RECEIVED
MAR 28 1996
OSTI

PNNL-10981

UC-810

Project Technical Information

Hanford Waste Vitrification Plant Hydrogen Generation Study

R. B. King
A. D. King, Jr.
N. K. Bhattacharyya
G. Vemparala
V. Vemparala
N. B. Turner
J. L. Walters

February 1996

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

Pacific Northwest National Laboratory
Richland, Washington 99352

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *mw*

MASTER

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.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Hanford Waste Vitrification Plant Hydrogen Generation Study

R. B. King
A. D. King, Jr.
N. K. Bhattacharyya
G. Vemparala
V. Vemparala
N. B. Turner
J. L. Walters

February 1996

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

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The purpose of the research supported by the Hanford Waste Vitrification Plant (HWVP) project of the Department of Energy through Battelle Pacific Northwest Laboratory (PNL) and summarized in this report was to gain a basic understanding of the hydrogen generation process and to predict the rate and amount of hydrogen generation during the treatment of HWVP feed simulants with formic acid. The objectives of the study were to determine the key feed components and process variables which enhance or inhibit the production of hydrogen. Information on the kinetics and stoichiometry of relevant formic acid reactions were sought to provide a basis for viable mechanistic proposals. The chemical reactions were characterized through the production and consumption of the key gaseous products such as H_2 , CO_2 , N_2O , NO , and NH_3 . For this reason this research program relied heavily on analyses of the gases produced and consumed during reactions of the HWVP feed simulants with formic acid under various conditions. Such analyses used gas chromatographic equipment and expertise at the University of Georgia for the separation and determination of H_2 , CO , CO_2 , N_2 , N_2O , and NO .

Simulants for the HWVP feed containing the major non-radioactive components Al, Cd, Fe, Mn, Nd, Ni, Si, Zr, Na, CO_3^{2-} , NO_3^- , and NO_2^- have been prepared. They have been used as media to evaluate the stability of formic acid towards hydrogen evolution by the reaction $HCO_2H \longrightarrow H_2 + CO_2$ catalyzed by the noble metals Ru, Rh, and/or Pd found in significant quantities in uranium fission products. In most cases the individual noble metals were used in separate experiments in closed small-scale (~550 mL) reactors to evaluate the effects of major feed simulant components such as NO_2^- , NO_3^- , Fe^{+3} , Al^{+3} , UO_2^{+2} and Cd^{+2} on their catalytic activities for formic acid decomposition. Reactions were monitored by using gas chromatography to analyze the CO_2 , H_2 , NO , and N_2O in the gas phase as a function of time.

Rhodium introduced as soluble $RhCl_3 \cdot 3H_2O$ was found to be the most active catalyst for hydrogen generation from formic acid above ~80°C in the presence of nitrite ion in accord with earlier observations from work supported by Westinghouse Savannah River Laboratory (WSRL) (King 1992a). The rate of this rhodium-catalyzed hydrogen production appears to be enhanced by the iron and aluminum present in the feed simulants, possibly by the stabilization of the active rhodium species by complexation on their oxide surfaces. The inherent homogeneous nature of the nitrite-promoted rhodium-catalyzed formic acid decomposition is suggested by the approximate first-order dependence of the hydrogen production rate on rhodium concentration and the lower activity of insoluble rhodium sources such as coprecipitated rhodium oxide or rhodium metal adsorbed on charcoal or alumina. Titration of the typical feed simulants containing carbonate and nitrite with formic acid in the presence of rhodium at the reaction temperature (~90°C) indicates that the nitrite-promoted rhodium-catalyzed decomposition of formic acid occurs only after formic acid has reacted with all of the carbonate and nitrite present to form CO_2 and NO/N_2O , respectively. The catalytic activities of ruthenium and palladium towards hydrogen generation from formic acid are quite different than those of rhodium in that they are inhibited rather than promoted by the presence of nitrite ion. Palladium is also an active catalyst for the reductions of nitrate and NO to N_2O in feed simulant media. Hydrogen generation has been observed in the formic acid titration of a nitrite-free

KfK feed simulant provided by PNL containing Ru, Rh, and Pd at the target Neutralized Current Acid Waste (NCAW) simulant composition. In a series of selected experiments, all of the nitrite nitrogen introduced in the slurry was accounted for within 10% in reactions leading to NO and N₂O. Some discrepancies were found in the carbon balance, perhaps attributed to reduction of nitrogen oxide or oxyacids to N₂O and/or NH₃ by formic acid.

Contents

Summary	iii
1.0 Introduction	1.1
2.0 Recommended Research	2.1
3.0 Background	3.1
4.0 Experimental Approach	4.1
4.1 Gas Analyses	4.1
4.2 Formic Acid Reactions	4.1
4.3 Feed Simulant Preparation	4.3
5.0 Results	5.1
5.1 Initial Screening Studies	5.1
5.1.1 Experiments with Rhodium	5.1
5.1.2 Experiments with Ruthenium	5.6
5.1.3 Experiments with Palladium	5.6
5.1.4 Ammonia Production	5.6
5.1.5 Comparison of Data on the WSRL and PNL Feed Simulants	5.8
5.2 Titration Studies Using the Syringe Pump	5.9
5.2.1 Experiments in the Absence of Noble Metals	5.11
5.2.2 Experiments in the Presence of Rhodium	5.14
5.2.3 Effect of the Type of Rhodium Source	5.14
5.2.4 Effect of Rhodium Concentration	5.16
5.2.5 Effect of Nitrite Concentration	5.20
5.2.6 Effect of Temperature	5.25
5.2.7 Mixed Metal Experiments	5.25

5.2.8 Tests with the KfK Feed Simulant Supplied by PNL	5.30
5.3 Some Observations on Carbon and Nitrogen Balance	5.31
5.3.1 Carbon Balance	5.33
5.3.2 Nitrite Nitrogen Balance	5.35
6.0 Discussion	6.1
7.0 Literature References	7.1
Appendix A: Protocol for the Preparation of the Major Component HWVP Feed Simulant: UGA-12M1	A.1
Appendix B: Summary of Reactions of Formic Acid with Feed Simulants Studied During the Course of this Project	B.1

Figures

1 Flow Chart for the Vitrification of Nuclear Wastes	1.1
2 Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrite	5.2
3 Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Iron	5.3
4 Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Aluminum	5.3
5 Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Uranium	5.4
6 Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Cadmium	5.5
7 Ruthenium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrite	5.7
8 Ruthenium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrate	5.8
9 Palladium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrite	5.9
10 Palladium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrate	5.10
11 Summary of the Effects of Nitrite and Nitrate on Hydrogen Generation Catalyzed by Palladium	5.10
12 Treatment of the UGA-12M1 Feed Simulant with Formic Acid in the Absence of Noble Metals Using the Syringe Pump	5.12
13 Treatment of the Iron-Free UGA-11XFe1 Feed Simulant with Formic Acid in the Absence of Noble Metals Using the Syringe Pump	5.13
14 Titration of a Carbonate-Free Feed Simulant Containing Nitrite with Formic Acid Added at the Rate of 0.453 mmol/min	5.14
15 Titration of the UGA-12M1 Feed Simulant with Formic Acid in the Presence of Rhodium Trichloride	5.15
16 Production of Hydrogen and Other Gases by Formic Acid Titration of the Feed Simulant UGA-13M+Rh1 in Which the Rhodium has been Coprecipitated Along with the Other Metals Using $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ as the Rhodium Source	5.17

17 Production of Hydrogen and Other Gases by Formic Acid Treatment of 50 mL of the Feed Simulant UGA-12M1A in the Presence of 0.1175 g of 5% Rhodium on Carbon	5.18
18 Production of Hydrogen and Other Gases by Formic Acid Treatment of 50 mL of the Feed Simulant UGA-12M1B in the Presence of 0.1175 g of 5% Rhodium on Alumina	5.19
19 Effect of Rhodium Concentration on Hydrogen Production Upon Treatment of 50 mL of UGA-12M1B Feed Simulant and 10 mL of Water with Formic Acid	5.21
20 Maximum Hydrogen Production Rate (mmole/min) Versus Rhodium Concentration ($[M] \times 10^{-3}$) in the Regime of Catalyst Activity	5.22
21 Production of CO_2 , H_2 , NO , and N_2O by Formic Acid Titration of the Feed Simulant UGA-11XN1 in the Presence of Rhodium at Four Different Nitrite Concentrations	5.23
22 Top: Hydrogen Production Versus Time for Four Different Nitrite Concentrations from the Formic Acid Titration of 50 mL UGA-11XN1 + 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ + 10 mL of Water; Bottom: Hydrogen Turnover Numbers (mmoles H_2 /mmoles Rh/24 hr) as a Function of Nitrite Concentration in the Experiments Depicted Individually in Figure 21	5.24
23 Effect of Sodium Nitrite Concentration on the Rhodium-Catalyzed Production of Hydrogen from Formic Acid in Feed Simulant Media	5.26
24 Hydrogen Evolution at Different Temperatures: 50 mL UGA-12M1C Feed Simulant, 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and 10 mL of Water	5.27
25 Generation of Hydrogen at 90°C after Pretreatment at 70°C for the Indicated Period of Time Using 50 mL UGA-12M1C, 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and 10 mL of Water	5.28
26 Titration of 50 mL of the Feed Simulant UGA-12M1C and 10 mL of Water with 85 mmoles of Formic Acid at 89-92°C in the Presence of Rh (7 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$), Ru (5 mg "hydrated ruthenium chloride), and/or Pd (5 mg PdCl_2)	5.29
27 Details of the NO and N_2O Evolution in the Experiments Depicted in Figure 26	5.30
28 Titration of 50 mL of the KfK Feed Simulant Supplied by PNL with Formic Acid Without Added Nitrite and with 1.5 g (21.4 mmoles) of Added Sodium Nitrite	5.32

Tables

1 Comparison of the Feed Simulant Compositions	3.2
2 Sources of the Components of the Feed Simulant Compositions	4.2
3 Some Analytical Data from PNL on Feed Simulant Samples	4.5
4 Production of Ammonia from the Decomposition of Formic Acid in Feed Simulants Containing Nitrite and Nitrate	5.11
5 Effect of the Amount of Rhodium on Hydrogen Production from Formic Acid. Experiment was conducted with 50 mL UGA12M1B feed simulant, 10 mL water, and 86 mmoles formic acid.	5.20
6 Carbon Dioxide Balance for the Experiments Depicted in the Figures of this Report	5.34
7 Nitrite Nitrogen Balance in the Experiments Depicted in Figure 21	5.35

1.0 Introduction

The most promising method for the disposal of highly radioactive nuclear wastes is a vitrification process in which the wastes are incorporated into borosilicate glass logs, the logs are sealed into welded stainless steel canisters, and the canisters are buried in suitably protected burial sites for disposal. The key features of this general scheme are outlined in Figure 1.

Feed preparation for the vitrification process requires use of formic acid for glass redox and melter feed rheology control. The operation of the glass melter and durability of the glass is affected by the oxidation state of the glass during processing. Formation of a conductive metallic sludge in an overreduced melt can result in a shortened melter lifetime. An overoxidized melt may lead to foaming and loss of ruthenium as volatile RuO_4 . Historically, foaming in the melter has been controlled by introduction of a reductant into the melter feed. For these reasons formic acid was selected by the Savannah River Laboratory (SRL) for its Defense Waste Processing Facility (DWPF) feeds as an acid which not only solubilizes the metals but also reduces mercury from Hg^{+2} and Hg_2^{+2} to mercury metal for subsequent steam stripping and manganese, the component believed to contribute to reboil in the melt, from MnO_2 to Mn^{+2} . Formic acid was also found to decrease the melter feed viscosity thereby enhancing the pumping in the plant.

