampshire. This electrode is designed to measure ammonia gas and to record the ammonia concentration as millivolts on a standard pH meter; an Orion 290A portable pH meter was used for these studies. The ammonia electrode was calibrated before each analysis using 0.1 *N*, 0.01 *N*, and 0.001 *N* NH_4Cl solutions made basic with 10 *N* sodium hydroxide.

4. Results

4.1 Ammonia analyses of previous runs.

The concentrations of ammonium ion produced by selected syringe pump titrations of various nitrite and/or nitrate-containing feed simulants with 88 wt % formic acid in the presence of various noble metals during the period July, 1992, to July 1993, were determined by ammonia analyses as outlined above. The ammonia analyses were performed on the residues remaining from the experiments, which had been stored in sealed screw cap bottles since completion of the experiments.

The results summarized in Table 1 indicate that the only experiments which produced significant quantities of ammonia (> 1 mmole) were the runs using the rhodium catalysts supported on charcoal or alumina (the 9/2/92 and 10/2/92 experiments, respectively). These experiments are also distinguished by the production of far too much carbon dioxide¹⁵ to arise solely from reactions of formic acid leading to carbonate decomposition, MnO_2 reduction to Mn^{2+} , nitrite reduction to N_2O , and formic acid decomposition to H_2 . In addition the final pH in both of these experiments is much higher (6.9) than the final pH in any of the other formic acid titrations (2.9 to 4.3). Production of each mole of ammonia by nitrate reduction can convert four moles of formic acid to carbon dioxide and neutralizes a fifth mole of formic acid to give formate, i.e.



The observed final pH of 6.9 is outside the range of the formic acid/formate buffer (pK of $\text{HCO}_2\text{H} = 3.7$) but in the range of the carbonic acid/bicarbonate buffer (pK_1 of $\text{H}_2\text{CO}_3 = 6.4$). Thus some of the carbon dioxide liberated by the formic acid forms the bicarbonate ion and thus cannot be measured in the gas phase.

Table 1
Ammonia Analyses on Samples from Selected Titrations of Feed Simulants
with Formic Acid During the Period July, 1992, to July 1993

Date	Sample (Amount, mL)	Catalyst (Amount, mg)	HCO ₂ H mL(added over min)	Temp °C	Final mmol H ₂	Final pH	Final NH ₃ mmoles
7/10/92	11XFe1(50)	RhCl ₃ ·3H ₂ O(14)	3.72(190)	93±2	1.4	4.3	0.0
4/27/93	12M1F	RhCl ₃ ·3H ₂ O(14)	3.63(190)	89±1	1.4	4.3	0.0
9/2/92	12M1A(50)	5% Rh/C(117)	3.53(190)	90±1	0.2	6.9	15.0
10/2/92	12M1B(50)	5% Rh/Al ₂ O ₃ (115)	3.67(190)	88-91	0.3	6.9	5.4
9/10/92	13M+Rh1(50)	RhCl ₃ ·3H ₂ O(14)	3.53(190)	90±2	4.8	4.1	0.1
8/19/92	13M+Rh1(50)	0	3.53(190)	91±2	0.4	3.9	0.3
11/17/92	12M1C(50)	RhCl ₃ ·3H ₂ O(14)	3.71(190)	70-90	1.4	3.5	0.2
12/18/92	12M1D(50)	RhCl ₃ ·3H ₂ O(14) CuCl ₂ (100mg)	3.40(185)	90±1	0.3	4.3	0.1
12/23/92	water(50) NaNO ₂ (1.5g)	RhCl ₃ ·3H ₂ O(14) CuCl ₂ (100mg)	3.71(190)	90±1	6.3	2.9	0.2
1/20/93	10M1EXNN'(50), NaNO ₂ (0.5g), NaNO ₃ (0.5g)	RhCl ₃ ·3H ₂ O(14)	3.75(190)	92±1	1.5	3.3	0.3
1/14/93	water(50) NaNO ₂ (1.5g)	RhCl ₃ ·3H ₂ O(14)	3.46(180)	91±1	10.0	2.6	0.3
1/21/93	10M1EXNN'(50), NaNO ₂ (0.1g), NaNO ₃ (0.5g)	RhCl ₃ ·3H ₂ O(14)	3.75(190)	90±1	11.7	3.3	0.2
1/22/93	10M1EXNN'(50), NaNO ₂ (0.025g), NaNO ₃ (0.5g)	RhCl ₃ ·3H ₂ O(14)	3.75(190)	91±1	4.5	3.2	0.2
4/8/93	10M1FXNN'(50), NaNO ₂ (1.5g), NaNO ₃ (0.5g)	RhCl ₃ ·3H ₂ O(14)	3.67(190)	100±1	1.6	4.3	0.1
7/9/93	12M1F(50)	RhCl ₃ ·3H ₂ O(14)	3.61(190)	91±1	1.9	4.1	0.2
5/11/93	11XFe1(50)	RhCl ₃ ·3H ₂ O(14)	3.65(190)	88±1	1.8	4.3	0.1
5/13/93	11XA11(50)	RhCl ₃ ·3H ₂ O(14)	3.65(190)	88±2	1.2	4.2	0.1
9/30/92	12M1B(50)	PdCl ₂ (12)	3.67(190)	90±2	0	5.4	0.4
6/30/92	11XN1(50)	PdCl ₂ (13)	3.42(118)	95±4	0.2	6.0	0.2
5/7/93	10M1EXNN'(50)	PdCl ₂ (15)	3.65(190)	88±1	1.0	4.6	0.3
1/8/93	water(60), NaNO ₂ (1.5g), HCO ₂ Na(6.2g)	PdCl ₂ (14)	0	92±1	0.1	10.6	0.1
1/9/93	water(60), NaNO ₂ (0.5g), HCO ₂ Na(6.2g)	PdCl ₂ (14)	0	92±2	1.4	10.0	0.8
1/13/93	water(60), HCO ₂ Na(6.2g)	PdCl ₂ (14)	0	90±2	1.4	9.6	0
12/3/92	11MDXC(50)	"RuCl ₃ ·3H ₂ O"(15)	3.53(182)	89±1	0	2.7	0.1
5/19/93	12M1F(50)	"RuCl ₃ ·3H ₂ O"(15)	3.63(190)	90±1	0	3.9	0.1

These observations suggest that ammonia production by the rhodium catalyzed reduction of nitrite or nitrate ion by formic acid is highly dependent on the form of the rhodium. Thus highly dispersed rhodium on alumina or charcoal is a very active catalyst whereas soluble rhodium compounds (such as the nitrorhodium complexes obtained from rhodium chloride and nitrite ion) are much less active catalysts. Furthermore, rhodium coprecipitated with the iron fraction in the feed simulant UGA-13+Rh1 is not an active catalyst even though the hydrous rhodium oxide is presumably dispersed in the other insoluble metal hydrous oxides.

4.2 Ammonia monitoring of runs with supported rhodium catalysts

The initial studies were performed using the UGA-12M1 feed simulant and 5% rhodium on charcoal or alumina since the ammonia analyses on reaction products from various experiments performed in 1992 summarized in Table 1 suggested that these supported rhodium metal catalysts produced the largest amounts of ammonia. Figures 1 and 2 show the production of H₂, NH₃, N₂O, NO, and CO₂ from the full feed simulant UGA-12M1H upon titration with 88 wt % formic acid in the presence of 5% Rh/C (Figure 1) and 5% Rh/Al₂O₃ (Figure 2), respectively, at 90°C. Both of these experiments using supported rhodium metal catalysts are seen to produce significant amounts of ammonia. In fact the amounts of ammonia produced in these experiments are significantly larger than the amounts of hydrogen.

The use of supported rhodium *metal* catalysts appears to be essential for the production of relatively large amounts of ammonia. Thus titration of the full feed simulant UGA-12M1H with 88 wt % formic acid in the presence of rhodium trichloride (Figure 3), which are the standard conditions used for many of the experiments run during the past year, is seen to produce much more hydrogen and much less ammonia. Since ammonia production appears to occur at the expense of hydrogen production, we suspect that the supported rhodium metal catalysts are functioning as hydrogenation catalysts for nitrite, nitrate, and/or nitrogen oxides. This idea is also supported by the observed decrease in nitric oxide concentration to zero in the experiments using supported rhodium catalysts producing significant amounts of ammonia.

A question of considerable interest is whether nitrite or nitrate is the source of the ammonia nitrogen. In this connection the nitrite-free feed simulant UGA-10GXNN1 was titrated with formic acid in the presence of sodium nitrate as well as 5% rhodium on charcoal (Figure 4). The amount of ammonia produced in this experiment (1.6 mmoles) was essentially identical to the amount of ammonia produced in an experiment using the full feed simulant UGA-12M1H containing nitrite (Figure 1). No nitrogen oxides were

observed in the experiment with the nitrite-free feed simulant indicating that rhodium cannot catalyze the formic acid reduction of *nitrate* to N_2O or NO .

Two other experiments indicate the role of supported rhodium metal catalysts in ammonia production from nitrogen-oxygen species and formic acid:

(1) The usual protocol for the preparation of UGA-10XNN' feed simulant was followed except that 0.284 g. of hydrated rhodium trichloride was added to the aluminum nitrate before precipitation of the aluminum hydroxide. The presence of rhodium(III) in the aluminum hydroxide precipitate was indicated by the tan color of the precipitate and a colorless supernatant liquid. Titration of this feed simulant with 88 wt % formic acid at $90^\circ C$ in the presence of sodium nitrate gave negligible amounts of ammonia and 0.4 mmoles of H_2 . This experiment suggests that supported rhodium must be the free metal (i.e., in the zero oxidation state) to exhibit high activity for the reduction of nitrate to ammonia by formic acid.

(2) Negligible amounts of ammonia were observed when the same UGA-10XNN'/ $NaNO_3$ mixture was titrated with 88 wt % formic acid at $90^\circ C$ in the presence of soluble rhodium trichloride rather than the 5% rhodium on carbon used in the experiment depicted in Figure 4.

Important conclusions suggested by the experiments outlined above concerning the rhodium-catalyzed reduction of nitrogen-oxygen compounds to ammonia by formic acid include the following:

- (1) Nitrate rather than nitrite is the principal source of ammonia.
- (2) Ammonia production appears to occur at the expense of hydrogen production.
- (3) Supported rhodium metal catalysts are more active than rhodium in any other form suggesting that ammonia production involves heterogeneous rather than homogeneous catalysis.

4.3 Studies with a nitrogen-free feed simulant

The protocol for the preparation of UGA-12M1 and related feed simulants uses nitrates as metal sources and therefore contains significant quantities of nitrate even if an alkali metal nitrate is not added later since residual nitrate remains even after thorough washing of the metal hydroxide/oxide precipitates. The presence of nitrate in the feed simulant complicates nitrogen balance studies such as those relating to the origin of ammonia. We have therefore developed the protocol described in Appendix B for the preparation of a nitrate-free (as well as nitrite-free) feed simulant. In connection with this protocol we were somewhat concerned whether the $KMnO_4/MnCl_2$ reaction would be a satisfactory method for the preparation of nitrate-free and organic-free MnO_2 because of the

possibility of permanganate oxidation of MnCl_2 to elemental chlorine, but apparently this is not significant in the pH range of feed simulant preparation. One liter of a carbonate-free version of this nitrogen-free feed simulant (designated as UGA-9M2XC) was prepared for initial nitrogen balance studies using the protocol in Appendix B.