Figure 1. Flow Chart for the Vitrification of Nuclear Wastes

2.0 Recommended Research

The information from this research project as well as from the previous work (King 1992a) supported by WSRL has been inferred exclusively by monitoring the production and consumption of gaseous products, particularly H_2 , CO_2 , N_2O , and NO , as a function of time. Additional useful information could be obtained by monitoring the composition of the liquid phase as a function of time. Of particular interest is the pH, redox potential and the production of NH_3/NH_4^+ . The monitoring of pH during the course of these reactions could be achieved by redesigning the apparatus to accommodate a pH electrode provided that an electrode can be found which can withstand the necessary pressures (up to 3 atmospheres) and temperatures (up to $100^\circ C$). A similar procedure could be used to monitor redox potential. Monitoring NH_3/NH_4^+ is potentially more difficult since use of an ammonia electrode requires making the solution sufficiently basic to generate NH_3 ; therefore continuous monitoring of NH_3 by this method is impossible. A possible alternative would be to modify the apparatus to remove periodically small liquid samples without disturbing the pressure or the gas phase. This would, of course, be analogous to what is actually done with the gas phase in the experiments reported here, where small gas samples are removed with an appropriate syringe. Still another alternative would be to redesign the entire experiment to use an open system at ambient pressure such as is used in the larger scale reactions at WSRL and PNL. This would allow the use of pH and other electrodes which cannot withstand elevated pressures but would also change the chemistry significantly since gaseous products, notably NO , would be removed from the reaction site as they are formed and therefore would not be available for further chemistry as is the case with the experiments discussed in this report.

Another question of interest is the nature of the nitrorhodium complexes involved in the nitrite-promoted rhodium-catalyzed formic acid decomposition [e.g., Equations (7) to (12)]. Most instructive would be the synthesis of model nitrorhodium compounds and the study of their chemical reactivity towards formic acid and formates, possibly using the observation of high field proton Nuclear Magnetic Resonance (NMR) resonances as indicators of rhodium hydride formation. In addition, the occurrence of the spin $1/2$ ^{103}Rh isotope in 100% natural abundance makes the resonances of hydrogens directly bonded to rhodium as distinctive doublets with characteristic $J(^{103}Rh-H)$ coupling constants.

3.0 Background

Laboratory and pilot scale studies using formic acid for the pretreatment of simulated nuclear wastes have been carried out both at WSRL and the PNL. Of particular significance was the observation in 1988 at PNL of hydrogen generation during treatment of an NCAW feed simulant with formic acid in a laboratory-scale apparatus (Wiemers 1988). Furthermore, in pilot-scale studies at SRL in 1990 significant levels (three to four times the lower flammability limit) of hydrogen were observed during preparation of a DWPF feed simulant (Hutson 1992).

The suggested cause of this unwanted hydrogen generation is the catalytic decomposition of formic acid, i.e.,

Possible catalysts are the noble metals ruthenium, rhodium, and palladium present in the wastes as uranium fission products (Choppin 1980). In this connection there is a strong precedent in the literature for the noble metal catalyzed decomposition of formic acid to hydrogen. The earliest studies by Müller and Loerpabel (1929) used salts of the six platinum group metals to effect the dehydrogenation of 10% formic acid containing dissolved sodium formate. Much more recent studies have focussed on various aspects of palladium-catalyzed formic acid decomposition including work by Ruthven and Upadhye (1971) on the catalytic decomposition of aqueous formic acid over palladium black, work by Aguiló (1969) on the palladium(II) catalyzed oxidation of formic acid in acetic acid solution, and work by Hill and Winterbottom (1988) on the palladium-catalyzed decomposition of formic acid/sodium formate solutions. Soluble derivatives of other noble metals including ruthenium carbonyls (Laine 1977) and the rhodium phosphine complex $\text{Rh}(\text{C}_6\text{H}_4\text{PPh}_2)(\text{PPh}_3)_2$ (Strauss 1979) have also been shown to be active homogeneous catalysts for formic acid decomposition. However, these ruthenium and rhodium derivatives contain carbonyl or phosphine ligands which are expected to modify greatly the underlying noble metal chemistry and which are unlikely to be present in the nuclear wastes being treated.

Initial studies at the University of Georgia on the noble metal catalyzed decomposition of formic acid in non-radioactive simulated nuclear wastes were supported by the WSRL. Results from this phase of the work were presented at a recent symposium on the Chemical Pretreatment of Nuclear Wastes (King 1992a). The compositions of the Defense Waste Processing Facility (DWPF) nuclear waste simulants used in the University of Georgia studies are compared with the HWVP NCAW feed simulant in Table 1.

The general objectives of the initial phase of this research project at the University of Georgia supported by WSRL were the elucidation of the origin of this hydrogen production and the development of practical methods for its inhibition. Initial experiments screened the four noble metals of interest, namely Ru, Rh, Pd, and Ag, for their catalytic activity for the decomposition of pure formic

Table 1. Comparison of the Feed Simulant Compositions

Amount, % by Weight (Dry Oxide Basis)

	DWPF		HWVP ^(a)
	IDMS (pH 11) HM Sludge Simulant	Low Nitrite Purex (pH = 12) Sludge Simulant	HWVP NCAW (pH 10 to 11) Slurry Simulant
Al(OH) ₃	25.0	12.3	14.1
BaSO ₄	0.22	0.51	0.27
B ₂ O ₃			0.0058
CdO			3.1
CeO ₂			0.65
Ca ₃ (PO ₄) ₂	0.097	0.25	1.93
CaCO ₃	1.48	5.1	0.58
CaSO ₄		0.47	
Cr ₂ O ₃	0.22	0.41	0.27
CsNO ₃	0.028	0.003	0.85
CuO	0.054	0.182	0.25
Fe(OH) ₃	25.9	51.2	28.8
GeO ₂			0.000155
Nd ₂ O ₃	2.34	0.25	3.5
KOH	0.17	0.40	0.24
La ₂ O ₃			0.66
Li ₂ O			0.000072
MgO	0.34	0.25	0.37
MnO ₂	6.6	7.3	2.18
MoO ₃			0.57
Na ₂ CO ₃	0.107	0.148	9.9
Na ₂ C ₂ O ₄			0.134
Na ₂ SO ₄	0.47	0.17	0.82
Na ₃ PO ₄	0.041	0.012	
NaCl	0.48	1.54	0.49
NaF	0.26	0.27	0.22
NaI		0.027	0.0000054
NaNO ₂	12.1	2.45	24.0
NaNO ₃	0.48	0.36	7.5
NaOH	1.37	3.51	1.4
Nb ₂ O ₅			0.0103
Ni(OH) ₂	1.31	4.5	2.9
PbSO ₄	0.22	0.51	0.71
Pr ₂ O ₃			0.156
Rb ₂ O			0.58

Table 1. (contd)

	DWPF		HWVP ^(a)
	IDMS (pH 11) HM Sludge Simulant	Low Nitrite Purex (pH = 12) Sludge Simulant	HWVP NCAW (pH 10 to 11) Slurry Simulant
Re ₂ O ₇ (for Tc)			0.24
Sb ₂ O ₃			0.0059
SeO ₂	0.002	0.003	0.0161
SiO ₂	5.0	1.67	4.1
Sm ₂ O ₃			0.077
SnO			0.0107
SrCO ₃	0.41	0.038	0.172
Ta ₂ O ₅			0.00338
TeO ₂	0.028	0.031	0.101
TiO ₂			0.66
Y ₂ O ₃			0.081
Zeolites	9.3	1.66	
ZnO	0.043	0.341	0.340
ZrO ₂	1.842	3.828	15.4

- (a) The data on the HWVP slurry are stated in a form comparable to the WSRL sludge simulant by assuming that the PO_4^{3-} ion is present as the Ca^{+2} salt, the CO_3^{2-} , SO_4^{2-} , Cl^- , F^- , I^- , NO_2^- , and NO_3^- ions (other than the amounts required for the Ba^{+2} , Cs^+ , and Sr^{+2}) are present as Na^+ salts, the oxides Al_2O_3 , K_2O , Na_2O (after subtracting the Na required as counterions for CO_3^{2-} , SO_4^{2-} , Cl^- , F^- , I^- , NO_2^- , and NO_3^-), and NiO are hydrated to hydroxides, and BaO , Cs_2O , and SrO are converted to BaSO_4 , CsNO_3 , and SrCO_3 , respectively.

acid (King 1992b). Subsequent experiments (King 1992a) investigated the catalytic activity of these noble metals for formic acid decomposition in non-radioactive sludges simulating the compositions of the feed to be used in the glass melter (see Table 1). The other components in the sludge simulants, particularly nitrite ion, were found to modify profoundly the catalytic activity of the noble metals of interest for formic acid decomposition. The important result from this phase of the research was the discovery that rhodium trichloride was the most active catalyst precursor for hydrogen evolution from the sludge simulant under the conditions of interest even though it was inactive as a catalyst precursor for hydrogen evolution from pure formic acid at the same temperature. The nitrite ion present in the sludge simulant was shown to be the critical component enhancing the catalytic activity of rhodium for formic acid decomposition. Organic aminopolycarboxylic acids such as ethylenediamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) showed some promise as inhibitors for hydrogen evolution under these conditions (King 1992b).

The feed preparation processes studied for WSRL are similar to those at HWVP. The slurry compositions are similar in many respects (Table 1). Furthermore, both processes involve the

addition of formic acid to the alkaline waste at an elevated temperature. For this reason the results of the WSRL work focusing on the DWPF sludges have direct application to HWVP hydrogen generation. Larger- scale WSRL and PNL testing, to which the smaller scale testing provides basic understanding of the hydrogen generation process, will provide input for equipment design and operating process steps needed to control hydrogen gas concentrations. The development information which could affect that equipment design is needed as far ahead of that design completion date as possible.

The purpose of the research supported by the HWVP project through PNL and summarized in this report was to gain a basic understanding of the hydrogen generation process and to predict the rate and amount of hydrogen generation during the treatment of the HWVP feed with formic acid. The objectives of the study were to determine the key feed components and process variables which enhance or inhibit the production of hydrogen. Information on the kinetics and stoichiometry of relevant formic acid reactions were sought to provide a basis for viable mechanistic proposals. The chemical reactions were characterized through the production and consumption of the key gaseous products such as H_2 , CO_2 , N_2O , NO and NH_3 . For this reason this research program relied heavily on analyses of the gases produced and consumed during reactions of the HWVP feed simulants with formic acid under various conditions. Such analyses used gas chromatographic equipment and expertise at the University of Georgia for the separation and determination of H_2 , CO , CO_2 , N_2 , N_2O , and NO .

4.0 Experimental Approach

Feed simulants were prepared on a one-liter scale from reagent grade chemicals listed in Table 2 according to the protocol summarized in Appendix A. Samples of these feed simulants (generally 40 to 50 mL) were treated with 88 wt% formic acid in a 550 mL closed glass reactor at 80 to 100°C. Gas samples were withdrawn periodically and analyzed for CO₂, H₂, NO, and N₂O by gas chromatography. The reaction mixtures remaining at the end of the experiment were submitted to PNL for NH₃ analyses. In the initial series of experiments, summarized in Section 5.1, all of the formic acid was added at the beginning of the experiment in a procedure similar to that used in the previous work supported by WSRL. During the course of this project this general experimental procedure was modified by using a syringe pump to deliver the formic acid at a slow measured rate into the reaction mixture at the desired reaction temperature.

4.1 Gas Analyses

Hydrogen analyses were performed using a Varian 90P gas chromatograph. The hydrogen was eluted on an 8 ft x 1/4 in. column packed with a 40/60 mesh 13x 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 6.5 ft 80/100 mesh Columnpak PQ and an 11 ft 13x 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 as part of the Quality Assurance protocol.

Nitrogen dioxide could not be determined by gas chromatography because of the $2\text{NO}_2 \leftrightarrow \text{N}_2\text{O}_4$ equilibrium. Ammonia was measured as soluble ammonium ion in the slurry. Ammonia analyses were conducted at PNL using a specific ion electrode technique.

4.2 Formic Acid Reactions

The reactions were conducted in a glass reaction vessel of ~250 mL or ~550 mL total capacity equipped with a threaded plug and O-ring adapter. A pressure gauge was attached to the system. The two side-arms of the vessel near the top were capped with rubber septa through which needles could be inserted to flush the system or for gas sampling purposes. 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. Magnetic stirring was used.