The experiments with this nitrogen-free feed simulant are summarized in Table 2. In all of these experiments 50 mL of UGA-9M2XC and 10 mL of water were titrated with 84 mmoles of 88 wt % formic acid at $90 \pm 1^\circ\text{C}$ in the presence of the indicated noble metal derivative and NaNO_2 and/or NaNO_3 where indicated. In addition Figure 5 compares the formic acid titration of this feed simulant in the presence of 5% rhodium on carbon and added NaNO_2 or added NaNO_3 . Both of these experiments are seen to produce ammonia, but the experiment with added nitrate produces more ammonia (1.2 mmoles NH_3) than the experiment with added nitrite (0.6 mmoles NH_3). Furthermore in the experiment with added nitrate, formation of ammonia began almost immediately upon addition of the formic acid at the reaction temperature whereas in the experiment with added nitrite, formation of ammonia began only after reaction of formic acid with nitrite ion was complete (Figure 5). This suggests that the nitrate ion produced by disproportionation of nitrous acid according to equation 4 is the source of ammonia in the experiment in which nitrogen is only added in the form of nitrite.



Figure 6 compares the formic acid titrations of the UGA-9M2XC feed simulant at 90°C using 5% Pd on carbon as the catalyst and either NaNO_2 or NaNO_3 as the nitrogen source. The reaction with NaNO_3 generated considerable amounts of NH_3 , H_2 , and N_2O whereas the reaction with NaNO_2 generated no hydrogen and a much smaller amount of ammonia.

The following additional points are of interest concerning the experiments summarized in Table 2:

- (1) If a rhodium catalyst is used, nitrogen oxides are observed only in experiments with added nitrite. The N_2O remains until the end of the experiment whereas the initially produced NO is consumed during the experiment. The maximum amount of NO observed during this experiment was 7.3 mmoles. Rhodium catalysts thus appear incapable of generating N_2O from *nitrate* in the presence of formic acid.
- (2) Insignificant H_2 is produced in the absence of nitrite even in the experiment with $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in accord with the requirement of added nitrite for the rhodium-catalyzed decomposition of formic acid to $\text{H}_2 + \text{CO}_2$ (equation 1) indicated in previous work.^{2,3}
- (3) Palladium catalysts, unlike rhodium catalysts, catalyze the reduction of nitrate to N_2O as well as NH_3 . Palladium(II) chloride is a considerably less active catalyst precursor

than 5% Pd/C for the production of H₂, N₂O, and NH₃ consistent with the relative activity of Pd catalysts for formic acid transfer hydrogenolysis of aryl halides.¹⁶

(4) Addition of the NaNO₃ to the feed simulant one day in advance of beginning the reaction in order to allow more time for adsorption onto the solid phases had no significant effect on the production of H₂ or NH₃ in experiments using either RhCl₃·3H₂O or 5% Pd on carbon (Table 2).

Table 2
Studies Using the Nitrogen-free and Carbonate-free Feed Simulant UGA-9M2XC

Additive(g)	Noble Metal(mg)	mmol H ₂	mmol CO ₂	mmol N ₂ O	mmol NO	mmol NH ₃	Final pH
none	none	0.0	3.1	0.0	0.0	0.0	2.9
none	RhCl ₃ ·3H ₂ O(14)	0.0	4.3	0.0	0.0	0.0	3.0
none	5% Rh/C(116)	0.0	12.0	0.0	0.0	0.0	3.9
NaNO ₃ (1.9)	5% Rh/C(118)	0.1	16.7	0.0	0.0	1.2	4.0
NaNO ₃ (1.9)	RhCl ₃ ·3H ₂ O(14)	0.4	6.5	0.0	0.0	0.0	3.2
NaNO ₃ (1.9) ^a	RhCl ₃ ·3H ₂ O(14)	0.4	5.5	0.0	0.0	0.0	3.0
NaNO ₃ (1.9)	5% Pd/C(120)	0.4	33.1	3.7	0.0	1.4	5.0
NaNO ₃ (1.9) ^a	5% Pd/C(120)	0.8	33.6	3.5	0.0	1.4	5.0
NaNO ₃ (1.9)	PdCl ₂ (13)	0.3	18.7	1.2	0.0	0.2	4.0
NaNO ₂ (1.5)	5% Rh/C(118)	0.0	19.4	6.9	0.0	0.6	4.2
NaNO ₂ (1.5)	RhCl ₃ ·3H ₂ O(14)	1.5	15.3	5.8	4.5	0.1	3.7
NaNO ₂ (1.5)	5% Pd/C(120)	0.0	15.2	6.1	3.3	0.2	3.8

^a In these experiments the NaNO₃ was added to the feed simulant at least 12 hr. before the experiment in order to allow time for adsorption of nitrate ion onto the solid phase before initiation of the reaction.

4.4 Carbon balance studies

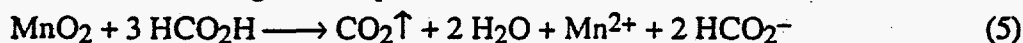
The carbon balance in the ammonia generation experiments is of interest. Table 3 compares the observed amounts of CO₂ with the total amount expected from carbonate acidification, MnO₂ reduction, H₂ generation, reduction of nitrite to N₂O, and reduction of nitrate to ammonia upon titration of the full metal nitrate-based feed simulant UGA-12M1 with formic acid in the presence of various rhodium catalysts. The experiments producing relatively large amounts of ammonia are seen to produce excess CO₂ even assuming the production of 4 mmoles of CO₂ for each mmole of NH₃ as required by equation 2 above.

A possible source of this excess CO₂ is partial reduction of the considerable amounts of iron(III) in the feed simulant to iron(II) under the conditions where nitrate is reduced to ammonia. This hypothesis is supported by the fact that the metal hydroxide precipitate obtained upon addition of base to samples for ammonia analysis is more green and less brown in samples containing appreciable amounts of ammonia suggesting that some reduction of iron(III) to iron(II) may be accompanying ammonia production. This possibility can be tested in the future by monitoring changes in the redox potential of the reaction mixture as ammonia is generated.

Table 3
Carbon Balance in the Titration of UGA-12M1 Feed Simulants with 88 wt % Formic Acid at 90°C in the Presence of Rhodium Catalysts

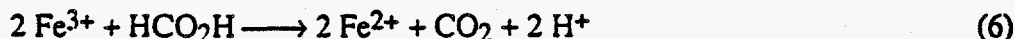
Sources of CO ₂	5% Rh/C Figure 1	5% Rh/Al ₂ O ₃ Figure 2	RhCl ₃ ·3H ₂ O Figure 3
Carbonate (1 mmole CO ₂ /mmole CO ₃ ²⁻)	6.2	6.2	6.2
MnO ₂ (1 mmole CO ₂ /mmole MnO ₂)	1.5	1.5	1.5
2NO ₂ ⁻ →N ₂ O (2 mmoles CO ₂ /mmole N ₂ O)	13.4	13.9	11.6
HCO ₂ H→H ₂ (1 mmole CO ₂ /mmole H ₂)	0.2	0.3	0.9
NO ₃ ⁻ →NH ₃ (4 mmoles CO ₂ /mmole NH ₃)	6.4	4.8	1.6
<i>Total mmoles CO₂ expected:</i>	27.7	26.7	21.8
<i>mmoles CO₂ observed</i>	30.4	30.3	20.4
<i>Excess CO₂ produced:</i>	2.7	3.6	-1.4

Some CO₂ balance observations were also made in the experiments using the nitrogen-free and carbonate-free feed simulant UGA-9M2XC summarized in Table 2. In these experiments the CO₂ produced in the absence of any additives (3.1 mmoles) must come from formic acid reduction of some of the metals in the feed simulant since this feed simulant contains no carbonate. Reduction of the 1.55 mmoles of MnO₂ present in 50 mL of UGA-9M2XC according to the equation



should give only 1.55 mmoles of CO₂ suggesting that the remainder of the observed 3.1 mmoles of CO₂ must come from reduction of Fe(OH)₃. The amount of CO₂ increases markedly in the presence of rhodium and the absence of any carbon sources other than the elemental carbon support of the 5% Rh/C suggesting that the formic acid reduction of

iron(III) to iron(II) can be catalyzed by addition of rhodium. The feed simulant is 0.45 M in iron(III) which means that the 50 mL of UGA-9M2XC contains 22.5 mmoles of Fe(III) which would give 11.2 mmoles of CO₂ according to the equation



The 12.0 mmoles of CO₂ observed in the experiment with 5% Rh/C but no added nitrogen species is very close to the 12.7 mmoles of CO₂ expected for complete reduction of 1.55 mmoles of MnO₂ and 22.5 mmoles of Fe(OH)₃. The predicted amount of CO₂ from the experiment in Table 2 with added nitrate from formic acid reduction of MnO₂ to Mn²⁺, Fe³⁺ to Fe²⁺, and nitrate to ammonia is 17.6 mmoles (Table 4) as compared with the 16.7 mmoles of CO₂ observed in this experiment.

Table 4
CO₂ Balance in the Titration of UGA-9M2XC with Formic Acid in the Presence of Nitrate at 90°C Listed in Table 2

CO ₂ from reduction of (50 mL)(0.0314 M) = 1.55 mmoles MnO ₂	1.5 mmoles
CO ₂ from reduction of (50 mL)(0.45 M) = 22.5 mmoles of Fe ³⁺ to Fe ²⁺	11.3 mmoles
CO ₂ from reduction of nitrate to 1.2 mmoles of ammonia	<u>4.8 mmoles</u>
<i>Total expected CO₂:</i>	<i>17.6 mmoles</i>

The predicted amount of CO₂ from the experiment in Table 2 with added *nitrite* from formic acid reduction of MnO₂ completely to Mn²⁺, Fe³⁺ completely to Fe²⁺, the 7.3 observed mmoles of NO completely to N₂O, the production of the remaining 3.3 mmoles of N₂O by nitrite reduction, and reduction of nitrate to the observed 0.6 mmoles of ammonia is 25.4 mmoles (Table 5) which compares with the observed 19.4 mmoles suggesting that reduction of Fe³⁺ to Fe²⁺ is incomplete in the presence of nitrite.

4.5 Limited component experiments

A series of limited component experiments was performed in order to gain a greater insight into the factors affecting ammonia formation. In these experiments solutions of the additives of interest in 60 mL of water in the presence of the noble metal derivative of interest were titrated at 90±1°C with 84 mmoles of 88 wt % formic acid using the syringe pump. Supported noble metal catalysts were used for these experiments since the previous experiments with feed simulants discussed above suggest that they are more active than soluble noble metal catalysts for formic acid reduction of nitrate and/or nitrite to ammonia.

The final compositions of the reaction mixtures (typically after 400 minutes reaction time) are summarized in Table 6. Two of the titrations of nitrate with formic acid in the presence of Pd/C are depicted in Figure 7.