Table 2. Sources of the Components of the Feed Simulant UGA-12M1

Component ^(a)	Molarity	Source	Amount ^(b)	Water solubility ^(c)
Al	0.226	Al(NO ₃) ₃ •9H ₂ O	84.8 g	63.7 g/100g @ 25°C
Cd	0.03	Cd(NO ₃) ₂ •4H ₂ O	9.2 g	215 g/100 g @ 25°C
Fe	0.45	Fe(NO ₃) ₃ •9H ₂ O	181.8 g	"soluble"
Mn	0.0314	KMnO ₄	2.0 g	6.38 g/100 g @ 20°C
		Mn(NO ₃) ₂ •6H ₂ O	5.4 g	426.4 g/100 g @ 0°C
Nd	0.0264	Nd(NO ₃) ₃ •6H ₂ O	11.6 g	152.9 g/100 g @ 25°C
Ni	0.0392	Ni(NO ₃) ₂ •6H ₂ O	11.6 g	238.5 g/100 g @ 0°C
Si	0.0854	SiO ₂	5.1 g	insoluble
Zr ^(d)	0.156	ZrO(NO ₃) ₂	36.1 g	soluble
Na ⁺	0.801 ^(e)	Na ₂ CO ₃ + NaNO ₃ + see below		see below
NaNO ₂				
CO ₃ ⁻²	0.125	Na ₂ CO ₃	13.2 g	7.1 g/100 g @ 0°C
NO ₃ ⁻	0.116	NaNO ₃	9.9 g	92.1 g/100g @ 25°C
NO ₂ ⁻	0.435	NaNO ₂	30.0 g	81.5 g/100 g @ 15°C

- (a) The insoluble components are present as Al(OH)₃, Fe(OH)₃, MnO₂, Nd₂O₃, Ni(OH)₂, SiO₂, and ZrO₂.
- (b) Amount of source chemical for a one-liter batch.
- (c) The water solubility figures for these salts are taken from the *Handbook of Chemistry and Physics*.
- (d) The amount of zirconyl nitrate per liter was increased from 36.1 g to 52.9 g after zirconium analyses by PNL suggested that the available material was the hexahydrate ZrO(NO₃)₂•6H₂O rather than the anhydrous salt.
- (e) 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.

The initial experiments were performed using a procedure closely related to the general procedure used for the earlier phase of this work supported by WSRL. In typical experiments a reaction vessel of the above type was charged with 40 mL of the sludge simulant and 2.1 mL of 88 wt% formic acid. After flushing the mixture with argon a weighed quantity of the noble metal compound or a known volume of an aqueous solution of a noble metal compound was added against an argon countercurrent. The system was then closed and the gas phase analyzed using the system described above. The solution was warmed to the desired reaction temperature (typically 80–100°C) and kept there using a temperature controller. 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.

A feature of the WSRL experimental procedure is the introduction of the entire amount of formic acid at the beginning of the experiment before bringing the reaction mixture to the reaction temperature. In order to simulate more closely the actual experimental conditions, the experimental procedure was revised so that the formic acid was introduced gradually into the reaction mixture only at the reaction temperature ($\sim 90^\circ\text{C}$) at a rate scaled to that used by PNL in the larger scale experiments. Such experiments require the gradual addition of ~ 1 mL of formic acid per hour to the hot reaction mixture. A Sage Instruments Model 355 syringe pump was used to drive 10 mL plastic BD disposable syringes of formic acid in these experiments. The pump was tested under the anticipated reaction conditions [e.g., Experiment 1.3 in the PNL Detailed Design Data Package (Wiemers 1991)]^(a) by setting it to deliver 2.1 mL of pure water over a 130 minute period. The actual amounts of water delivered during this period in two experiments were found to be 2.14 mL and 2.16 mL. The syringe pump was then used to deliver 88 wt% formic acid below the surface of the feed simulant in a closed reactor such as that described above. The standard rate of addition of formic acid was $0.0194\text{ mL/min} = 1.164\text{ mL/hr}$ corresponding to $0.448\text{ mmol HCO}_2\text{H/min}$ or $26.88\text{ mmol HCO}_2\text{H/hr}$. The setting on the syringe pump to achieve this rate of addition was checked weekly with either formic acid or pure water. In a typical run 88 wt% formic acid was added at this rate for a total of 190 minutes corresponding to a total of 85.1 mmol of formic acid.

In order to minimize weighing errors a stock aqueous solution of 1.4 mg/mL of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was prepared. Many runs used 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ corresponding to 10 mL of this stock solution. In order to keep the total volume the same in all of the experiments using the syringe pump, 10 mL of water was always added even if this rhodium stock solution was not used. For brevity $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is abbreviated as " RhCl_3 " in many of the figures.

A summary of all of the runs completed through the transmittal of the draft report (November 1992) is listed in Appendix B.

4.3 Feed Simulant Preparation

The objective of the protocol was the preparation of a representative HWVP feed simulant containing the major components present in $\geq 3\%$ concentrations using Table 1 as the basis for the choice of the feed simulant composition. The major component feed simulant contained 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 in which one or more components were omitted or additional components added, this feed simulant was 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. Different batches of the

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

feed simulants of the same nominal composition were distinguished by designations such as UGA-12M1, UGA-12M1A, UGA-12M1B, etc. Variations of this feed simulant were also prepared leaving out the redox component Fe, the metals Al or Cd, and the anions nitrite, nitrate, and carbonate. In the feed simulant prepared without the addition of nitrate ion as sodium nitrate the metal ions were still introduced as their nitrate salts but the water washing of the oxide/hydroxide precipitates can be assumed to remove at least most of the nitrate ion introduced with the metal ions. The iron-free feed simulant based on this protocol was called UGA-11XFe1; the nitrite-free feed simulant based on this protocol was called UGA-11XN1; and an iron-free and nitrite-free feed simulant was called UGA-10XFeN1 with the first number indicating the number of components, etc. In most of this work the noble metals of interest were added as soluble compounds (mainly chlorides but occasionally nitrates) to individual aliquots of the feed simulant immediately before carrying out the hydrogen generation studies.

The commercially available inorganic salts used as sources of the 12 components of the feed simulant UGA-12M1 are listed in Table 2. Analyzed reagent grade chemicals except for the neodymium and zirconium nitrates were used as sources of the metals and ions. Neodymium and zirconium nitrates were not available as reagent grade chemicals but were purchased from Aldrich Chemical Company as 99.9% neodymium nitrate hexahydrate and zirconyl nitrate, respectively. In the feed simulants prepared during most of the work the zirconium nitrate was assumed to be anhydrous in the absence of information to the contrary. However, a zirconium analysis from PNL suggested that the zirconyl nitrate used for the feed simulant preparation was actually the hexahydrate $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ rather than the anhydrous salt indicated in Table 2 (ID 92-09927). As a result of this the amount of zirconyl nitrate per liter for the feed simulant protocol was increased from 36.1 g to 52.9 g for the preparation of UGA-12M1C and subsequent feed simulants.

The protocol for preparing the feed simulant is given in Appendix A. All of the chemicals for the feed simulant preparation were weighed on an electronic balance certified to ± 0.1 g.

The compositions of the initially prepared feed simulants were checked by the Inorganic Analysis Group of the Pacific Northwest Laboratory. The metals were determined by inductively coupled argon plasma emission spectrometry and the ions were determined by ion chromatography. Results are listed in Table 3. Some of the variances can be explained as follows:

1. Low values for aluminum can arise because of solubility of $\text{Al}(\text{OH})_3$ in excess base.
2. The zirconium source was assumed to be the anhydrous salt $\text{ZrO}(\text{NO}_3)_2$ but was later found by zirconium analyses to be the hexahydrate $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ thereby accounting for the low values of zirconium in the feed simulants analyzed.
3. The silicon values are known to be consistently low owing to poor recovery during sample preparation.

4. Sodium is used as a counterion for introduction of nitrate, nitrite, and carbonate and is therefore of variable concentration depending on how many of these anions are introduced.
5. Low values of nitrite ion were found. The reason for this is not clear at the present time. The nitrogen balance studies (Section 5.3.2) were done on nitrite-free feed simulant UGA-11XN1 to which the desired amount of sodium nitrite was added immediately before the experiment in order to avoid uncertainty in the amount of nitrite present.

Table 3. Some Analytical Data from PNL on Feed Simulant Samples

Element	Concentration, Moles/liter				
	Target	10XFeN1	11XFe1	11XN1	12M1
Al	0.226	0.235	0.182	0.076	0.090
Cd	0.03	0.030	0.023	0.024	0.029
Fe	0.45	<0.001	<0.001	0.345	0.418
Mn	0.0314	0.034	0.026	0.024	0.029
Na	0.801	0.355	0.644	0.286	0.689
Ni	0.0392	0.037	0.029	0.031	0.037
Si	0.0854	0.028	0.028	0.029	0.037
Zr	0.156	0.118	0.090	0.083	0.101
<u>Ion</u>					
NO ₂ ⁻	0.435	< 0.003	0.169	<0.003	0.124
NO ₃ ⁻	0.116	0.135	0.115	0.099	0.079

5.0 Results

5.1 Initial Screening Studies

These initial screening studies were conducted using the WSRL methodology for the purpose of comparison. Thus all of the formic acid was introduced at the beginning of the experiment as 88 wt% formic acid before the reaction mixture was brought to the desired reaction temperature. All of these experiments were done in reaction vessels of ~250 mL total capacity.

5.1.1 Experiments with Rhodium

The effects of the presence of nitrite, iron, aluminum, uranium, and cadmium on the rhodium-catalyzed decomposition of formic acid in feed simulant media were examined. The results are summarized below.

5.1.1.1 Nitrite

Hydrogen generation from the nitrite-containing feed simulant UGA-12M1 and the corresponding feed simulant without nitrite, namely UGA-11XN1, are compared in Figure 2 under essentially identical conditions. The promoter effect of nitrite is clearly indicated in Figure 2. Thus in the presence of nitrite a total of ~6 mmol of H_2 was generated over 300 minutes whereas only a total of ~0.3 mmol of H_2 was generated in the absence of nitrite even after 450 minutes. No NO or N_2O were observed in the experiments with the UGA-11XN1 feed simulant, which contains nitrate but not nitrite, indicating that rhodium is not able to catalyze the formic acid reduction of nitrate. In addition, the amount of CO_2 produced in the experiment is reduced from 18.6 mmoles in the feed simulant containing nitrite, namely UGA-12M1, to only 10.0 mmoles in the nitrite-free feed simulant, UGA-11XN1, corresponding to the absence of nitrite reduction by formic acid in the latter experiment.

5.1.1.2 Iron

Iron can influence the catalytic properties of rhodium and other noble metal through the redox properties of the Fe(II)/Fe(III) couple ($E^\circ = 0.77$ V for Fe^{3+}/Fe^{2+} in acid solution) (Cotton and Wilkinson, 1988). Figure 3 shows the generation of gases from the treatment of the iron-free feed simulant UGA-11XFe1 with formic acid. Compared with the UGA-12M1 feed simulant, relatively little H_2 (~1.4 mmole) is observed suggesting that iron, like nitrite, enhances the apparent catalytic activity of rhodium for formic acid decomposition. Iron is present in feed simulants as iron(III) oxide. The preferential reduction of iron(III) to iron(II) over the reduction of catalytically active rhodium(III) or rhodium(I) species to relatively inactive rhodium metal by formic acid could account

Figure 2. Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrite

for the apparent ability of iron to promote this catalytic reaction. The generation rates and amounts of CO₂, N₂O, and NO appear not to be affected by the absence of iron.

5.1.1.3 Aluminum

Aluminum oxide can influence the catalytic properties of rhodium and other noble metals by stabilizing reactive intermediates by chemical anchoring on the oxide surface. Figure 4 shows the generation of gases from the treatment of the aluminum-free feed simulant UGA-11XA11 with formic acid. Again the generation of H₂ is greatly reduced in the absence of aluminum thereby providing experimental evidence for the role of the aluminum oxide surface in stabilizing reactive intermediates.

Figure 3. Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Iron

Figure 4. Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Aluminum

5.1.1.4 Uranium

Uranium is not present in the feed simulants even though residual uranium from the nuclear fuel is a major component of the actual nuclear wastes. For this reason the effect of added uranyl ion on the rhodium-catalyzed hydrogen generation from formic acid in the feed simulants was investigated. In this connection a 40 mL sample of UGA-12M1 to which 0.4 g of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ had been

added was treated with 2.1 mL of formic acid (Figure 5). Comparison of Figure 5 with the corresponding experiment in the absence of added uranyl (Figure 2, top) indicates that the presence of uranyl ion has no significant effect on hydrogen generation in these systems.