Table 5
CO₂ Balance in the Titration of UGA-9M2XC with Formic Acid in the Presence of Nitrite at 90°C Listed in Table 2

CO ₂ from reduction of (50 mL)(0.0314 M) = 1.55 mmoles MnO ₂	1.5 mmoles
CO ₂ from reduction of (50 mL)(0.45 M) = 22.5 mmoles of Fe ³⁺ to Fe ²⁺	11.3 mmoles
CO ₂ from reduction of 7.3 mmoles of NO to 3.6 mmoles of N ₂ O	3.6 mmoles
CO ₂ from reduction of nitrite to (6.9-3.6) = 3.3 mmoles of N ₂ O	6.6 mmoles
CO ₂ from reduction of nitrate to 0.6 mmoles of ammonia	<u>2.4 mmoles</u>
<i>Total expected CO₂:</i>	<i>25.4 mmoles</i>

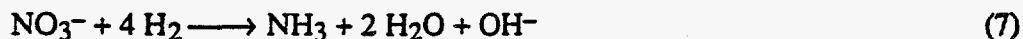
The following points are of interest concerning these limited component experiments:

- (1) The CO₂ produced in the Rh/C experiment with Fe(OH)₃ indicates essentially complete formic acid reduction of the 22.5 mmoles of Fe³⁺ present to Fe²⁺ probably catalyzed by the supported rhodium catalyst. The final color of this reaction mixture was pale green consistent with the high conversion of Fe³⁺ to Fe²⁺.
- (2) Substantial amounts of hydrogen are produced in the Rh/Al₂O₃ experiment with added NaNO₂ but not in the experiments with NaNO₃. This again indicates the role of nitrite as a promoter for the rhodium catalysts for hydrogen generation from formic acid as suggested from previous work.^{2,3}
- (3) Although RhCl₃·3H₂O does not produce NH₃ from nitrite at least in feed simulant experiments, Rh/C produces a significant amount of NH₃ (1.5 mmoles) but very little H₂ (0.2 mmoles) from nitrite. The production of H₂, N₂O, and NH₃ accounts for essentially all of the CO₂ since $0.2 + (5.8 \times 2) + (1.5 \times 3) = 16.3$ mmoles as compared with the observed 17.1 mmoles.
- (4) Pd/Al₂O₃ is more efficient than Pd/C at catalyzing the formic acid reduction of *nitrite* to ammonia. In addition Pd/Al₂O₃ but not Pd/C catalyzes formic acid decomposition to hydrogen in the presence of nitrite.
- (5) The experiment with 1.9 g of NaNO₃ using Pd/C had to be stopped after 138 min after the addition of only 61.3 mmoles of formic acid because of excessive pressure (e.g.,

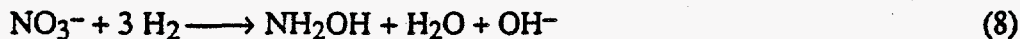
36.1 mmol of CO_2) and produced ~ 5.4 mmol of N_2 in addition to the gases listed above. The production of relatively large amounts of NH_3 (2.9 mmol) led to an unusually high final pH (7.0). Use of a smaller amount of NaNO_3 (0.5 g) allowed the reaction to be carried out to completion and led to the generation of considerable amounts of H_2 . The maximum H_2 generated in this experiment with 0.5 g of NaNO_3 was 2.1 mmol, but the amount of H_2 present in this experiment decreased to 1.1 mmol as 0.7 mmol of NH_3 was generated in the later stages of the reaction. This suggests that the NH_3 arises from H_2 reduction of a higher oxidation state nitrogen intermediate. Furthermore, a comparison of the otherwise identical experiments using 1.9 g and 0.5 g of NaNO_3 suggests that if the nitrate concentration is high enough, all of the H_2 generated by formic acid decomposition is used for the reduction of nitrate to NH_3 rather than being evolved as H_2 gas.

(6) Supported ruthenium catalysts are not active for the formic acid reduction of either nitrite or nitrate to ammonia, at least under the reaction conditions of interest in this work. Supported ruthenium catalysts are only active for formic acid decomposition to hydrogen in the absence of both nitrite and nitrate (Table 6).

The effect of NaNO_3 concentration on the Pd/C catalyzed reduction of nitrate with formic acid was investigated at a range of nitrate concentrations (Table 7). At intermediate nitrate concentrations (5.9 and 11.7 mmol $\text{NaNO}_3/60$ mL) some of the initially produced H_2 was subsequently consumed suggesting a metal-catalyzed hydrogenation of nitrate to ammonia according to the following equation:



The final pH in such experiments was 2.0 ± 0.3 which is close to the reported range for the hydrogenation of nitrate ion in the presence of a 5% Pd/C catalyst in aqueous phosphoric acid.^{12,13,14} Under such conditions nitrate is reported to be hydrogenated not only to ammonia but also to hydroxylamine according to the following equation:



This suggests that hydroxylamine might be a byproduct on the formic acid treatment of nuclear wastes containing nitrate or even nitrite ion. Future experiments designed to detect hydroxylamine in the products from the formic acid treatment of nitrate-containing feed simulants, possibly using electrochemical methods, will be of interest.

Table 6
Formation of Ammonia and Hydrogen in Limited Component Experiments

Additive(g)	Noble Metal(mg)	mmol H ₂	mmol CO ₂	mmol N ₂ O	mmol NO	mmol NH ₃	Final pH
none	5% Rh/C(112)	1.0	1.1	0.0	0.0	0.0	1.8
NaNO ₃ (0.5)	5%Rh/C(115)	0.2	1.5	0.0	0.0	0.2	1.8
Fe/NaNO ₃ ^a	5%Rh/C(115)	0.0	13.8	0.0	0.0	0.3	3.7
NaNO ₃ (0.5)	5%Rh/Al ₂ O ₃ (115)	0.1	0.6	0.0	0.0	0.0	1.9
NaNO ₂ (1.5)	5%Rh/Al ₂ O ₃ (117)	1.4	15.1	5.1	2.3	1.9	3.2
NaNO ₂ (1.6)	5% Rh/C(118)	0.2	17.1	5.8	0.0	1.5	3.2
NaNO ₂ (1.5)	5% Pd/C(120)	0.0	10.3	6.7	2.4	0.1	3.2
NaNO ₂ (1.5)	5% Pd/Al ₂ O ₃ (120)	1.0	12.2	6.0	2.5	0.4	3.1
NaNO ₃ (1.9)	5% Pd/C(120)	0.0	36.1	1.6	0.0	2.9	7.0
NaNO ₃ (1.0)	5% Pd/C(120)	0.6	7.3	0.0	0.0	0.8	2.2
NaNO ₃ (0.5)	5% Pd/C(120)	1.1	8.0	0.0	0.0	0.7	2.3
NaNO ₃ (0.2)	5% Pd/C(120)	4.4	4.9	0.0	0.0	0.1	1.9
none	5% Pd/C(120)	3.8	3.5	0.0	0.0	0.0	1.8
NaNO ₂ (1.5)	5% Ru/Al ₂ O ₃ (110)	0.0	6.7	4.5	6.5	0.0	3.1
NaNO ₂ (1.5)	5% Ru/C(110)	0.0	6.2	4.3	6.1	0.0	3.1
NaNO ₃ (1.9)	5% Ru/C(110)	0.0	0.6	0.0	0.0	0.0	1.8
none	5% Ru/C(110)	0.2	0.4	0.0	0.0	0.0	1.8

^a50 mL of a 0.45 M aqueous slurry of Fe(OH)₃, 10 mL of water, 0.5 g. of sodium nitrate, and 115 mg of 5% rhodium on carbon was used for this experiment.

Table 7
Effect of Nitrate Concentration on the Pd/C Catalyzed Reduction of Nitrate
with Formic Acid^a

NaNO ₃ mmol	H ₂ mmol ^b	CO ₂ mmol	N ₂ O mmol	N ₂ mmol	NH ₃ mmol	final pH
0	3.8(12.2)	3.5	0	0	0	1.8
2.4	4.4(11.4)	4.9	0	0	0.1	1.9
5.9	1.1 ^c	8.0	0	0	0.7	2.3
11.7	0.6(17.7) ^d	7.3	0	0	0.8	2.2
22.3	0 ^e	36.4	1.6	5.3	2.9	7.0

^aAll experiments were performed using 60 mL of water and 120 mg 5% Pd/C.

^bThe rate of H₂ production is given in parentheses in mmoles/day.

^cMaximum H₂ produced = 2.1 mmoles at 80 min. Too few points were obtained to give a reliable H₂ production rate. Rate of NH₃ increase = 2.7 mmoles/day. Rate of H₂ decrease during NH₃ production = 4.3 mmoles/day.

^dMaximum H₂ produced = 1.2 mmoles at 69 min. Rate of NH₃ increase = 4.1 mmoles/day. Rate of H₂ decrease during NH₃ production = 2.7 mmoles/day.

^eThe reaction was stopped after 138 min owing to excessive pressure. No H₂ was observed during any stage of the process.

5.0 Literature References

- (1) G. R. Choppin and J. Rydberg, *Nuclear Chemistry: Theory and Applications*, Pergamon, Oxford, 1980, p 505.
- (2) R. B. King; A. D. King, Jr.; N. K. Bhattacharyya, C. M. King, and L. F. Landon, in *Chemical Pretreatment of Nuclear Waste for Disposal*, W. W. Schulz and E. P. Horwitz, eds., Plenum, New York, in press.
- (3) R. B. King et al., *Hanford Waste Vitrification Plant Hydrogen Generation Study*, Technical report dated April, 1993, to the Battelle Pacific Northwest Laboratory for the Hanford Waste Vitrification Technology Development Project under Contract No. 125770-A-A2.
- (4) R. L. Augustine, *Catalytic Hydrogenation*, Dekker, New York, 1965.
- (5) P. N. Rylander, *Catalytic Hydrogenation over Platinum Metals*, Academic Press, New York, 1967.
- (6) M. Freifelder, *Practical Catalytic Hydrogenation*, Wiley-Interscience, New York, 1971.
- (7) P. N. Rylander, *Hydrogenation Methods*, Academic Press, London, 1985.
- (8) L. Červený, ed., *Catalytic Hydrogenation*, Elsevier, Amsterdam, 1986.
- (9) I. D. Entwistle, A. E. Jackson, R. A. W. Johnstone, and R. P. Telford, *J. Chem. Soc. Perkin I*, 443 (1977).
- (10) N. A. Cortese and R. F. Heck, *J. Org. Chem.*, 42, 3491 (1977)
- (11) S. Ram and R. E. Ehrenkauf, *Tetrahedron Letters*, 25, 3415 (1984).
- (12) V. L. Lopatin, K. A. Lezhneva, N. V. Kul'kova, and M. I. Temkin, *Kinetika i Kataliz*, 20, 373 (1979); Engl. Transl., 20, 302 (1979).
- (13) H. Kinza, *Kinetika i Kataliz*, 23, 1511 (1982); Engl. Transl., 23, 1290 (1982).
- (14) M. I. Temkin, N. V. Kul'kova, and V. L. Lopatin, *Kinetika i Kataliz*, 23, 1514 (1982); Engl. Transl., 23, 1294 (1982).
- (15) Table 6 in the report R. B. King, et al., *Hanford Waste Vitrification Plan Hydrogen Generation Study*, April, 1993.
- (16) M. K. Anwer, D. B. Sherman, J. G. Roney, and A. F. Spatola, *J. Org. Chem.*, 54, 1283 (1990).

Figure Captions

Figure 1: Titration of 50 mL UGA-12M1H, 10 mL of water, and 0.118 g. 5% Rh/C with 85 mmoles of 88 wt % formic acid at $90\pm 1^\circ\text{C}$.

Figure 2: Titration of 50 mL UGA-12M1H, 10 mL of water, and 0.118 g. 5% Rh/Al₂O₃ with 85 mmoles of 88 wt % formic acid at $90\pm 1^\circ\text{C}$.

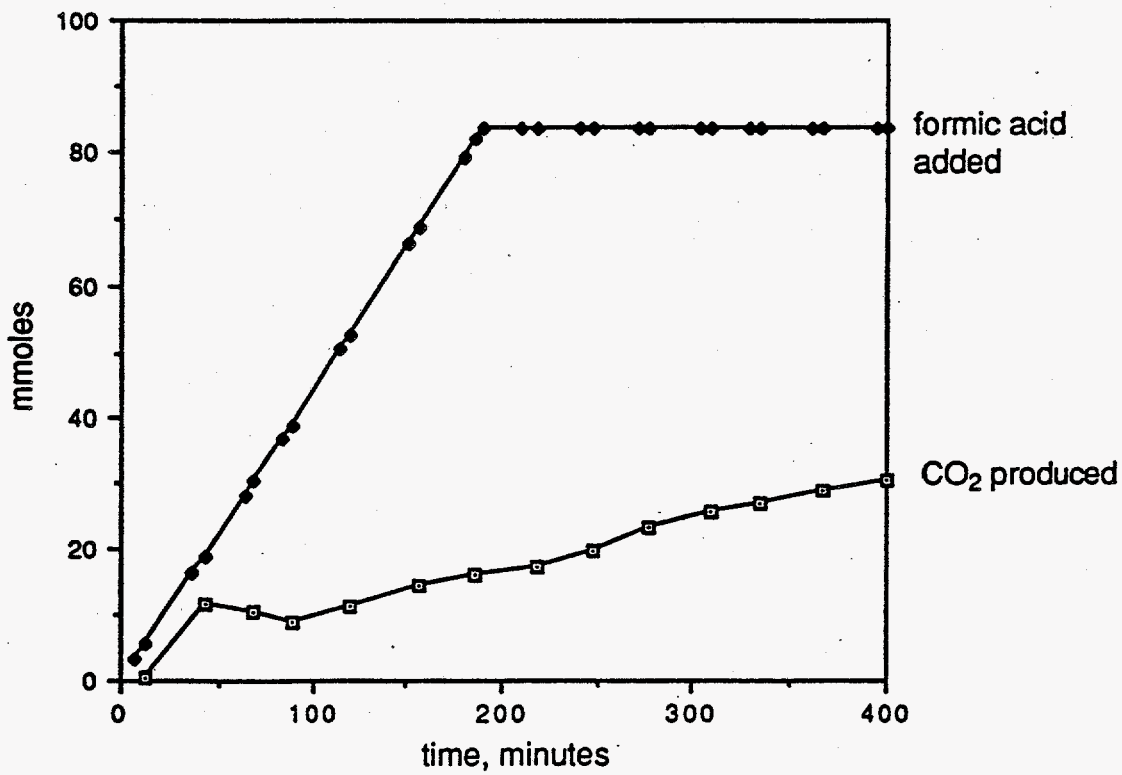
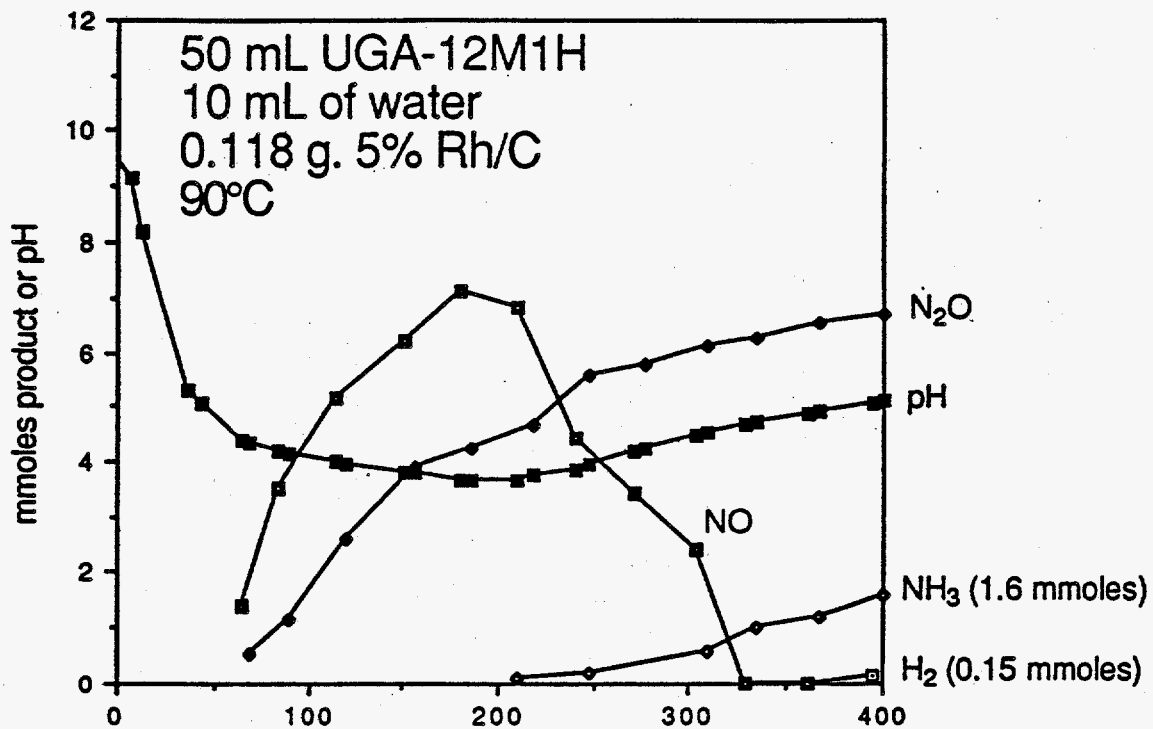
Figure 3: Titration of 50 mL UGA-12M1H, 10 mL of water, and 14 mg of RhCl₃·3H₂O with 85 mmoles of 88 wt % formic acid at $90\pm 1^\circ\text{C}$.

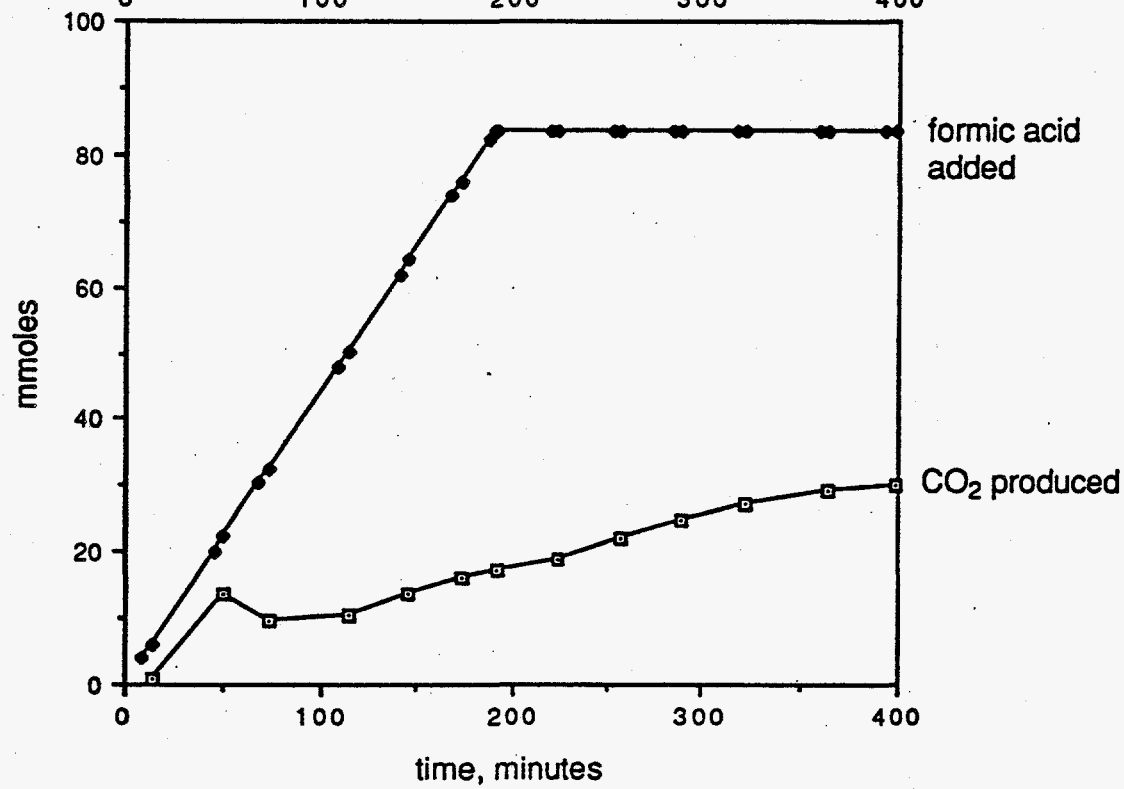
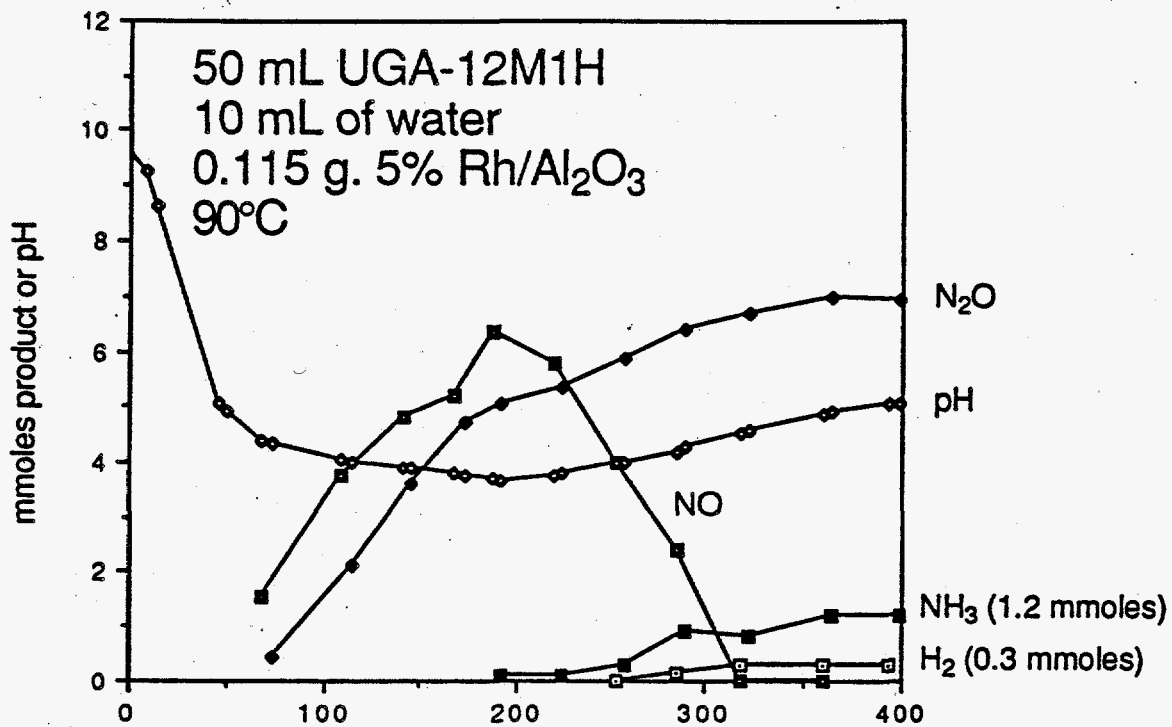
Figure 4: Titration of 50 mL UGA-10XNN'1G, 10 mL of water, 0.5 g NaNO₃, and 0.118 g. 5% Rh/C with 85 mmoles of 88 wt % formic acid at $90\pm 1^\circ\text{C}$. No nitrogen oxides or H₂ were observed in this experiment.