5.1.1.5 Cadmium

The standard feed simulant UGA-12M1 contains cadmium as one of its components. In the previous phase of this work supported by WSRL mercury or its compounds was found to inhibit hydrogen production from formic acid in a Rh/nitrite system in a feed simulant closely related to those studied in the current project (King 1992a). Since cadmium is a congener of mercury in the Periodic Table, it appeared that cadmium could also be an inhibitor of hydrogen production in this system. For this reason a sample of feed simulant, UGA-10XCdN1, was prepared omitting cadmium and nitrite from the protocol. A sample of this feed simulant spiked with nitrite ion (to make up for the nitrite ion omitted in its preparation) exhibited similar hydrogen (and NO/N₂O) evolution behavior as the standard feed simulant containing cadmium (Figure 6). However, a total of only 0.7 mmoles of H₂ was produced in the experiment without cadmium as compared with 1.8 mmoles of H₂ in a comparable experiment with cadmium suggesting some role of the co-precipitated cadmium hydroxide similar to that of aluminum oxide (Section 5.1.1.3) in hydrogen generation. The much lower hydrogen production in the experiment with cadmium depicted in Figure 6 (top) relative to Figure 2 may be related to the gradual addition of formic acid using the syringe pump in the Figure 6 experiment as compared with the addition of all of the Figure 2 experiment.

Figure 5. Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Uranium

Figure 6. Rhodium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Cadmium. (In contrast to the experiments depicted in Figures 2 to 5, the syringe pump was used to add a total of 88 mmoles of formic acid over a period of ~190 minutes.)

5.1.2 Experiments with Ruthenium

Figure 7 compares the hydrogen generation from formic acid catalyzed by ruthenium in the presence (top) and absence (bottom) of nitrite and in the presence of nitrate using the feed simulants UGA-12M1 and UGA-11XN1, respectively. Relative to the nitrite-containing simulant, significant amounts of hydrogen (~0.4 mmoles) were observed in the absence of nitrite indicating that nitrite is an inhibitor for the ruthenium-catalyzed production of hydrogen from formic acid in feed simulant media. Figure 8 shows the hydrogen generation from formic acid catalyzed by ruthenium in the absence of nitrite and added nitrate (the only nitrate present was that which was not washed out of the precipitated oxides and hydroxides). The increased production of hydrogen in the feed simulant prepared without added nitrate as well as nitrite (~1.1 mmoles versus only ~0.4 mmoles with added nitrate but no nitrite) suggests that both of these nitrogen oxyanions can inhibit the ruthenium-catalyzed production of hydrogen from formic acid. However, ruthenium appears to be incapable of catalyzing the reduction of nitrate to NO or N₂O as indicated by the absence of these gases in the experiment with the UGA-11XN1 feed simulant containing nitrate but not nitrite (Figure 7 bottom). Omission of aluminum had no significant effect on hydrogen generation from formic acid by ruthenium in the absence of both nitrite and nitrate. Thus an experiment using the aluminum-free, nitrite-free, and nitrate-free feed simulant UGA-9XAINN'1 gave essentially identical results to that depicted in Figure 8 using the aluminum-containing but nitrite-free and nitrate-free feed simulant UGA-10XNN'1.

5.1.3 Experiments with Palladium

Figure 9 compares the hydrogen generation from formic acid catalyzed by palladium in the presence (top) and absence (bottom) of nitrite using the feed simulants UGA-12M1 and UGA-11XN1, respectively. Negligible amounts of hydrogen (0.23 mmoles) were observed in the presence of both nitrate and nitrite, and only very small amounts of hydrogen (0.63 mmoles) were observed in the absence of nitrite but the presence of nitrate. More dramatically the production of N₂O was observed when nitrite was absent but nitrate was present indicating that palladium can catalyze the reduction of nitrate by formic acid to N₂O. Significant H₂ generation (a total of 2.6 mmoles) was observed upon treatment of a nitrite-free simulant without added nitrate (UGA-10XNN'1) with formic acid in the presence of palladium indicating that both nitrate and nitrite inhibit the catalytic activity of palladium for hydrogen production from formic acid, Figure 10. The effects of nitrite and nitrate on the palladium-catalyzed hydrogen generation from formic acid in the feed simulants are summarized in Figure 11.

5.1.4 Ammonia Production

The ability of the noble metals to catalyze the reduction of nitrite and occasionally even nitrate by formic acid as indicated by the production of NO and N₂O raises the question as to whether the

Figure 7. Ruthenium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrite

reduction of the nitrogen oxyanions and oxyacids all the way to ammonia can occur under the conditions of these experiments. Unfortunately, ammonia unlike NO and N₂O cannot be monitored during these experiments. However, the reaction mixtures remaining from the treatment of the feed simulant UGA-12M1 with formic acid in the presence of each of the noble metals (Ru, Rh, and Pd) were analyzed for NH₄⁺ by the PNL. The results are summarized in Table 4. These preliminary

Figure 8. Ruthenium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrate

analytical data suggest that the rhodium catalyst system, which is the most active of the three noble metals in the presence of nitrite, is also the most active catalyst for the reduction of nitrogen oxides and oxyanions to ammonia.

5.1.5 Comparison of Data on the WSRL and PNL Feed Simulants

The amount of data from the WSRL project that can be directly compared with the data from the current project is rather limited because many of the WSRL experiments were performed with much larger amounts of rhodium (e.g., 0.2 mmole of RhCl₃·3H₂O) than the present work and under otherwise different conditions. Qualitatively, similar trends in hydrogen generation were observed.

An experiment with 30 mL of the WSRL DWPF low nitrite Purex (pH =12) sludge simulant using 14 mg RhCl₃·3H₂O and 1.6 mL of 88 wt% formic acid at 100 ± 2°C gave a turnover number of 80 mmoles of H₂/mmole Rh/24 hr, corresponding to 0.1 mmoles/min/liter H₂ production. This can be compared with 0.56 mmoles/min/liter H₂ production for the experiment with 40 mL of UGA-12M1 feed simulant using the same amount of RhCl₃·3H₂O but somewhat larger amount of formic acid (2.1 mmoles) at 99 ± 1°C. The much higher rate of hydrogen production per unit volume in the experiment using the HWVP feed simulant as compared with the DWPF feed simulant could relate to the larger amount of formic acid used. Experiments are clearly needed in which the activities of the rhodium for hydrogen generation from formic acid are compared in HWVP and DWPF simulants under otherwise identical conditions.

Figure 9. Palladium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrite

5.2 Titration Studies Using the Syringe Pump

The syringe pump provides a method of introducing formic acid into the feed simulant at a controlled steady rate at the desired reaction temperature. Use of the syringe pump thus corresponds to an acid titration of the feed simulant mixture. The data discussed in Section 5.2 were obtained using the titration method. A larger reaction vessel of ~550 mL total capacity was used for all of the titration studies with the syringe pump in order to minimize the generation of excessive pressures during some of the experiments.

Figure 10. Palladium-Catalyzed Formic Acid Decomposition in Feed Simulants: Effect of Nitrate

Figure 11. Summary of the Effects of Nitrite and Nitrate on Hydrogen Generation Catalyzed by Palladium

Table 4. Production of Ammonia from the Decomposition of Formic Acid in Feed Simulants Containing Nitrite and Nitrate (UGA-12M1)^(a)

<u>Metal</u>	<u>Date of Run</u>	<u>Amount of Soluble NH₄⁺ Ion Measured in Slurry</u>	<u>Max. H₂ Measured</u>
Rh	May 6, 1992	1.17 mmoles	6.0 mmoles
Ru	May 7, 1992	0.75 mmoles	0
Pd	May 8, 1992	0.23 mmoles	0.2 mmoles

(a) Ammonium ion analyses were performed by the Pacific Northwest Laboratory.

5.2.1 Experiments in the Absence of Noble Metals

Figure 12 summarizes the evolution of the gases CO₂, NO, and N₂O as a function of time when the feed simulant UGA-12M1 is titrated with 2.3 mL of 88 wt% formic acid added over a period of 118 minutes in the absence of added noble metals. Hydrogen was not observed in the absence of noble metals. In the first stage of the reaction CO₂ is generated from the carbonate ion by the two-stage reaction:

In this regime CO₂ is produced without any accompanying nitrogen oxides. The production of ~9 mmoles of CO₂ in this regime is more than expected by decomposition of the 50 mL x 0.125 M = 6.25 mmoles of carbonate present in the feed simulant used by the first 12.5 mmoles of formic acid introduced; however, an additional 50 x 0.03 M = 1.5 mmoles of CO₂ can be produced by rapid reduction of MnO₂ to Mn²⁺ in this initial regime. The excess CO₂ in this initial regime is unlikely to arise from formic acid reduction of any of the iron(III) since a similar titration of the iron-free feed simulant UGA-11XFe1 with formic acid gives even more CO₂ in this initial regime (Figure 13).

After decomposition of the carbonate in the feed simulant to give CO₂ by Equation (2) is complete the additional formic acid decomposes the nitrite according to the following reactions:

Figure 12. Treatment of the UGA-12M1 Feed Simulant with Formic Acid in the Absence of Noble Metals Using the Syringe Pump. (Top: the entire experiment; Bottom: the initial portion of the experiment when formic acid was added [i.e., the first 118 minutes].)

Figure 13. Treatment of the Iron-Free UGA-11XFe1 Feed Simulant with Formic Acid in the Absence of Noble Metals of Noble Metals Using the Syringe Pump

Decomposition (disproportionation) of Nitrous Acid:

Reduction of Nitrite:

Since nitrous acid ($\text{pK} = 5.22$) is a stronger acid than the bicarbonate ion ($\text{pK} = 6.38$) (Cotton 1988) generation of nitrous acid from nitrite is only expected to occur after all of the bicarbonate ion has been converted to CO_2 [Equation (2b)]. This point is illustrated further in Figure 14 summarizing an experiment using the feed simulant UGA-9XNN'C (50 mL) spiked with nitrite (1.38 g NaNO_2) so that carbonate is absent but nitrite is present. In this case production of NO [Equation (3)] is seen to start immediately upon introduction of the formic acid since there is no carbonate to consume the formic acid initially added by Equation (2). Production of N_2O [Equation (4)] is seen to lag the production of NO and is accompanied by production of twice the corresponding amount of CO_2 in accord with the stoichiometry in Equation (4). Since rhodium is present, H_2 is generated at the late stages of this reaction.

Figure 14. Titration of a Carbonate-Free Feed Simulant Containing Nitrite with Formic Acid Added at the Rate of 0.453 mmol/min.

5.2.2 Experiments in the Presence of Rhodium

Figure 15 summarizes the titration of the UGA-12M1 feed simulant with formic acid in the presence of 14 mg of RhCl₃·3H₂O under conditions otherwise identical to the experiment in Figure 12. Hydrogen production is seen to begin only after all of the carbonate has been converted to CO₂ [Equations (2a) and (2b)] and the nitrite to NO and N₂O [Equations (3) and (4)]. *This suggests that one method of limiting hydrogen production during the treatment of nuclear wastes with formic acid is to limit the amount of formic acid to that required for conversion of all of the carbonate to CO₂ and the nitrite to NO and N₂O.*

5.2.3 Effect of the Type of Rhodium Source

All of the previous work has used soluble rhodium compounds, mainly the commercial "rhodium trichloride trihydrate" as the rhodium source. Two rather different methods of introducing rhodium in an insoluble form have been investigated.

In the first method rhodium was introduced into the complete feed simulant by coprecipitation in the iron fraction in the standard feed simulant preparation procedure (Appendix A) using hydrated rhodium trichloride as the rhodium source; the feed simulant prepared in this manner is designated as UGA-13M+Rh. Treatment of this feed simulant with 88 wt% formic acid led to some

Figure 15. Titration of the UGA-12M1 Feed Simulant with Formic Acid in the Presence of Rhodium Trichloride

hydrogen production (Figure 16) but far less than was found in the experiments where rhodium was introduced as the soluble "rhodium trichloride trihydrate." Thus only 0.66 mmoles of H_2 was present at the end of a typical experiment of this type. The usual production of NO and N_2O was observed in this experiment. As usual the CO_2 production from carbonate and the NO/ N_2O production from nitrite was essentially complete before onset of H_2 production.

In the second method rhodium was introduced as a 5% dispersion of the metal on charcoal (Figure 17) or alumina (Figure 18) using 0.1175 g of 5% Rh/C or 0.115 g of 5% Rh/ Al_2O_3 , respectively, corresponding to the amount of rhodium in the 14 mg of $RhCl_3 \cdot 3H_2O$ used in the standard experiments. The observed behavior with these solid 5% rhodium dispersions was very different from the observed behavior with hydrated rhodium trichloride in the following ways:

1. Only a very small amount of H_2 was produced (0.16 mmoles and 0.28 mmoles at the end of the experiments with 5% Rh/C and 5% Rh/ Al_2O_3 , respectively).
2. The initially produced NO but not the N_2O was almost entirely consumed during the course of the experiment. For example, a maximum of 9.29 mmoles of NO was measured after 216 minutes but only 1.25 mmoles of NO remained at the end of the experiment with 5% Rh/C.

These experiments support the observation that insoluble sources of rhodium are less active than soluble sources of rhodium for the hydrogen production in nitrite-containing feed simulant media. In addition, the drastically reduced production of H_2 and the consumption of NO as the reaction proceeds suggests that rhodium dispersed on carbon is an active catalyst for the hydrogenation of NO.

5.2.4 Effect of Rhodium Concentration

A series of six experiments was performed using 50 mL of the feed simulant UGA12M1B, 10 mL of water, a total of 86 mmoles of formic acid added to each experiment at a steady rate by means of the syringe pump, and amounts of hydrated rhodium trichloride ranging from 1.4 mg (0.0056 mmoles) to 14 mg (0.056 mmoles) in a more detailed attempt to assess the minimum amount of rhodium needed to catalyze hydrogen evolution from formic acid. The experiment using 14 mg corresponds to the target rhodium composition. The results are summarized in Table 5. Hydrogen evolution as a function of time for the four experiments producing hydrogen is depicted in Figure 19. Figure 20 plots the hydrogen production rate in mmol/min during the time that the catalyst is active versus the rhodium concentration. Within the considerable experimental errors of an experiment of this type the rate of hydrogen production is seen to be first order in rhodium concentration according to the following equation:

$$H_2 \text{ production (mmol/min)} = -0.92 + 8030[Rh, M] \quad R^2 = 0.952 \quad (5)$$

50 mL UGA 13M + Rh1 + 10% water
 $90 \pm 1^\circ\text{C}$

Figure 16. Production of Hydrogen and Other Gases by Formic Acid Titration of the Feed Simulant UGA-13M+Rh1 in Which the Rhodium has been Coprecipitated Along with the Other Metals Using $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ as the Rhodium Source

50 mL UGA 12M1A + 10 mL water + 0.1175 g 5% Rh/C
 $90 \pm 1^\circ \text{C}$

Figure 17. Production of Hydrogen and Other Gases by Formic Acid Treatment of 50 mL of the Feed Simulant UGA-12M1A in the Presence of 0.1175 g of 5% Rhodium on Carbon

50 mL UGA12M1B + 10 mL water + 115 mg 5% Rh/Al₂O₃

Figure 18. Production of Hydrogen and Other Gases by Formic Acid Treatment of 50 mL of the Feed Simulant UGA-12M1B in the Presence of 0.1175 g of 5% Rhodium on Alumina

Table 5. Effect of the Amount of Rhodium on Hydrogen Production from Formic Acid. Experiment was conducted with 50 mL UGA-12M1B feed simulant, 10 mL water, and 86 mmoles formic acid.

	<u>mmoles of gas at end of experiment</u>				
<u>mg RhCl₃·3H₂O</u>	<u>H₂</u>	<u>CO₂</u>	<u>N₂O</u>	<u>NO</u>	<u>Final pH</u>
1.4	~0	17.5	4.75	8.57	3.57
2.8	~0	18.16	5.97	4.23	4.18
5.6	0.25	18.07	5.27	5.77	3.57
8.4	0.63	18.00	4.54	7.57	3.64
11.2	1.14	19.46	5.05	5.94	3.79
14.0	1.31	20.22	4.99	6.70	3.67

It appears that about 5 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ corresponding to about 2 mg of rhodium metal is needed before appreciable hydrogen evolution is observed under these conditions. Extrapolating these results to a large scale experiment using 6,000 gallons of feed simulant (= ~23,000 liters) suggests that

$$(0.005 \text{ g } \text{RhCl}_3 \cdot 3\text{H}_2\text{O}) \left(\frac{23,000 \text{ liter}}{0.05 \text{ liter}} \right) = 2,300 \text{ g } \text{RhCl}_3 \cdot 3\text{H}_2\text{O} \quad (6)$$

would be required for a large scale run to mimic the behavior observed in the lowest concentration of rhodium found to give hydrogen.

The pH at the end of these experiments was found to be rather insensitive to the amount of rhodium used and the amount of hydrogen produced. This relates to the fact that the maximum 1.3 mmoles of H_2 produced in these experiments is a small fraction of the ~86 mmoles of formic acid introduced in each experiment.

5.2.5 Effect of Nitrite Concentration

Since nitrite ion has been shown to promote the catalytic activity of rhodium for formic acid decomposition in feed simulant media, it was of interest to investigate the effect of nitrite concentration on the reaction rate. In this series of experiments 50 mL samples of the nitrite-free feed simulant UGA-11XN1 were spiked with various amounts of sodium nitrite and 14 mg of rhodium trichloride trihydrate in 10 mL of water in the usual ~550 mL closed glass reactor before being treated with 88 wt% formic acid using the syringe pump. The composition of the gas phase was analyzed by gas chromatography in the usual manner. Results from four experiments of this type are depicted

Figure 19. Effect of Rhodium Concentration on Hydrogen Production Upon Treatment of 50 mL of UGA-12M1B Feed Simulant and 10 mL of Water with Formic Acid. (Top: mmoles of hydrogen as a function of time for runs using 5.6, 8.4, 11.2, and 14.0 mg $RhCl_3 \cdot 3H_2O$. Bottom: addition of formic acid as a function of time.)

Figure 20. Maximum Hydrogen Production Rate (mmole/minute) Versus Rhodium Concentration ($[M] \times 10^{-3}$) in the Regime of Catalyst Activity

individually in Figure 21 and are compared in Figure 22. The experiment with the largest amount of sodium nitrite, namely 1.5 g NaNO_2 , corresponds to the concentration of nitrite present in the complete feed simulants UGA-12M.

The data depicted in Figures 21 and 22 indicate that the rate of H_2 production is relatively insensitive to nitrite concentration, at least in this concentration range. The expected production of NO and N_2O was observed in all of the experiments. There were no major qualitative differences, and the amounts of nitrogen oxides appeared roughly proportional to the amount of sodium nitrite used.

Another question of interest is the minimum amount of nitrite needed to promote this reaction. Accordingly, 50 mL of the nitrite-free simulant, UGA-10M1EXNN', 10 mL water, and 0.5 g of sodium nitrate was titrated at 90°C with 88 wt% formic acid using the syringe pump in the presence of 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (0.054 mmoles) and varying amounts of NaNO_2 , ranging from 11.6 mg (0.17 mmoles) to 0.5 g (Figure 23: top), considerable amounts of hydrogen were produced in all of these experiments, even in the experiment with only 11.6 mg NaNO_2 (corresponding to a NO_2^-/Rh ratio of ~ 3) where ~ 4 mmoles of H_2 was produced at the end of the experiment. This contrasts with

Figure 21. Production of CO_2 , H_2 , NO , and N_2O by Formic Acid Titration of the Feed Simulant UGA-11XN1 in the Presence of Rhodium at Four Different Nitrite Concentrations

Figure 22. Top: Hydrogen Production Versus Time for Four Different Nitrite Concentrations from the Formic Acid Titration of 50 mL UGA-11XN1 + 14 mg RhCl₃·3H₂O + 10 mL of Water; Bottom: Hydrogen Turnover Numbers (mmoles H₂/mmoles Rh/24 hr) as a Function of Nitrite Concentration in the Experiments Depicted Individually in Figure 21.

the production of only 0.4 mmole of H_2 at the end of a similar experiment where no nitrite at all was added (Figure 23: bottom). This confirms that nitrite is a promoter for the rhodium-catalyzed decomposition of formic acid but that stoichiometric amounts of nitrite corresponding to formation of a trinitrorhodium derivative suffice for catalyst promotion.

5.2.6 Effect of Temperature

In order to evaluate the effect of temperature on the rhodium-catalyzed hydrogen generation rate from formic acid, 50 mL of the standard UGA-12M1C feed simulant and 10 mL of an aqueous solution of $RhCl_3 \cdot 3H_2O$ (1.4 mg $RhCl_3 \cdot 3H_2O/mL$) in a ~250 mL closed glass reactor was treated with a total of 85 mmoles of formic acid using the syringe pump. The composition of the gas phase was analyzed by gas chromatography in the usual manner. Results from five experiments of this type at temperatures ranging from 77°C to 94°C are depicted in Figure 24. As expected the rate of hydrogen production increases with increasing temperature with a hydrogen production rate of 0.29 mmol H_2 /minute/liter feed simulant at 94°C. Hydrogen production at temperatures below ~85°C was so slow that meaningful rates could not be obtained from the slope of the hydrogen production curve. *It thus appears that hydrogen production can be shut off at temperatures below ~75°C.*

A practical question is whether the activity of the rhodium catalyst system for hydrogen generation from formic acid can be destroyed by treating the reaction mixture with formic acid at a temperature below which hydrogen generation takes place and then heating the mixture further at such a temperature before bringing the mixture to 90 to 100°C to complete the reaction. In order to test this possibility 50 mL of the feed simulant, UGA-12M1C, 10 mL of water, and 14 mg of $RhCl_3 \cdot 3H_2O$ was treated at 70°C with 85.3 mmoles of formic acid over 190 minutes using the syringe pump. In five experiments the reaction mixture was held at 70°C for various periods of time ranging from the 190 minutes required for the formic acid addition to 25 hours before heating to 90°C. Figure 25 shows the hydrogen generation at 90°C for such reaction mixtures pretreated at 70°C for 190 min, 6 h, and 9 h before heating to 90°C. The induction period for hydrogen generation at 90°C is seen to increase as the pretreatment time at 70°C increases although the rate of hydrogen generation after initiation appears to be the same. Experiments in which the mixture was kept at 70°C for 12 h and for 25 h show no hydrogen generation after heating to 90°C for at least five hours. Thus pretreatment of the reaction mixture at 70°C has some promise as a method for inhibiting the unwanted hydrogen generation provided that the pretreatment is carried out for a sufficiently long time.

5.2.7 Mixed Metal Experiments

In the actual nuclear wastes modelled by this work all three noble metals ruthenium, rhodium, and palladium are present. For this reason the effect of mixtures of these noble metals on hydrogen generation and on the nitrogen oxide chemistry in the feed simulants are of interest. In order to assess this point a mixture of 50 mL of the feed simulant UGA-12M1C, 10 mL of water, and 7 mg of

Effect of NaNO_2 concentration on H_2 production

Figure 23. Effect of Sodium Nitrite Concentration on the Rhodium-Catalyzed Production of Hydrogen From Formic Acid in Feed Simulant Media (Top: A Comparison of Hydrogen Evolution in Experiments Using 11.6 mg, 25 mg, 100 mg, and 500 mg of Sodium Nitrite Added to Nitrite-Free Feed Simulant; Bottom: Hydrogen Evolution from the Nitrite-Free Feed Simulant UGA-10M1EXNN' in the Presence of 0.5 g of Sodium Nitrate.)

Figure 24. Hydrogen Evolution at Different Temperatures: 50 mL UGA-12M1C Feed Simulant, 14 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and 10 mL of Water

Figure 25. Generation of Hydrogen at 90°C After Pretreatment at 70°C for the Indicated Period of Time Using 50 mL UGA-12M1C, 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, and 10 mL of Water

$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, 5 mg of commercial "hydrated ruthenium trichloride," and/or 5 mg of PdCl_2 was titrated with 85 mmoles of formic acid at 88–91°C in the usual manner. The reason for using only 7 mg of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ rather than the 14 mg used for most of the other syringe pump experiments was to keep the pressure generated in experiments with all of the noble metal combinations within the limits of the apparatus. Otherwise mixed metal experiments using 14 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and palladium chloride were found to generate pressures beyond the maximum of 30 psig where problems with leaks begin to occur (see Section 4.2). Experiments were done using pure Rh as well as all three possible binary mixtures Rh + Ru, Rh + Pd, and Ru + Pd; the gas evolution plots are depicted in Figure 26. The control experiment using only rhodium resulted in the generation of a total of 0.25 mmoles of hydrogen which was essentially unchanged in the Rh + Ru mixed metal system but increased to 0.67 mmoles in the Rh + Pd mixed metal system.