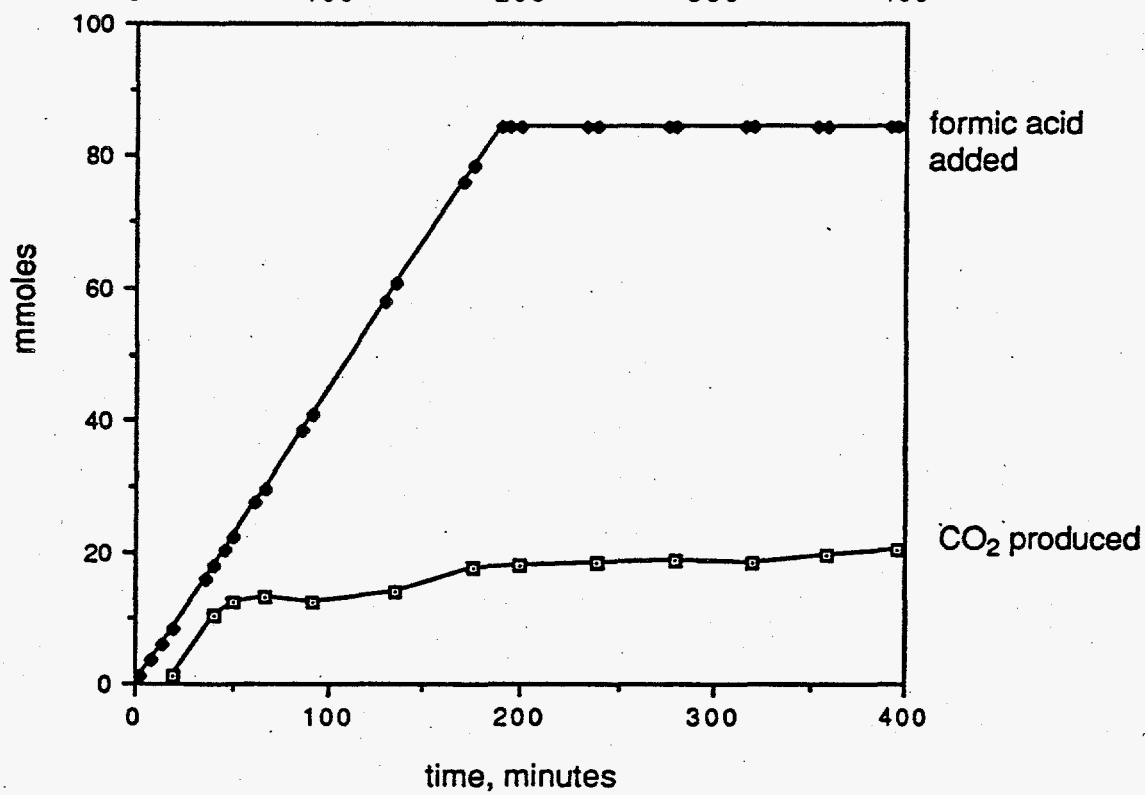
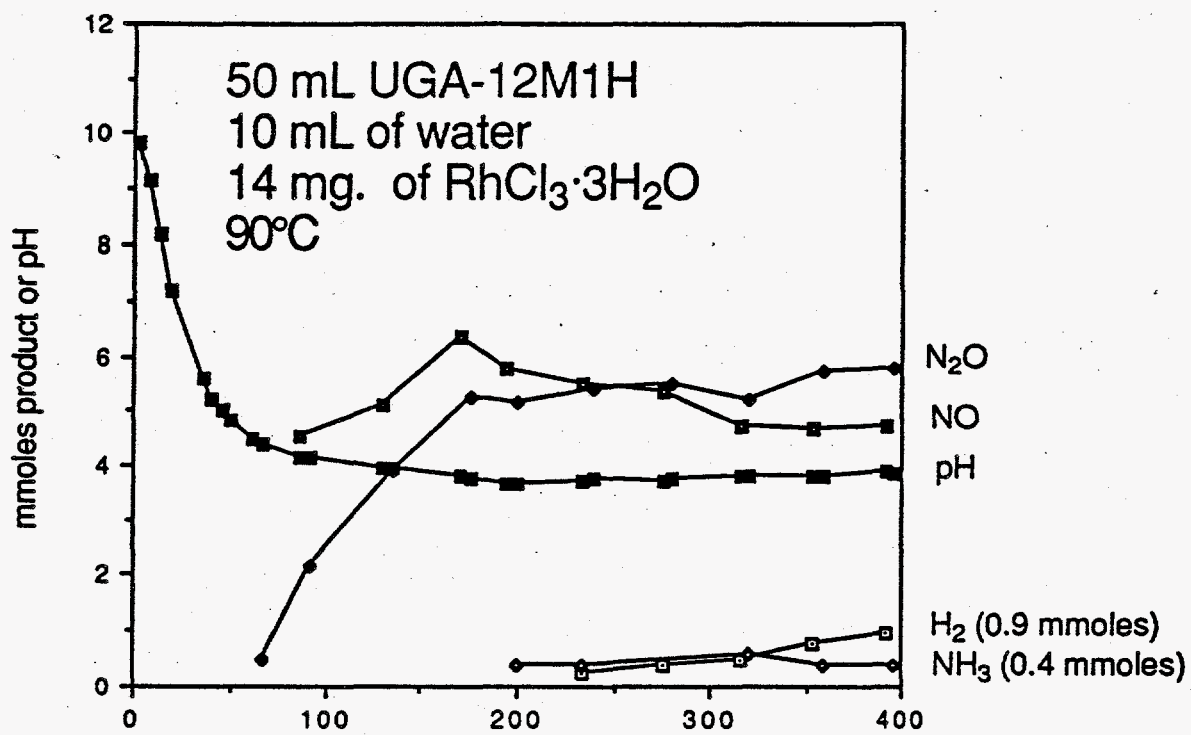
Figure 5: Comparison of the effects of added NaNO₂ and NaNO₃ in the titration of 50 mL of the nitrite- and carbonate-free feed simulant UGA-9M2XC, 10 mL of water, and 118 mg of 5% Rh/C with 85 mmoles of 88 wt % formic acid at $90\pm 1^\circ\text{C}$.

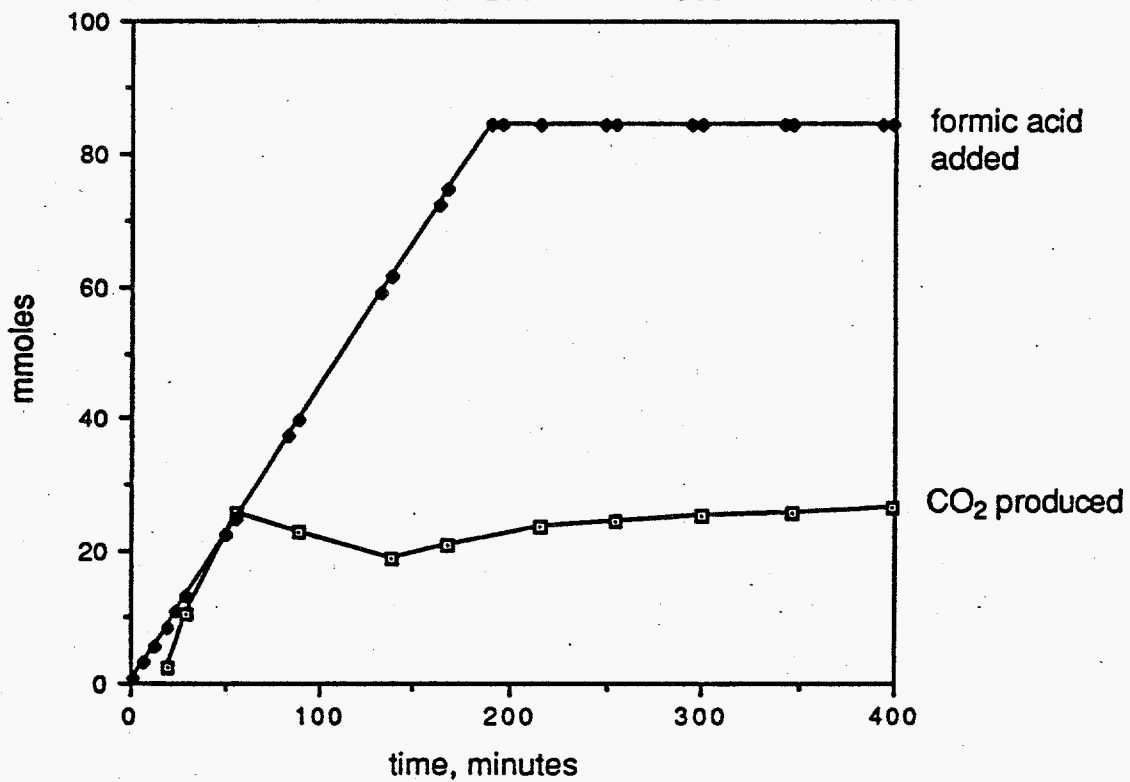
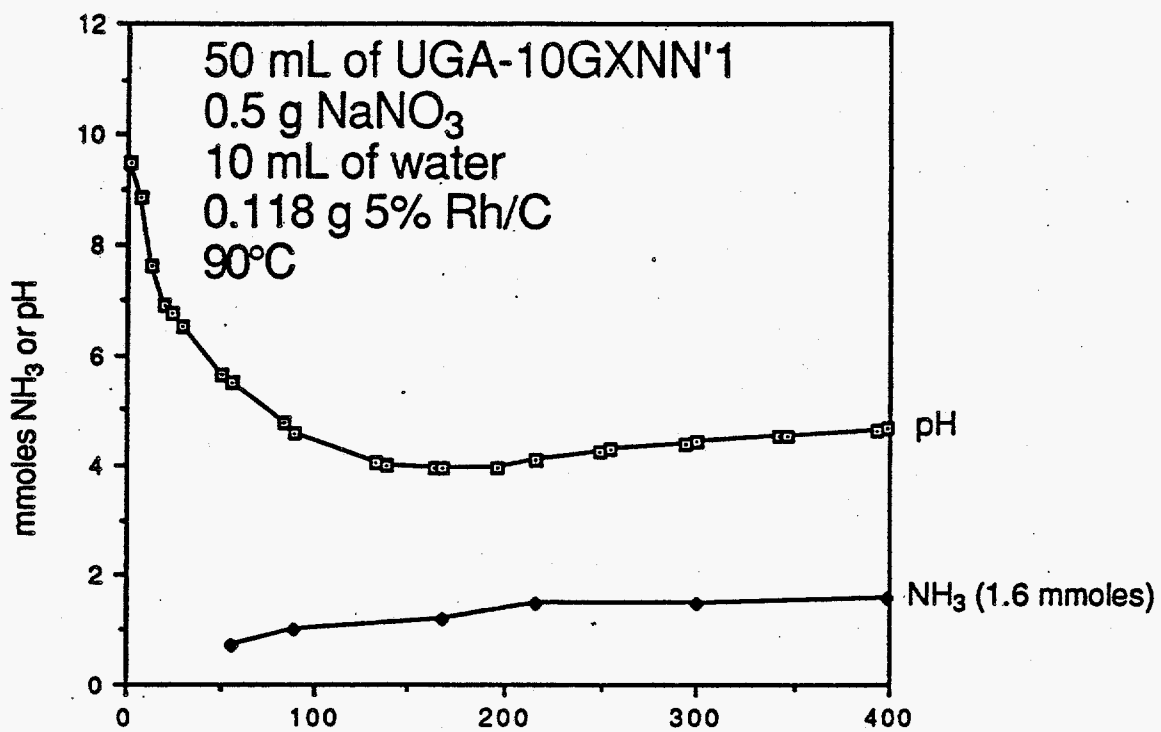
Figure 6: Comparison of the effects of added NaNO₂ and NaNO₃ in the titration of 50 mL of the nitrite- and carbonate-free feed simulant UGA-9M2XC, 10 mL of water, and 120 mg of 5% Pd/C with 85 mmoles of 88 wt % formic acid at $90\pm 1^\circ\text{C}$.

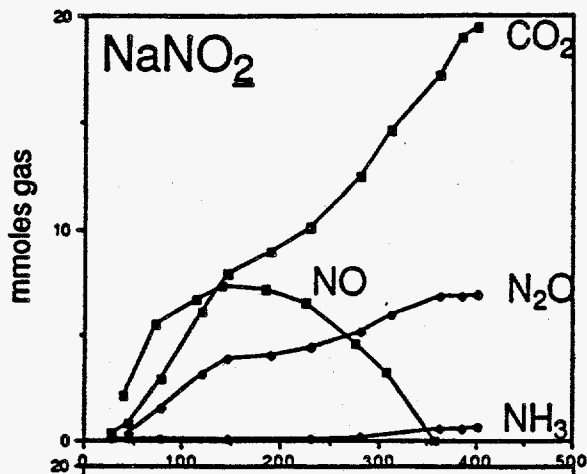
Figure 7: Effect of NaNO₃ concentration in its titration with formic acid in the presence of 5% Pd/C.





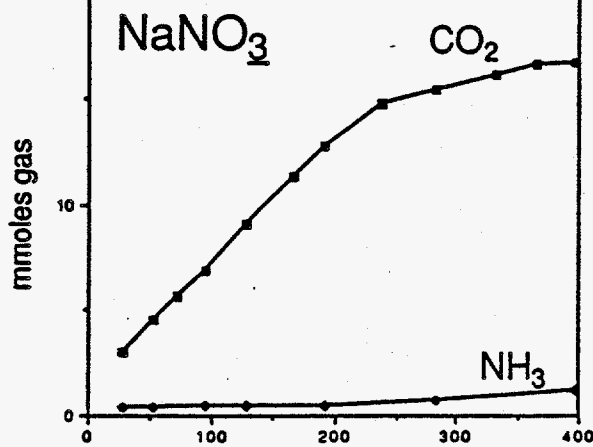






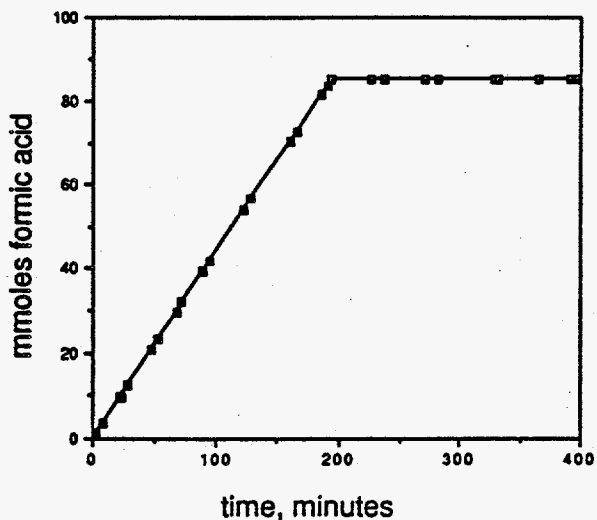
50 mL of UGA-9M2XC
 10 mL of water
 118 mg 5% Rh on C
1.5 g NaNO₂
 90 ± 1°C

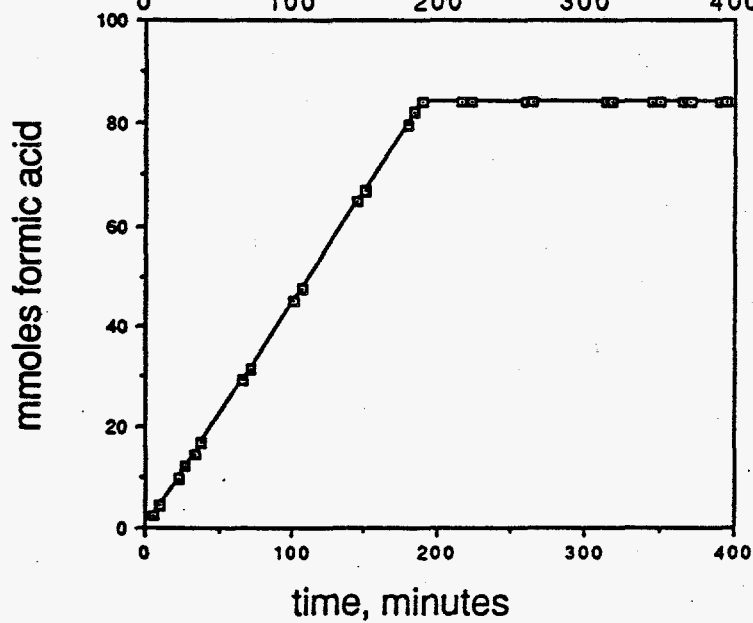
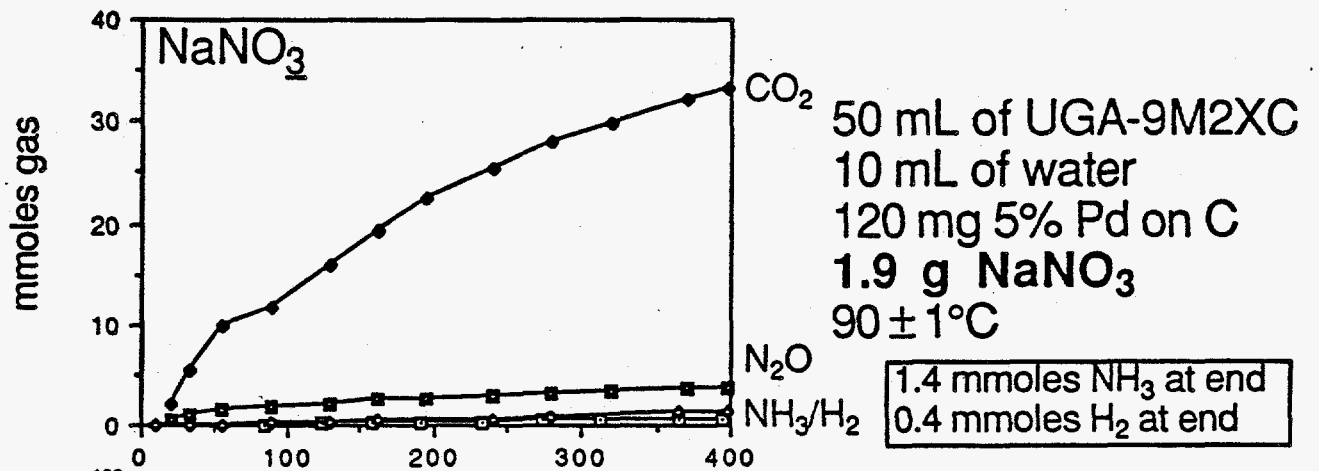
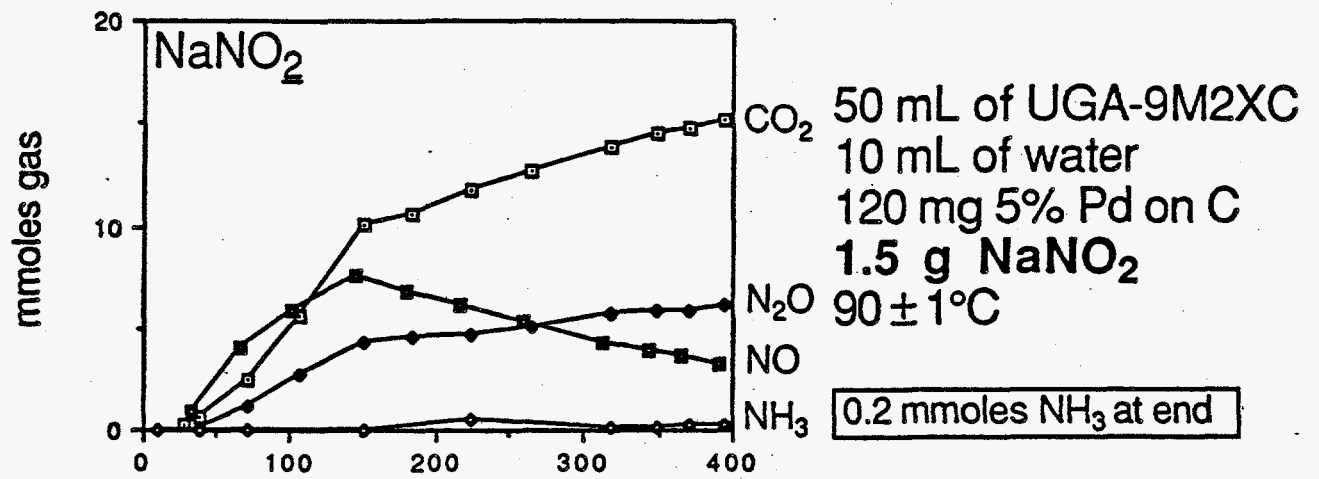
0.6 mmoles NH₃ at end

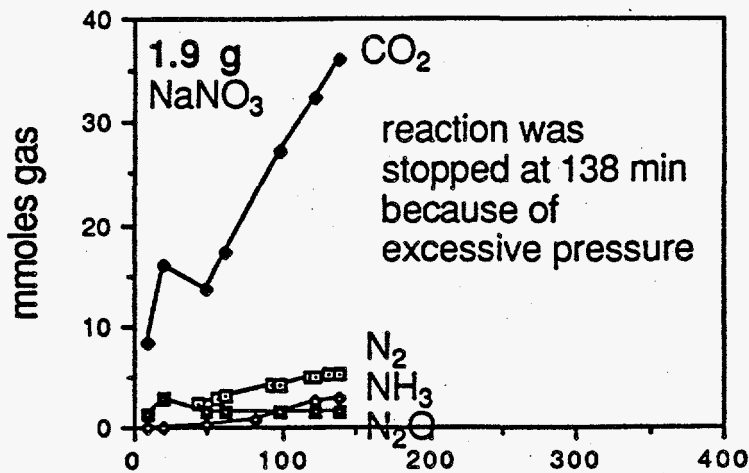


50 mL of UGA-9M2XC
 10 mL of water
 118 mg 5% Rh on C
1.86 g NaNO₃
 90 ± 1°C

1.2 mmoles NH₃ at end

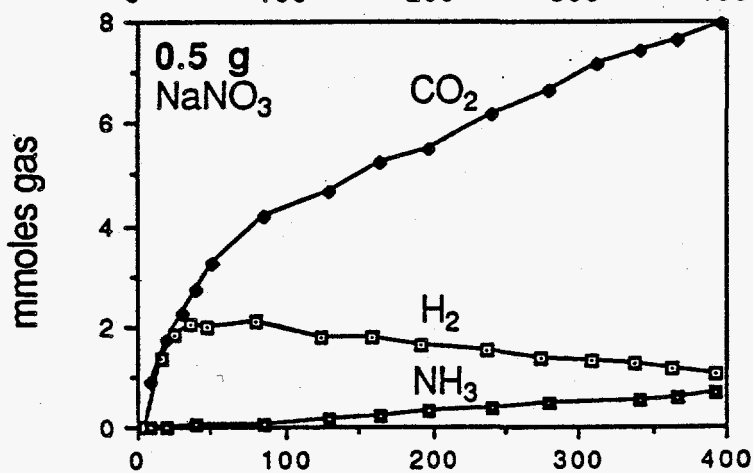






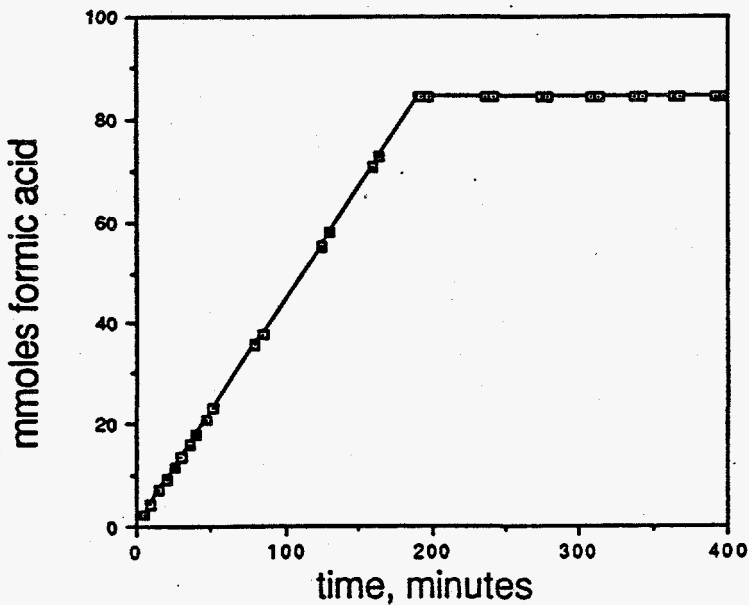
60 mL of water
 1.9 g of NaNO₃
 120 mg of 5% Pd/C
 90 ± 1°C

2.9 mmoles of NH₃ at end



60 mL of water
 0.5 g of NaNO₃
 120 mg of 5% Pd/C
 90 ± 1°C

rate of NH₃ production =
 0.62 rate of H₂ consumption



Appendix A

Summary of Reactions of Formic Acid with Feed Simulants Studied During the Course of this Project