The presence or absence of palladium in these mixed metal systems had a dramatic effect on the nitrogen oxide chemistry (Figure 27). In the experiments without palladium (i.e., either pure Rh or Rh + Ru) the amounts of NO and N_2O generated from the nitrite/nitrous acid chemistry [i.e., Equations (3) and (4)] reached a constant level at the end of the nitrite decomposition regime and stayed at that level for the remainder of the experiment. However, in the experiments with palladium (i.e., either Rh + Pd, or Ru + Pd) about 75% of the NO originally generated was consumed apparently mainly reduced to N_2O by the equation

Figure 26. Titration of 50 mL of the Feed Simulant UGA-12M1C and 10 mL of Water with 85 mmoles of Formic Acid at 89-92°C in the Presence of Rh (7 mg $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$), Ru (5 mg "hydrated ruthenium chloride), and/or Pd (5 mg PdCl_2)

Figure 27. Details of the NO and N₂O Evolution in the Experiments Depicted in Figure 26

In the Pd + Rh mixed metal experiment 5.9 mmoles of NO are consumed during the time that an additional 2.7 mmoles of N₂O are produced corresponding to an (NO consumed)/(N₂O produced) ratio of $5.9/2.7 = 2.2$ relative to the "ideal" value of 2.0 predicted by Equation (7). Similarly, in the Pd + Ru mixed metal experiment 5.7 mmoles of NO are consumed during the time that an additional 3.3 mmoles of N₂O are produced corresponding to an (NO consumed)/(N₂O produced) ratio of $5.7/3.3 = 1.7$ relative to the "ideal" value of 2.0 predicted by Equation (7). These observations suggest the specific ability of palladium to catalyze the reduction of NO to N₂O in these feed simulant media.

5.2.8 Tests with the KfK Feed Simulant Supplied by PNL

In order to relate the information from this research project to the feed simulants studied by PNL a sample of a KfK German feed simulant was supplied by the PNL. The label on the bottle reported this feed simulant to contain 0.7% Ca(OH)₂, 4.38% Al(OH)₃, 0.29% MoO₃, and 5.36% Zr(OH)₄. Subsequently provided analytical data (from the PNL on October 14, 1992) indicated this

feed simulant to contain no nitrite, 0.035 moles/liter of nitrate, 0.125 moles/liter of carbonate, 0.304 moles/liter of sodium, and amounts of other metals, including the noble metals ruthenium, rhodium, and palladium at the target NCAW simulant composition for 125 g waste oxides/liter loading. Two experiments with this KfK feed simulant are depicted in Figure 28. In the first experiment (Figure 28, top) a 50 mL sample of this feed simulant was titrated with a total of 168 mmoles of formic acid over a period of 400 minutes. The observed hydrogen evolution (1.74 mmoles) was similar to that observed when UGA12-M1 was titrated with formic acid in the presence of rhodium trichloride under otherwise similar conditions (e.g., Figure 15). However, at least some of the hydrogen evolution could arise from ruthenium or palladium catalyzed decomposition of formic acid since nitrite is not present in this experiment and nitrite was shown to inhibit the ruthenium and palladium catalyzed decompositions of formic acid (Figures 7 and 9). No nitrogen oxides were observed in this experiment even though palladium has been shown to catalyze the reduction of nitrate to N_2O (Figure 9).

The second experiment (Figure 28, middle) was performed in order to assess the effect of added nitrite on the catalytic activity of the noble metals in the KfK feed simulant. In this experiment a mixture of 50 mL of the KfK feed simulant, 1.5 g (21.4 mmoles) of sodium nitrite, and 10 mL of water was treated with a total of 127.2 mmoles of formic acid over a period of 285 minutes. The amount of hydrogen generation (a total of 1.26 mmoles) was slightly less than that observed in the previous nitrite-free experiment (Figure 28, top). The decrease in the amount of H_2 generated in the presence of nitrite might simply be a consequence of the smaller amount of formic acid used in this experiment, namely 127 mmoles versus 168 mmoles. In addition, NO and N_2O were observed in the experiment with added nitrite. The maximum amount of NO generated was 14.7 mmoles but 3.6 mmoles of this was consumed in the later stages of this experiment with the production of an additional 1.6 mmoles of N_2O during this period of time. This is consistent with the reduction of NO to N_2O by the palladium present in the system by Equation (6) (compare Figure 27).

5.3 Some Observations on Carbon and Nitrogen Balance

The carbon balance in these experiments was examined by comparing the amount of observed CO_2 at the end of the experiment with that expected from known reactions producing CO_2 . Similarly a partial nitrogen balance was examined in the experiments (Figure 21) by comparing the known amounts of nitrite added to a nitrite-free simulant with the amounts of nitrogen in the N_2O and NO measured at the end of the experiment.

Figure 28. Titration of 50 mL of the KfK Feed Simulant Supplied by PNL with Formic Acid Without Added Nitrite and with 1.5 g (21.4 mmoles) of Added Sodium Nitrite

5.3.1 Carbon Balance

Carbon dioxide has the following obvious major sources:

- (1) Acidification of carbonate, i.e.

Production of CO_2 from this source is constant for a given quantity of a given feed simulant and corresponds simply to one mmol of CO_2 for each mmol of carbonate in the feed simulant.

- (2) Formic acid reduction of MnO_2 to manganese(II), i.e.

Production of CO_2 from this source is also constant for a given quantity of a given feed simulant and corresponds simply to one mmol of CO_2 for each mmol of MnO_2 in the feed simulant. Since the $\text{KMnO}_4/\text{Mn}^{+2}$ ratio in the preparation of the feed simulant was controlled to convert all of the manganese in the feed simulant to MnO_2 (Appendix A), the amount of MnO_2 in the feed simulant can be considered to be equivalent to the total manganese introduced into the feed simulant.

- (3) Formic acid reduction of nitrite ion to N_2O , i.e.

Each mmol of N_2O produced by nitrite reduction should correspond to *two* mmol of CO_2 .

- (4) Formic acid reduction of *nitrate* ion, i.e.

This process does not appear to occur in most of the systems studied but can occur when nitrite-free feed simulants are treated with formic acid in the presence of palladium (e.g., Figure 9). Each mmol of N_2O produced by nitrate reduction should correspond to *four* mmol of CO_2 .

- (5) Formic acid decomposition to CO_2 and H_2 , i.e.

Each mmol of H_2 produced by formic acid decomposition should correspond to one mmol of CO_2 .

Table 6 compares the total amount of CO_2 expected from all of these sources with that observed experimentally for the experiments depicted in the figures in this report.

Table 6. Carbon Dioxide Balance for the Experiments Depicted in the Figures of this Report

<u>Test Number</u>	<u>Expected CO₂ from (mmoles):</u>				<u>Total CO₂ (mmoles)</u>		<u>Comments</u>
	<u>CO₃⁻²</u>	<u>MnO₂</u>	<u>N₂O</u>	<u>H₂</u>	<u>Calculated</u>	<u>Found</u>	
Fig 2 top	5.0	1.2	10.8	6.2	23.2	18.6	
Fig 2 bottom	5.0	1.2	0	0.4	6.6	10.0	CO ₂ high
Fig 3	5.0	1.2	8.4	0.8	15.4	17.3	
Fig 4	5.0	1.2	6.2	2.0	14.4	20.7	CO ₂ high
Fig 5	5.0	1.2	6.4	4.7	17.3	18.0	
Fig 6	6.2	1.5	10.0	0.7	18.4	18.8	
Fig 7 top	5.0	1.2	10.4	0.0	16.6	12.2	CO ₂ low
Fig 7 bottom	5.0	1.2	0	0.4	6.6	4.8	CO ₂ low
Fig 8	5.0	1.2	0	1.5	7.7	5.8	CO ₂ low
Fig 9 top	5.0	1.2	16.6	0.0	22.8	17.8	CO ₂ low
Fig 9 bottom	5.0	1.2	9.6 ^(a)	0.6	16.4	18.9	
Fig 10	5.0	1.2	0	2.6	8.8	11.4	CO ₂ high
Fig 12 top	6.2	1.5	7.6	0	15.3	13.5	
Fig 12 bottom	6.2	1.5	4.0	0	11.7	12.0	
Fig 13	6.2	1.5	8.0	0	15.7	19.3	CO ₂ high
Fig 14	0	1.5	11.2	1.3	14.0	14.8	
Fig 15	6.2	1.5	9.8	1.3	18.8	22.2	CO ₂ high
Fig 16	6.2	1.5	7.8	1.4	16.9	18.3	
Fig 17	6.2	1.5	12.8	0.3	20.8	31.0	CO ₂ high
Fig 18	6.2	1.5	13.9	0.6	22.2	25.7	
Fig 21a	6.2	1.5	5.8	2.5	16.0	18.2	
Fig 21b	6.2	1.5	7.0	2.0	16.7	19.3	
Fig 21c	6.2	1.5	11.6	2.5	21.8	28.0	CO ₂ high
Fig 21d	6.2	1.5	12.0	3.6	23.3	21.9	
Fig 26a	6.2	1.5	10.6	0.3	18.6	18.3	
Fig 26b	6.2	1.5	10.8	0.4	19.2	19.1	
Fig 26c	6.2	1.5	15.4	0.7	18.9	22.2	
Fig 26d	6.2	1.5	16.2	0	23.9	22.0	

(a) This N₂O is assumed to come from the reduction of nitrate since no nitrite was present.

There are a number of possible reasons for the discrepancies in Table 6 between the observed amounts of CO_2 and those calculated to arise from carbonate decomposition [Equation (8)], MnO_2 reduction [Equation (9)], nitrite reduction [Equation (10)], or formic acid decomposition [Equation (12)]. Thus further reduction of nitrogen oxides or oxyacids to ammonia would result in additional CO_2 as was clearly found in a number of the experiments with rhodium as the added noble metal. By far the largest excess CO_2 was produced when rhodium was introduced as a Rh/C catalyst (Figure 17) suggesting that this form of rhodium might be the most effective catalyst for the reduction of nitrogen oxides to ammonia although this has not yet been verified by ammonia analyses. In addition, the production of CO_2 from the reduction of *nitrate* to N_2O [Equation (11)] or ammonia has not been considered except for the experiment in which N_2O was produced from a nitrite-free feed simulant (UGA-11XN1) in the presence of palladium (Figure 9 bottom).

5.3.2 Nitrite Nitrogen Balance

Another question of interest is the fate of the nitrogen in the nitrite ion. Reaction of nitrite ion with formic acid can lead to the production of NO by disproportionation of nitrous acid [Equations (3a)–(3c)] and N_2O [Equation (4)] by nitrite reduction. Each mmole of nitrite undergoing nitrous acid disproportionation leads to 2/3 mmoles of NO and 1/3 mmole of nitrate. Therefore observation of 1 mmole of NO corresponds to the decomposition of 1.5 mmoles of nitrite ion by disproportionation. Each mmole of nitrite undergoing reduction to N_2O leads to 1/2 mmole of N_2O . Therefore observation of 1 mmole of N_2O corresponds to the reduction of 2 mmoles of nitrite ion. Using this stoichiometry Table 7 summarizes the nitrogen balance from these processes in the experiments depicted in Figure 21 in which controlled amounts of sodium nitrite were added to a nitrite-free feed simulant prior to the experiment. In all cases all of the added sodium nitrite appears to be consumed by these two processes within a $\pm 10\%$ experimental error.

Table 7. Nitrite Nitrogen Balance in the Experiments Depicted in Figure 21.

Experiment	Disproportionation to NO	Reduction to N_2O	Total mmoles Nitrite Reacting	mmoles Nitrite Added
Fig 21a	2.4	5.8	8.2	8.7
Fig 21b	6.9	7.0	13.9	13.0
Fig 21c	7.6	11.6	19.2	17.4
Fig 21d	8.4	12.0	20.4	21.7

6.0 Discussion

The experiments discussed in this report confirm the earlier observations (King 1992a) that rhodium is the most active catalyst for formic acid decomposition in feed simulant media in the presence of nitrite. Attempts to obtain definitive mechanistic information on this system have been complicated by the limited catalyst lifetime and the presence of solid oxide/hydroxide phases as well as the large number of components in this system. For this reason even the question as to whether the observed nitrite-promoted rhodium catalysis of formic acid decomposition is a homogeneous or heterogeneous process has been difficult to resolve. Attempts to determine the rate dependence on rhodium concentration yield ambiguous results unless the experimental conditions are very carefully controlled including use of the same batch of feed simulant and careful control of the reaction temperature. However, the clear indication of first order dependence of the reaction rate on rhodium concentration provided by the data summarized in Figures 19 and 20 suggests that the observed nitrite-promoted rhodium catalysis of formate decomposition is a homogeneous process involving a soluble rhodium complex as an intermediate. The fundamental homogeneous nature of this process is also suggested by the higher rate of hydrogen production when soluble $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ is used as a rhodium source as compared with insoluble rhodium sources such as coprecipitated rhodium, Rh/C , or $\text{Rh/Al}_2\text{O}_3$.