Date	Feed (ml)	Additive (g)	Noble Metal (mg)	Amount of 88 wt % Formic Acid(time)	Temperature °C	Total Time (minutes)	mmoles H ₂	mmoles NH ₃	Final pH
8/6/93	12M1H (50)	0	RhCl ₃ ·3H ₂ O(14)	3.63 mL(190 min)	89-90°	396	0.94	0.4	3.85
8/12/93	12M1H (50)	0	5%Rh/C(118)	3.63 mL(190 min)	90±1°	400	0.15	1.6	5.09
8/13/93	12M1H (50)	0	5%Rh/Al ₂ O ₃ (116)	3.63 mL(190 min)	90±1°	398	0.30	1.2	5.06
8/17/93	10MIGXNN' (50)	NaNO ₃ (0.5)	5%Rh/C(117)	3.65 mL(190 min)	90±1°	398	trace	1.6	4.66
8/18/93	10MIGXNN' (50)	NaNO ₃ (0.5)	RhCl ₃ ·3H ₂ O(14)	3.65 mL(190 min)	90±1°	403	0.0	0.0	3.18
8/19/93	10MIGXNN' (50)	NaNO ₃ (0.5)	Rh coppt w. Al ₂ O ₃	3.65 mL(190 min)	90±1°	395	0.22	-0	3.19
8/20/93	10MIGXNN' (50)	NaNO ₃ (0.5),NaNO ₂ (1.5)	Rh coppt w. Al ₂ O ₃	3.65 mL(190 min)	90±1°	396	0.40	-0	3.89
8/24/93	12M1H (50)	0	PdCl ₂ (12)	3.63 mL(190 min)	90±1°	395	0.0	-0	4.07
8/25/93	10XNN' (50)	NaNO ₃ (0.5)	PdCl ₂ (12)	3.63 mL(190 min)	90±1°	394	0.26	0.8	4.62
8/26/93	12M1H (50)	0	PdCl ₂ (13)	3.63 mL(190 min)	90±1°	236	0	-0	5.24
8/31/93	H ₂ O (60)	NaNO ₃ (0.5)	5%Rh/C(115)	3.61 mL(190 min)	90±1°	391	0.21	0.2	1.80
9/1/93	H ₂ O (60)	NaNO ₃ (0.5)	5%Rh/Al ₂ O ₃ (115)	3.61 mL(190 min)	90±1°	395	0.05	0	1.94
9/2/93	H ₂ O (60)	NaNO ₂ (1.5)	5%Rh/Al ₂ O ₃ (117)	3.61 mL(190 min)	90±1°	395	1.44	1.94	3.17
9/3/93	0.45M Fe(OH) ₃ (50)	NaNO ₃ (0.5)	5%Rh/Al ₂ O ₃ (115)	3.61 mL(190 min)	90±1°	388	0	0.3	3.69
9/8/93	9M2XC (50)	0	0	3.63 mL(195 min)	90±1°	403	0	0	2.95
9/9/93	9M2XC (50)	0	5%Rh/C(116)	3.63 mL(195 min)	90±1°	396	0	0	3.92
9/10/93	9M2XC (50)	0	RhCl ₃ ·3H ₂ O(14)	3.63 mL(195 min)	90±1°	402	0	0	3.03
9/14/93	9M2XC (50)	NaNO ₂ (1.5)	5%Rh/C(118)	3.69 mL(195 min)	90±1°	402	0	0.63	4.21
9/15/93	9M2XC (50)	NaNO ₃ (1.86)	5%Rh/C(118)	3.69 mL(195 min)	90±1°	397	0.09	1.2	4.04

Date	Feed (ml)	Additive (g)	Noble Metal (mg)	Formic Acid(time)	°C	(minutes)	H ₂	NH ₃	pH
10/1/93	H ₂ O (60)	NaNO ₂ (1.5)	5%Rh/C(118)	3.63 mL(190 min)	90±1°	401	0.21	1.5	3.21
10/5/93	9M2XC (50)	NaNO ₂ (1.5)	RhCl ₃ ·3H ₂ O(14)	3.63 mL(190 min)	90±1°	396	1.68		3.59
10/6/93	9M2XC (50)	NaNO ₃ (1.9)	RhCl ₃ ·3H ₂ O(14)	3.63 mL(190 min)	90±1°	399	0.41	0.03	3.17
10/7/93	9M2XC (50)	NaNO ₂ (1.5)	5%Pd/C(120)	3.63 mL(190 min)	90±1°	394	0	0.2	3.77
10/8/93	9M2XC (50)	NaNO ₃ (1.9)	5%Pd/C(120)	3.63 mL(190 min)	90±1°	399	0.45	1.4	5.05
10/12/93	9M2XC (50)	NaNO ₂ (1.5)	RhCl ₃ ·3H ₂ O(14)	3.65 mL(190 min)	90±1°	397	1.46	0.05	3.68
10/13/93	H ₂ O (60)	NaNO ₂ (1.5)	5%Pd/C(120)	3.65 mL(190 min)	90±1°	397	0	0.05	3.20
10/14/93	H ₂ O (60)	NaNO ₃ (1.9)	5%Pd/C(120)	2.65 mL(138 min)	90±1°	138	0	2.88	7.04
10/15/93	H ₂ O (60)	NaNO ₃ (0.5)	5%Pd/C(120)	3.65 mL(190 min)	90±1°	397	1.06	0.7	2.28
10/20/93	9M2XC (50)	NaNO ₃ (1.9) "aged" 12 hr	5%Pd/C(120)	3.65 mL(190 min)	90±1°	398	0.76	1.44	5.01
10/21/93	9M2XC (50)	NaNO ₃ (1.9) "aged" 12 hr	RhCl ₃ ·3H ₂ O(14)	3.65 mL(190 min)	90±1°	394	0.41	0	3.05
10/22/93	9M2XC (50)	NaNO ₃ (1.9)	PdCl ₂ (13)	3.65 mL(190 min)	90±1°	400	0.31	0.19	3.96
10/26/93	9M2XC (50)	NaNO ₂ (1.5)	PdCl ₂ (13)	3.65 mL(190 min)	90±1°	401	0	0.04	3.73
10/27/93	H ₂ O (60)	0	5%Pd/C(120)	3.65 mL(190 min)	90±1°	403	3.81	0	1.84
10/28/93	H ₂ O (60)	NaNO ₃ (0.2)	5%Pd/C(120)	3.65 mL(190 min)	90±1°	395	4.39	0.1	1.89
10/29/93	H ₂ O (60)	NaNO ₃ (1.0)	5%Pd/C(120)	3.65 mL(190 min)	90±1°	397	0.59	0.82	2.23
11/2/93	H ₂ O (60)	NaNO ₂ (0.2)	RhCl ₃ ·3H ₂ O(14)	3.61 mL(190 min)	90±1°	391	0.34	0.33	2.4
11/3/93	H ₂ O (60)	NaNO ₂ (1.0)	RhCl ₃ ·3H ₂ O(14)	3.61 mL(190 min)	90±1°	345	14.86	0.36	3.1
11/4/93	H ₂ O (60)	NaNO ₂ (0.7)	RhCl ₃ ·3H ₂ O(14)	3.61 mL(190 min)	90±1°	394	10.90	0.47	2.9
11/5/93	H ₂ O (60)	NaNO ₂ (0.5)	RhCl ₃ ·3H ₂ O(14)	3.61 mL(190 min)	90±1°	400	0.81	0.44	2.7
11/9/93	H ₂ O (60)	0	RhCl ₃ ·3H ₂ O(14)	3.61 mL(190 min)	90±1°	394	0	0	2.1
11/10/93	H ₂ O (60)	NaNO ₂ (1.5)	5%Ru/C(110)	3.61 mL(190 min)	90±1°	396	0	0	3.07
11/11/93	H ₂ O (60)	NaNO ₃ (1.9)	5%Ru/C(110)	3.61 mL(190 min)	90±1°	400	0	0	1.76

Date	Feed (ml)	Additive (g)	Noble Metal (mg)	Amount of 88 wt % Formic Acid(time)	Temperature °C	Total Time (minutes)	mmoles H ₂	mmoles NH ₃	Final pH
11/12/93	H ₂ O (60)	0	5%Ru/C(112)	3.61 mL(190 min)	90±1°	397	0.96	0	1.81
11/16/93	H ₂ O (60)	NaNO ₂ (0.8)	RhCl ₃ ·3H ₂ O(14)	3.65 mL(190 min)	90±1°	396	11.12	0.29	2.9
11/17/93	H ₂ O (60)	NaNO ₂ (1.5)	5%Pd/Al ₂ O ₃ (120)	3.65 mL(190 min)	90±1°	396	0.98	0.45	3.13
11/18/93	H ₂ O (60)	NaNO ₂ (1.5)	5%Ru/Al ₂ O ₃ (110)	3.65 mL(190 min)	90±1°	398	0	0	3.10
11/19/93	H ₂ O (60)	0	5%Ru/C(110)	3.65 mL(190 min)	90±1°	399	0.21	0	1.85

FEED SIMULANT COMPOSITION

The Hanford Waste Vitrification Plant (HWVP) feed simulant prepared at the University of Georgia contains the major components present in $\geq 3\%$ concentrations using Table 1 of the original University of Georgia proposal¹ as the basis for the choice of the feed simulant composition. The major component feed simulant thus contains 12 components, namely the nine metals Al, Cd, Fe, Mn, Nd, Ni, Na, Si, and Zr and the three anions NO_2^- , NO_3^- , and CO_3^{2-} . In order to distinguish this feed simulant from other feed simulants to be prepared later in this work, this feed simulant is given the code name UGA-12M1, with the "12" corresponding to the 12 components, the "M" indicating that the components are the major components, and the "1" indicating that this is the first feed simulant of this type to be prepared during the course of this research project. In the early stages of the research to evaluate the role of the noble metals Ru, Rh, and Pd in hydrogen generation, variations of this feed simulant leaving out the redox component Fe and the metal complex forming component nitrite were also prepared. The iron-free feed simulant based on this protocol is called UGA-11XFe1, the nitrite-free feed simulant based on this protocol is called UGA-11XN1, and an iron-free and nitrite-free feed simulant is called UGA-10XFeN1 with the first number indicating the number of components. In most cases the noble metals of interest were added as chlorides or nitrates to individual aliquots of the feed simulant immediately before carrying out the hydrogen and ammonia generation studies.

The commercially available inorganic salts used as sources of the 12 components of the feed simulant UGA-12M1 are listed in Table 1A.

¹Research proposal entitled *Waste Vitrification Plant Feed Preparation Hydrogen Study* submitted to the Pacific Northwest Laboratories by the University of Georgia Research Foundation in August, 1991.

Table 1A
Sources of the Components of the Feed Simulant UGA-12M1

Component*	Molarity	Source	Amount‡	Water solubility§
Al	0.226	Al(NO ₃) ₃ ·9H ₂ O	84.78 g	63.7 g/100g @ 25°C
Cd	0.03	Cd(NO ₃) ₂ ·4H ₂ O	9.25 g	215 g/100 g @ 25°C
Fe	0.45	Fe(NO ₃) ₃ ·9H ₂ O	181.80 g	"soluble"
Mn	0.0314	{ KMnO ₄ Mn(NO ₃) ₂ ·6H ₂ O	{ 1.98 g 5.41 g	{ 6.38 g/100 g @ 20°C 426.4 g/100 g @ 0°C
Nd	0.0264	Nd(NO ₃) ₃ ·6H ₂ O	11.57 g	152.9 g/100 g @ 25°C
Ni	0.0392	Ni(NO ₃) ₂ ·6H ₂ O	11.57 g	238.5 g/100 g @ 0°C
Si	0.0854	SiO ₂	5.13 g	insoluble
Zr	0.156	ZrO(NO ₃) ₂	36.07 g	soluble
Na ⁺	0.801†	Na ₂ CO ₃ + NaNO ₃ + NaNO ₂	see below	see below
CO ₃ ²⁻	0.125	Na ₂ CO ₃	13.25 g	7.1 g/100 g @ 0°C
NO ₃ ⁻	0.116	NaNO ₃	9.86 g	92.1 g/100g @ 25°C
NO ₂ ⁻	0.435	NaNO ₂	30.02 g	81.5 g/100 g @ 15°C

* The insoluble components are present as Al(OH)₃, Fe(OH)₃, MnO₂, Nd₂O₃, Ni(OH)₂, SiO₂, ZrO₂.