The role of nitrite ion as a promoter suggests the role of soluble nitrorrhodium complexes as intermediates in the rhodium-catalyzed decomposition of formic acid. In this connection rhodium trichloride was reported more than a century ago (Leidie 1890) to react with excess nitrite ion in boiling water to give salts of the hexanitrorhodate anion, $[\text{Rh}(\text{NO}_2)_6]^{-3}$. Three of the six nitro groups in the hexanitrorhodate ion are reported to be labile upon treatment with strong oxidants (Kukushkin 1977) or amidosulfuric acid (Mel'chakova 1967) indicating the feasibility of opening up catalytic sites on the central rhodium atom under the conditions of formic acid decomposition. These vacant sites on the central rhodium atom can be used both for anchoring onto an insoluble hydrous oxide support as well as for coordination with formic acid prior to its decomposition.

The reaction of hydrated rhodium trichloride with nitrite ion to give the hexanitrorhodate ion can be summarized by the following equation:

The lability of three of the six nitro groups in hexanitrorhodate can be summarized by the following equations in which nitro groups are successively replaced by more labile aquo ligands:

Formate can then displace the aquo ligands by reactions such as the following:

Coordinated formate can undergo a hydrogen shift from carbon to a vacant rhodium site with carbon dioxide evolution to generate a rhodium hydride according to the following equation:

Hydrolysis of the rhodium hydride, possibly acid catalyzed, can then result in the observed hydrogen evolution, i.e.,

The resulting hydroxorhodium complex can then be protonated by formic acid to give the original diaquo derivative, i.e.,

The net sum of Equations (15)–(18) is the observed formic acid decomposition

In this mechanistic scheme nitrite ion is essential to the reaction but excess nitrite can inhibit the reaction by tying up catalytic sites forming $[\text{Rh}(\text{NO}_2)_6]^{-3}$ [see Equation (14a)]. The balance between the requirement of nitrite to make active nitrorhodium intermediates but the ability of excess nitrite to inhibit the reaction can account for the observed insensitivity of the reaction rate to nitrite concentration.

The nitrorhodium catalysts involved in formic acid decomposition appear to have a limited lifetime and appear to decompose to much less catalytically active metallic rhodium under the reducing reaction conditions created by the formic acid. The enhancement of hydrogen generation in the presence of the large quantities of iron (Figures 2 and 3) or aluminum (Figures 2 and 4) in the feed simulants can be attributed to the stabilization of the nitrorhodium intermediate towards destructive reduction to metallic rhodium by chemical bonding to the oxide surface through surface hydroxyl groups. In addition, the presence of large amounts iron(III) can inhibit destruction of the catalytically active nitrorhodium species by sacrificial reduction of the iron(III) to iron(II) in preference to the reduction of the rhodium catalyst.

The role of nitrite ion as a promoter for the rhodium-catalyzed formic acid decomposition is contrasted by its role as an inhibitor for the ruthenium-catalyzed (Figure 7) and palladium-catalyzed

(Figure 9) decompositions of formic acid. In the case of ruthenium, the presence of nitrite ion could convert the metal to less catalytically active ruthenium nitrosyl derivatives; this possibility has not yet been explored. Palladium is of interest since it is even capable of catalyzing reductions of *nitrate* to N_2O (Figure 9) and NO to N_2O (Figure 26). This suggests that the inhibitory role of nitrite and even nitrate in the palladium-catalyzed generation of hydrogen from formic acid may relate to their sacrificial reduction in the presence of palladium.

Titration of the feed simulants with formic acid in the presence of rhodium using the syringe pump is also informative with regard to the pH dependence of the nitrite-promoted rhodium-catalyzed hydrogen evolution from formic acid. Addition of formic acid first decomposes the carbonate according to Equations (2a) and (2b) to give CO_2 . When all of the carbonate is decomposed, further addition of formic acid decomposes the nitrite to give NO and N_2O according to Equations (3) and (4). Hydrogen evolution from formic acid only takes place after essentially all of the carbonate is decomposed to CO_2 and all of the nitrite to NO and N_2O and thus requires lower pH's than these other processes. From the practical point of view these observations suggest that one method of limiting hydrogen production during the treatment of nuclear wastes with formic acid is to limit the amount of formic acid to that required for conversion of all of the carbonate to CO_2 and the nitrite to NO and N_2O .

7.0 Literature References

Aguiló, A. 1969. *Journal of Catalysis*, 13, 283.

Choppin, G. R., and J. Rydberg. 1980. *Nuclear Chemistry: Theory and Applications*, Pergamon, Oxford. p. 505.

Cotton, F. A., and G. Wilkinson. 1988. *Advanced Inorganic Chemistry*, fifth edition, Wiley, New York. p. 245 (HCO_3^-), p. 327 (HNO_2), and p. 714 [Fe(II)/Fe(III)].

Hill, S. P., and J. M. Winterbottom. 1988. *Journal Chemical Tech. Biotechnology*, 41, 121.

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

ID 92-09927, p. 10 of September 28, 1992, memorandum.

King, R. B., A. D. King, Jr., N. K. Bhattacharyya, C. M. King, and L. F. Landon. 1992a. Presentation at the Symposium on *Chemical Pretreatment of Nuclear Wastes for Disposal* held in conjunction with the Fall 1992 National Meeting of the American Chemical Society, Washington, D.C., August, 1992. Abstract I&EC 0119, manuscript in preparation.

King, R. B., A. D. King, Jr., and N. K. Bhattacharyya. 1992b. Presented to the Division of Inorganic Chemistry at the Fall 1992 National Meeting of the American Chemical Society, Washington, D.C., August 1992, abstract INOR 124.

Kukushkin, Yu. N., and O. V. Stefanova. 1977. *Russian Journal of Inorganic Chemistry*, 1977, 22, 1844.

Laine, R. M., R. B. Rinker, and P. C. Ford. 1977. *Journal American Chemical Society*, 99, 252.

Leidié, E. 1890. *Compt. Rend.* 1890, 111, 106.

Mel'chakova, N. V., G. P. Ozerova, and V. M. Peshkova. 1967. *Russian Journal of Inorganic Chemistry*, 1967, 12, 577.

Muller, E. and W. Loerpabel. 1929. *Monatshefte*, 53/54, 825.

Ruthven, D. M. and R. S. Upadhye. 1971. *J. Catalysis*, 21, 39.

Strauss, S. H., K. H. Whitmire, and D. F. Shriver. 1979. *Journal Organometal. Chemistry*, 174, C59.

Wiemers, K. D. 1988. Evaluation of Process Offgases Released During the Formating of Simulated HWVP Feed. Presented at the American Institute of Chemical Engineers 1988 Summer National Meeting. August 21-24, 1988. Denver, Colorado.

Appendix A

Protocol for the Preparation of the Major Component HWVP Feed Simulant: UGA-12M1

Appendix A

Protocol for the Preparation of the Major Component HWVP Feed Simulant: UGA-12M1

A flow chart for the protocol for the preparation of UGA-12M1 major component feed simulant is depicted in Figure A.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 A.1. Outline of the Scheme for the Preparation of UGA-12M1 Major Component Feed Simulant

(A) Precipitation of MnO_2

The precipitation of MnO_2 uses the reaction of KMnO_4 with $\text{Mn}(\text{NO}_3)_2$ according to the following general equation which is used to calculate the stoichiometry:

Dissolve 5.41 g of $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 100 mL of water. Agitate the solution and maintain the temperature in the range 35–40°C. In a separate vessel dissolve 1.98 g of KMnO_4 in 100 mL of water, agitate the solution and warm to 35–40°C. Add the warm KMnO_4 solution to the $\text{Mn}(\text{NO}_3)_2$

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 181.80 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 9.25 g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 11.40 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 11.57 g of $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, and 36.07 g of $\text{ZrO}(\text{NO}_3)_2$. After all of these solid nitrates 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 nitric acid. Record the final pH.

Feed simulants containing noble metals of interest (Ru, Rh, and/or Pd) coprecipitated as oxides can be prepared by introducing the noble metals as water-soluble nitrates along with the nitrates of Fe, Cd, Ni, Zr, and Nd in this oxide/hydroxide precipitation step. A revised protocol will be submitted before the research project reaches this point.

(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 84.78 g of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 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 nitric 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 nitrate formed as a byproduct upon treatment of the various metal nitrates with sodium hydroxide. The precipitates are washed by decantation with distilled water until the wash liquid is free of nitrate 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 (NaNO_3) as determined by its conductivity compared with pure water. The nitrate concentration of the wash liquid can also be monitored by a nitrate-selective electrode and/or ion chromatography if these analytical methods are available.

(E) Addition of SiO_2 , Na_2CO_3 , NaNO_2 , and NaNO_3

Remove by decantation enough of the final wash water for both the $\text{MnO}_2/\text{Fe}(\text{OH})_3/\text{Cd}(\text{OH})_2/\text{Ni}(\text{OH})_2/\text{Nd}_2\text{O}_3/\text{ZrO}_2$ and the $\text{Al}(\text{OH})_3$ slurries so that the total volumes of each slurry is no more than ~350 mL. Then add the $\text{Al}(\text{OH})_3$ slurry to the $\text{MnO}_2/\text{Fe}(\text{OH})_3/\text{Cd}(\text{OH})_2/\text{Ni}(\text{OH})_2/\text{Nd}_2\text{O}_3/\text{ZrO}_2$ slurry using a minimum of wash water to wash the $\text{Al}(\text{OH})_3$ slurry into the other vessel. Then add with stirring 5.13 g of SiO_2 , 13.25 g of Na_2CO_3 , 30.02 g of NaNO_2 , and 9.86 g of NaNO_3 making sure that the sodium salts do not contain any clumps that might dissolve slowly. The SiO_2 will remain insoluble but the three sodium salts 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.

Appendix B

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

Appendix B **Summary of Reactions of Formic Acid with Feed Simulants Studied** **During the Course of this Project(a)**

Date	Feed Simulant	Noble Metal(l)	Syringe Pump	Amount of Formic Acid(2)	Temperature °C	Total Time (minutes)	Total H ₂ Produced (mmoles)	Final pH
5/6/92	12MI(40 mL)	RhCl ₃ (14 mg)	no	2.1 mL	99±1°	534	6.16	6.41
5/7/92	12MI(40 mL)	RuCl ₃ (48 mg)	no	2.1 mL	~98°	769	0.10	5.81
5/8/92	12MI(40 mL)	PdCl ₂ (12 mg)	no	2.1 mL	~99°	514	0.23	7.41
5/11/92	11XNI(40 mL)	RhCl ₃ (14 mg)	no	2.1 mL	~97°	1249	0.31	8.15
5/12/92	11XNI(40 mL)	RuCl ₃ (14 mg)	no	2.1 mL	~98°	2957	2.10	4.53
5/14/92	11XNI(40 mL)	PdCl ₂ (13 mg)	no	2.1 mL	~96°	1060	0.63	5.90
5/15/92	10XFeNI(40 mL)	RhCl ₃ (14 mg)	no	2.1 mL	~96°	3256	0.65	3.95
5/20/92	10XFeNI(40 mL)	PdCl ₂ (14 mg)	no	2.1 mL	98-95°	1315	1.07	5.60
5/21/92	11XNI(40 mL)	Pd(NO ₃) ₂ (16.5 mg)	no	2.1 mL	97°	1301	1.07	6.47
5/22/92	10XFeNI(40 mL)	Pd(NO ₃) ₂ (15.5 mg)	no	2.1 mL	~100°	730	0.61	6.50
5/26/92	10XFeNI(40 mL)	RuCl ₃ (13 mg)	no	2.1 mL	~94°	694	0.44	7.69
6/2/92	11XFeI(40 mL)	PdCl ₂ (13.5 mg)	no	2.1 mL	98°	1441	0.11	7.61
6/3/92	11XFeI(40 mL)	RuCl ₃ (13 mg)	no	2.1 mL	94-100°	2779	1.11	~8.0
6/8/92	10XNNI(40 mL)	PdCl ₂ (13.5 mg)	no	2.1 mL	94-95°	1576	5.50	5.89
6/10/92	10XNNI(40 mL)	RhCl ₃ (14 mg)	no	2.1 mL	94±1°	1746	0.17	6.06
6/11/92	10XNNI(40 mL)	RuCl ₃ (13 mg)	no	2.1 mL	96±2°	3185	1.4	4.03
6/15/92	10XNNI(40 mL)	PdCl ₂ (12.9 mg)	no	2.1 mL	95±1°	1315	2.58	5.88
6/16/92	12MI(40 mL)	PdCl ₂ (13 mg)	no	2.1 mL	96±2°	1420	0	8.73