† The nominal Na⁺ concentration in the simulant is 0.88 M because of additional Na⁺ from the NaOH precipitant incompletely washed from the oxide/hydroxide precipitates.

‡ Amount for a one-liter batch.

§ The water solubility figures for these salts are taken from the *Handbook of Chemistry and Physics*.

Appendix B

PROTOCOL FOR THE PREPARATION OF A NITROGEN-FREE MAJOR COMPONENT HWVP FEED SIMULANT FROM METAL CHLORIDES: UGA-10M2

R. B. King and N. K. Bhattacharyya, Department of Chemistry, University of Georgia, Athens, Georgia 30602

Introduction

The objective of this procedure is to prepare a valid nitrogen-free Hanford Waste Vitrification Plant (HWVP) feed simulant containing the major components present in $\geq 3\%$ concentrations using Table 1 of the University of Georgia proposal¹ as the basis for the choice of the feed simulant composition. The major component feed simulant thus will contain 10 components, namely the nine metals Al, Cd, Fe, Mn, Nd, Ni, Na, Si, and Zr and the anion CO_3^{2-} . Metal chlorides rather than metal nitrates will be used as metal sources since experience has shown that feed simulants prepared from metal nitrates (e.g., UGA-12M1 and other feed simulants prepared according to this protocol) contain considerable amounts of nitrate ion in the metal hydroxide precipitates even after considerable washing. The nitrogen-free feed simulant is of interest in studies of the nitrogen balance and ammonia generation during reactions of the feed simulant with formic acid or other reducing acids since the only source of nitrogen is any nitrate and/or nitrate added in known amounts to the nitrogen-free feed simulant prior to the reaction.

In order to distinguish this feed simulant from other feed simulants prepared in this work, this feed simulant will be given the code name UGA-10M2, with the "10" corresponding to the 10 components, the "M" indicating that the components are the major components, and the "2" indicating that this is the first feed simulant of this type to be prepared during the course of this research project. In the early stages of the research to evaluate the role of the noble metals Ru, Rh, and Pd in hydrogen generation, variations of this feed simulant leaving out the redox component Fe and the metal complex forming component nitrite will also be prepared. The iron-free feed simulant based on this protocol will be called UGA-9XFe2, and an iron-free and aluminum-free feed simulant will be called UGA-8XFeAl2 with the first number indicating the number of components. In these

¹Research proposal entitled *Waste Vitrification Plant Feed Preparation Hydrogen Study* submitted to the Pacific Northwest Laboratories by the University of Georgia Research Foundation in August, 1991.

initial studies the noble metals of interest will be added as chlorides to individual aliquots of the feed simulant immediately before carrying out the ammonia generation and nitrogen balance studies. In later studies the noble metals will be introduced into the feed simulant preparation along with other metals precipitated as oxides or hydroxides.

The commercially available inorganic salts used as sources of the 12 components of the feed simulant UGA-10M12 are listed in Table 1.

Table 1
Sources of the Components of the Feed Simulant UGA-10M2

Component*	Molarity	Source	Amount‡	Water solubility§
Al	0.226	AlCl ₃ ·6H ₂ O	54.6 g	"soluble"
Cd	0.03	2 CdCl ₂ ·5H ₂ O	6.9 g	168 g/100 g @ 20°C
Fe	0.45	FeCl ₃ ·6H ₂ O	121.6 g	91.9 g/100 g @ 20°C
Mn	0.0314	{ KMnO ₄ MnCl ₂ ·4H ₂ O	{ 2.0 g 3.7 g	{ 6.38 g/100 g @ 20°C 151 g/100 g @ 0°C
Nd	0.0264	NdCl ₃ ·6H ₂ O	9.5 g	246g/100 g @ 25°C
Ni	0.0392	NiCl ₂ ·6H ₂ O	9.3 g	254 g/100 g @ 0°C
Si	0.0854	SiO ₂	5.13 g	insoluble
Zr	0.156	ZrOCl ₂ ·8H ₂ O	50.3 g	soluble
Na ⁺	0.250	Na ₂ CO ₃	see below	see below
CO ₃ ²⁻	0.125	Na ₂ CO ₃	13.25 g	7.1 g./100 g @ 0°C

* The insoluble components are present as Al(OH)₃, Fe(OH)₃, MnO₂, Nd₂O₃, Ni(OH)₂, SiO₂, ZrO₂.

‡ Amount for a one-liter batch.

§ The water solubility figures for these salts are taken from the *Handbook of Chemistry and Physics*.

Protocol

A flow chart for the protocol for the preparation of UGA-10M2 major component feed simulant is depicted in Figure 1. The individual steps are described below. Before beginning the procedure the vessel containing the final feed simulant is marked at a volume of one liter with tape to facilitate dilution to the correct final volume.

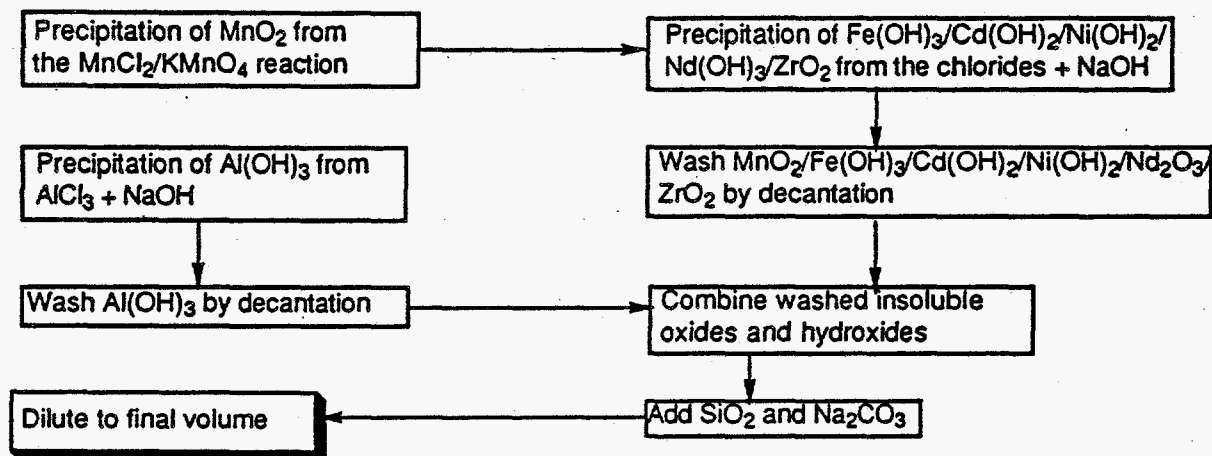
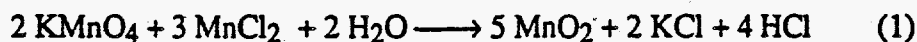


Figure 1: Outline of the scheme for the preparation of the nitrogen-free UGA-10M2 major component feed simulant.

(A) Precipitation of MnO₂.

The precipitation of MnO₂ uses the reaction of KMnO₄ with MnCl₂ according to the following general equation which is used to calculate the stoichiometry:



This procedure should be conducted in a hood because of the possibility of a side reaction of chloride with permanganate resulting in evolution of the toxic Cl₂.

Dissolve 3.7 g. of MnCl₂·4H₂O in 100 mL of water. Agitate the solution and maintain the temperature in the range 35–40°C. In a separate vessel dissolve 2.0 g. of KMnO₄ in 100 mL of water, agitate the solution and warm to 35–40°C. Add the warm KMnO₄ solution to the MnCl₂ solution slowly with constant stirring maintaining the temperature in the 35–40°C range. When the precipitation is complete, measure the pH. Allow the solution to cool.

(B) Precipitation of $\text{Fe}(\text{OH})_3/\text{Cd}(\text{OH})_2/\text{Ni}(\text{OH})_2/\text{Nd}_2\text{O}_3/\text{ZrO}_2$.

Add to the above slurry 500 mL of water and then add successively with constant stirring 121.6 g. of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 6.9 g. of $2 \text{CdCl}_2 \cdot 5\text{H}_2\text{O}$, 9.3 g. of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 9.5 g. of $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$, and 50.3 g. of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. After all of these solid chlorides have dissolved, add 10 M aqueous NaOH with constant stirring at such a rate (~1 to 5 mL/minute) that the temperature is maintained below 40°C during the addition. Monitor the pH of the slurry during the addition of NaOH and stop addition of the NaOH when the pH is in the range 10–11. If the end point is missed, backtitrate with hydrochloric acid. Record the final pH.

(C) Precipitation of $\text{Al}(\text{OH})_3$.

The $\text{Al}(\text{OH})_3$ must be precipitated in a separate vessel since a lower pH must be used to avoid loss of the aluminum through dissolution in excess NaOH to give soluble $\text{Al}(\text{OH})_4^-$. To prepare the $\text{Al}(\text{OH})_3$ dissolve 54.6 g. of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 500 mL of water. While agitating the solution add 10 M NaOH at such a rate (~1 to 5 mL/minute) that the temperature is maintained below 40°C during the course of the addition. Monitor the pH of the slurry during the addition of the NaOH. Stop the addition of NaOH when the pH is between 7 and 7.5 using hydrochloric acid to backtitrate if necessary.

(D) Washing the Oxide/Hydroxide Precipitates.

The purpose of washing the precipitates is to remove soluble components, particularly the sodium chloride formed as a byproduct upon treatment of the various metal chlorides with sodium hydroxide. The precipitates are washed by decantation with distilled water until the wash liquid is free of chloride and other salts. This is readily determined by measuring the conductivity of the wash liquid and comparing it with pure water. The precipitates of $\text{MnO}_2/\text{Fe}(\text{OH})_3/\text{Cd}(\text{OH})_2/\text{Ni}(\text{OH})_2/\text{Nd}_2\text{O}_3/\text{ZrO}_2$ and of $\text{Al}(\text{OH})_3$ are each allowed to settle until their volume does not decrease significantly. The supernatant liquids are then removed by decantation. Each remaining precipitate is then stirred separately with at least three times its volume of pure water for a *minimum* of ten minutes after no further change is observed. The resulting slurry is then allowed to settle until the precipitate volume does not decrease significantly (a *minimum* of 12 hours and possibly as much as three days). The supernatant liquid is then removed by decantation and its conductivity checked. This washing procedure is repeated in the same way for at least a second time and until the water does not contain significant amounts of electrolytes (NaCl) as determined by its conductivity compared with pure water. The nitrate concentration of the wash liquid can also be monitored by a chloride-selective electrode and/or ion chromatography if these analytical methods are available.

(E) Addition of SiO₂ and Na₂CO₃.

Remove by decantation enough of the final wash water for both the MnO₂/Fe(OH)₃/Cd(OH)₂/Ni(OH)₂/Nd₂O₃/ZrO₂ and the Al(OH)₃ slurries so that the total volumes of each slurry is no more than ~350 mL. Then add the Al(OH)₃ slurry to the MnO₂/Fe(OH)₃/Cd(OH)₂/Ni(OH)₂/Nd₂O₃/ZrO₂ slurry using a minimum of wash water to wash the Al(OH)₃ slurry into the other vessel. Then add with stirring 5.13 g. of SiO₂ and 13.25 g. of Na₂CO₃ making sure that the Na₂CO₃ does not contain any clumps that might dissolve slowly. The SiO₂ will remain insoluble but the Na₂CO₃ will dissolve. Dilute the final slurry to one liter and package in a screw cap bottle. After shaking the bottle well remove a reference sample of 25 mL of the slurry, place in a secondary container, and send it in a labelled bottle to Karyn Wiemers P7-14, PNL HWVP Technology Development Project, Battelle Pacific Northwest Laboratories, P. O. Box 999, Richland, Washington 99352. Also retain the final 25 mL of each sample of feed simulant after completion of the hydrogen generation studies as an additional reference sample for analysis.