6/17/92	10XNN ¹ (40 mL) + NaNO ₂ (1.2 g)	PdCl ₂ (13 mg)	no	2.1 mL	94°	1401	0	7.28
6/18/92	11XAII(40 mL)	PdCl ₂ (13 mg)	no	2.1 mL	96±1°	1406	0	8.91
6/19/92	9XAINN ¹ (40 mL)	PdCl ₂ (13 mg)	no	2.1 mL	93-96°	420	1.63	4.64
6/19/92	12MI(40 mL) + UO ₂ (NO ₃) ₂ (0.4 g) ⁽³⁾	RhCl ₃ (14 mg)	no	2.1 mL	96±1°	319	1.47	6.66
6/22/92	12MI(40 mL) + UO ₂ (NO ₃) ₂ (0.4 g) ⁽³⁾	RhCl ₃ (14 mg)	no	2.1 mL	94±1°	532	4.68	9.07 (leak?)
6/23/92	11XAII(40 mL)	RhCl ₃ (14 mg)	no	2.1 mL	94-95°	1418	2.04	8.82
6/24/92	9XAINN ¹ (40 mL)	RhCl ₃ (14 mg)	no	2.1 mL	97±2°	1426	0.07	5.23
6/24/92	11XAII(40 mL)	RuCl ₃ (13 mg)	no	2.1 mL	94±1°	2731	0.08	4.57
6/25/92	9XAINN ¹ (40 mL)	RuCl ₃ (14 mg)	no	2.1 mL	98-99°	1543	0.77	3.58
7/7/92	10XNN ¹ (40 mL)	PdCl ₂ (13.2 mg)	no	2.1 mL	98±2°	1503	4.05	4.45
6/26/92	12MI(50 mL)	none	yes	2.31 mL(118 min)	92-95°	216	0	4.77
6/30/92	11XNI(50 mL)	PdCl ₂ (13 mg)	yes	2.31 mL(118 min)	92-99°	254	0.25	6.04
7/1/92	10XNN ¹ (50 mL)	PdCl ₂ (13 mg)	yes	2.31 mL(118 min)	92-99°	337	0.23	4.87
7/7/92	12MI(50 mL)	RhCl ₃ (14 mg) + PdCl ₂ (13 mg)	yes	2.31 mL(118 min)	93±1°	288	0	7.23
7/8/92	10XNN ¹ (50 mL)	Pd(NO ₃) ₂ (16 mg)	yes	2.31 mL(118 min)	94-97°	222	1.20	5.91
7/9/92	11XFeI(50 mL)	0	yes	3.72 mL(190 min)	96±2°	368	0	4.05
7/10/92	11XFeI(50 mL)	RhCl ₃ (14 mg)	yes	3.72 mL(190 min)	93±2°	295	1.40	4.25
7/17/92	12MI(50 mL)	RhCl ₃ (14 mg)	yes	3.72 mL(190 min)	92±2°	385	1.81	3.66
7/22/92	12MI(50 mL)	RhCl ₃ (8.4 mg)	yes	3.72 mL(190 min)	90±1°	481	3.34	4.31

7/23/92	12M1A(50 mL)	RhCl ₃ (5.6 mg)	yes	3.72 mL(190 min)	96±2°	532	2.13	4.03
7/24/92	12M1A(50 mL)	RhCl ₃ (11.2 mg)	yes	3.72 mL(190 min)	93±1°	397	1.08	4.32
7/30/92	11XN1(50 mL) + NaNO ₂ (0.9 g)	RhCl ₃ (14 mg)	yes	3.60 mL(190 min)	91-92°	392	1.98	3.96
8/4/92	11XN1(50 mL) + NaNO ₂ (1.2 g)	RhCl ₃ (14 mg)	yes	3.59 mL(191 min)	97±3°	311	2.49	4.8
8/5/92	11XN1(50 mL) + NaNO ₂ (0.6 g)	RhCl ₃ (14 mg)	yes	3.57 mL(190 min)	91±1°	411	2.52	3.32
8/6/92	11XN1(50 mL) + NaNO ₂ (1.5 g)	RhCl ₃ (14 mg)	yes	3.65 mL(194 min)	93±1°	348	1.81	3.84
8/7/92	12M1A(50 mL)	RhCl ₃ (2.8 mg)	yes	3.57 mL(190 min)	90±2°	391	0.13	4.17
8/12/92	12M1A(50 mL)	RhCl ₃ (8.4 mg)	yes	3.63 mL(190 min)	90±1°	404	0.55	3.97
8/13/92	12M1A(50 mL)	RhCl ₃ (11.2 mg)	yes	3.63 mL(190 min)	88±1°	399	0.54	4.08
8/18/92	German Feed (50 mL)	0	yes	3.53 mL(190 min)	90±1°	391	1.74	4.54
8/19/92	13M+Rh1(50 mL)	0	yes	3.53 mL(190 min)	91±2°	400	0.39	3.89
8/21/92	13M+Rh1(50 mL)	0	yes	3.53 mL(190 min)	87-90°	403	1.44	3.63
9/1/92	13M+Rh1(50 mL)	0	yes	3.53 mL(190 min)	90±1°	399	0.66	4.29
9/2/92	12M1A(50 mL)	5% Rh/C(117.5 mg)	yes	3.53 mL(190 min)	90±1°	342	0.16	6.95
9/4/92	9XNN'C(50 mL) + Na ₂ CO ₃ (0.7 g) + NaNO ₃ (0.5 g) + NaNO ₂ (1.5 g)	0	yes	3.53 mL(190 min)	89±1°	399	0.27	3.85
9/9/92	German Feed(50 mL) + NaNO ₂ (1.5 g)	0	yes	3.53 mL(190 min)	90°	399	0.59	4.93
9/10/92	13M+Rh1(50 mL)	RhCl ₃ (14 mg)	yes	3.53 mL(190 min)	90±2°	400	4.79	4.06

9/11/92	13M+Rh1(50 mL)	PdCl ₂ (12 mg)	yes	3.53 mL(190 min)	90±2°	269	0	6.09
9/15/92	12M1B(50 mL)	RhCl ₃ (1.4 mg)	yes	3.55 mL(190 min)	92±1°	400	0	3.57
9/16/92	12M1B(50 mL)	RhCl ₃ (2.8 mg)	yes	3.55 mL(190 min)	92±2°	400	0	4.18
9/17/92	12M1B(50 mL)	RhCl ₃ (5.6 mg)	yes	3.55 mL(190 min)	90±2°	399	0.25	3.57
9/23/92	12M1B(50 mL)	RhCl ₃ (8.4 mg)	yes	3.44 mL(180 min)	93±1°	403	1.14	3.79
9/24/92	12M1B(50 mL)	RhCl ₃ (11.2 mg)	yes	3.63 mL(190 min)	91±1°	403	1.14	3.79
9/25/92	12M1B(50 mL)	RhCl ₃ (14 mg)	yes	3.63 mL(190 min)	90±2°	400	1.31	3.67
9/29/92	12M1B(50 mL)	RhCl ₃ (8.4 mg)	yes	3.67 mL(190 min)	89±1°	402	0.63	3.64
9/30/92	12M1B(50 mL)	PdCl ₂ (12 mg)	yes	3.67 mL(190 min)	90±2°	261	0	5.4
10/1/92	12M1B(50 mL)	RhCl ₃ (8.4 mg) + PdCl ₂ (5 mg)	yes	3.67 mL(190 min)	89±1°	407	0.53	3.92
10/2/92	12M1B(50 mL)	5% Rh/Al ₂ O ₃ (115 mg)	yes	3.67 mL(190 min)	88-91°	400	0.28	6.88
10/6/92	12M1B(50 mL)	RhCl ₃ (14 mg)	yes	3.67 mL(190 min)	78±1°	399	0.35	3.53
10/8/92	12M1B(50 mL)	RhCl ₃ (14 mg)	yes	3.67 mL(190 min)	93±1°	396	2.38	3.80
10/9/92	12M1B(50 mL)	RhCl ₃ (14 mg)	yes	3.80 mL(190 min)	86±1°	396	0.50	3.46
10/13/92	12M1B(50 mL)	RhCl ₃ (14 mg)	yes	3.69 mL(180 min)	86±1°	398	0.51	4.06
10/14/92	10XCdN1(50 mL) + NaNO ₂ (1.5 g)	RhCl ₃ (14 mg)	yes	3.69 mL(190 min)	89±1°	395	0.66	3.76
10/15/92	13M+Rh1(50 mL)	RhCl ₃ (8.4 mg) + RuCl ₃ (5 mg)	yes	3.69 mL(190 min)	90±2°	366	1.10	3.78
10/16/92	13M+Rh1(50 mL)	RuCl ₃ (5 mg) + PdCl ₂ (5 mg) + RhCl ₃ (2.8 mg)	yes	3.69 mL(190 min)	88±1°	398	0.27	4.83

10/22/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.69 mL(190 min)	89±1°	399	0.93	3.87
10/23/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.69 mL(190 min)	94±1°	400	2.95	4.11
10/28/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.66 mL(190 min)	77±2°	398	0.12	3.72
10/29/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.66 mL(190 min)	85±1°	402	0.26	3.79
10/30/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.66 mL(190 min)	88±1°	397	0.66	3.68
11/3/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.66 mL(190 min)	88±1°	395	0.80	3.95
11/4/92	German Feed(50 mL) + NaNO ₂ (1.5 g)	0	yes	5.49 mL(248 min)	88±1°	487	1.26	4.74
11/5/92	12M1C(50 mL)	RhCl ₃ (15 mg)	yes	3.66 mL(190 min)	70°(25 hr) → 90°	1869	0	6.08
11/10/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.69 mL(190 min)	70°(190 min) → 90°	401	1.48	5.72
11/11/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.69 mL(190 min)	70°(6 hr) → 90°	521	1.12	5.72
11/12/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.69 mL(190 min)	70°(12 hr) → 90°	874	0	5.22
11/17/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.71 mL(190 min)	70°(9 hr) → 90°	708	1.36	3.49
11/18/92	12M1C(50 mL)	RhCl ₃ (14 mg)	yes	3.71 mL(190 min)	89±1°	397	1.10	3.98
11/19/92	12M1C(50 mL)	RhCl ₃ (7.0 mg) + PdCl ₂ (5 mg)	yes	3.71 mL(190 min)	90±1°	403	0.67	4.12
11/20/92	12M1C(50 mL)	RhCl ₃ (7.0 mg)	yes	3.71 mL(190 min)	90±1°	398	0.25	3.59
11/24/92	12M1C(50 mL)	PdCl ₂ (5 mg) + RuCl ₃ (5 mg)	yes	3.68 mL(190 min)	89±1°	402	0	4.08

11/25/92	12M1C(50 mL)	RhCl ₃ (7.0 mg) + RuCl ₃ (5 mg)	yes	3.68 mL(190 min)	90±1°	398	0.26	3.86
----------	--------------	--	-----	------------------	-------	-----	------	------

Notes:

- (a) Some tests conducted subsequent to completion of the draft report (approximately the end of November 1992), are discussed in text, however, are not listed in Appendix B. A revision of the table will be provided in a subsequent report.
- (1) The weights of RhCl₃ and RuCl₃ are those of the commercial trihydrates; the RhCl₃ was introduced in an aqueous solution that led to the addition of 10 mL of additional water in each experiment.
- (2) The formic acid was added as the indicated amount of 88% formic acid. The time required to add the entire amount of formic acid is given in parentheses for the experiments using the syringe pump.
- (3) Uranyl nitrate was introduced as the indicated amount of the hexahydrate UO₂(NO₃)₂·6H₂O.