

Thermochemical Nitrate Reduction

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Introduction

Better alternatives to tank storage of radioactive waste are being evaluated as part of the overall cleanup mission at the U.S. Department of Energy's (DOE) Hanford Site. Two strategies being pursued for stabilizing the waste for permanent disposal are grouting and vitrification. The use of these stabilization techniques must take into account the constituents of the waste in terms of operation and cost effects. One component being addressed is nitrate; the amount of nitrate contained within the waste in the 177 underground storage tanks at Hanford is estimated to be 200 million pounds (DOE 1987).

The nitrate in the tank waste is predicted to have a profound influence on the performance assessment of the grout facility since most nitrate compounds are readily soluble in water. Consequently, nitrate could easily be leached from grout, with the potential of reaching the groundwater in concentrations exceeding state and federal government standards. Reducing the nitrate content also lowers costs, particularly for those wastes targeted for vitrification, by minimizing the amount of waste needing to be stabilized.

The thermochemical reduction technique discussed here is a method for preprocessing the tank waste to remove selected constituents, which is an approach being investigated to reduce the environmental risk and cost and maximize the technical feasibility of waste disposal. Specifically, this report presents the results of a preliminary experimental effort focused on thermochemically converting nitrate to environmentally benign nitrogen and water.

Conclusions and Recommendations

In the thermochemical reduction procedure, ~3 wt% NO_3^- solutions were mixed with six different reducing agents (ammonia, formate, urea, glucose, methane, hydrogen) in a buffered aqueous solution. The individual mixtures were then placed in a 1-L batch reactor and reacted at approximately 200°C to 350°C and 600 to 2800 psig for 0.5 to 3 h.

The preliminary experiments conducted here demonstrated the feasibility of using lower temperatures and a pressurized aqueous environment to minimize the amount of nitrate in Hanford tank waste. Of the reducing agents studied, formate was effective under both acidic (pH 4) and basic (pH 13) conditions. Ammonia was effective under only acidic conditions. The other reducing agents were tested only in basic solutions; the ease of nitrate conversion in the basic solutions descends in the following order: formate > glucose > urea > hydrogen > ammonia \approx methane.

Further investigations are warranted for nitrate reduction at a more fundamental level to gain insight about the mechanism of the reaction. Such a study would lend itself well to the use of Raman spectroscopy and a specially designed reaction cell so that transient chemical species, in particular, those of nitrogen, could be monitored throughout the course of the reaction. This experimental approach could lead to a better understanding of the apparent induction period for the nitrate reduction that has been observed in this study and reported by others (Kelm, Oser, and Drobnik 1986; Cecille and Kelm 1986).

An expanded data base, including more detailed examination of the pH and temperature dependence of the reaction with various reducing agents, is needed to facilitate engineering feasibility studies. These studies would focus on identifying optimum conversion conditions for the more promising reducing agents, as well as continue screening tests to identify new reducing agents with improved performance characteristics. These studies should be conducted with improved analytical tools in order to secure better accounting of the different nitrogen products produced in the reaction, with particular emphasis on N_2 , NO_2 , NO , N_2O , and NH_3 .

Background

A variety of methods have been studied for removing nitrate from hazardous wastes, water, and process streams. Methods applicable to aqueous media include ion exchange, extraction, membranes, distillation, and chemical and biological denitrification. Ion exchange, extraction, membrane, and distillation techniques leave the nitrate radical unchanged, which creates yet another disposal problem. If the nitrate is going to be reused, a recovery operation is needed. For radioactive wastes, methods of nitrate reclamation and reuse are continuing to be investigated. The use of nitrate in a form such as ammonium nitrate for fertilizer suffers from liability and product acceptance issues related to its being derived from a mixed waste. Use of nitrate in the form of nitric acid in nuclear fuel manufacturing and reprocessing faces a limited demand for nitric acid.

Chemical and biological methods decompose nitrate into other chemical species, the nature of which depend upon the reaction conditions. Biological denitrification methods suffer from slow rates, pH sensitivity, and microbe poisoning by elevated levels of nitrates and a host of other compounds, and the ammonia byproduct requires disposal. The method finds its greatest application in nitrate removal from dilute waste streams, such as those at sewage treatment plants or groundwater, where nitrate levels are usually less than 2000 ppm.

A number of thermochemical methods have been examined for denitrification of dry nitrate wastes (Dotson et al. 1975; Meile et al. 1982, 1983). Moderately high (300°C to 500°C) to high temperatures (>500°C) can be employed to thermally decompose NO_3^- into O_2 , N_2 , and NO_x . The amount of undesirable NO_x formation is a function of temperature, heating rate, and co-reactant composition. Thermochemical methods of nitrate destruction can achieve denitrification at lower temperatures by employing a chemical reducing agent such as Fe^{++} or ammonia.

A variety of chemical reducing agents have been examined in aqueous media. Gunderloy et al. (1970) examined the denitrification of dilute nitrate ion solutions (44 to 220 ppm NO_3^-) under both basic and acidic anaerobic conditions at 85°F for 48 h in the presence of ferric and cupric ion catalysts. The relative effectiveness of NO_3^- reduction was $\text{Fe}^{++} \approx \text{iron powder} \approx \text{N}_2\text{H}_2 > \text{glucose} \gg \text{CO} \approx \text{CH}_2\text{O} \approx \text{carbon} \approx \text{SO}_2 \approx 0$. Other investigators have reported the chemical denitrification of nitrate solutions with sugar (Bray 1963), formaldehyde (Forsman and Oberg 1963), and formic acid (Bradley and Goodlett 1972).

Meile and Johnson (1982) reported that denitrification of dilute solutions of nitric acid is achieved by refluxing the solution for 3 h in the presence of chemical reducing agents. The nitrate destruction effectiveness of the reducing agents decreased in the order: formic acid (96%) > formaldehyde (54%) > sucrose (17%) > urea (8%) > ferrous sulfamate (6%) > sulfamic acid (0%) \approx and hydrogen peroxide (0%). The best nitrate destruction yields were obtained in a two-step process of 1) adding H_2SO_4 to the waste and distilling off the resultant HNO_3 and 2) refluxing the HNO_3 for 3 h with formic acid. If the HNO_3 was not distilled out of the H_2SO_4 mix, a nickel catalyst was required to obtain high destruction yields. However, high (4400 ppm) NO_x gas was obtained in the offgas.

Meile and Johnson (1982) also reported on high-temperature nitrate destruction in a high-temperature fluid wall reactor. At temperatures of 2200°C, 96% NO_3^- destruction with low NO_x concentrations in the products was achieved in the presence of carbon black. In the absence of the carbon black, only 80% nitrate destruction occurred. Slightly better nitrate destruction was obtained in the presence of carbon black in a molten salt reactor at 1000°C, while only 25% destruction was observed with urea as the reducing agent in a muffle furnace at 400°C.

An ideal destruction method would convert the nitrate into molecular nitrogen and water without producing problematic reaction byproducts such as ammonia or nitrogen oxides. A low-temperature selective method has yet to be developed that is practical and cost effective for the complete destruction of high concentrations of nitrate in aqueous solutions. The system described in this report was designed to thermochemically reduce nitrate at practical rates at temperatures lower than tested by previous researchers and to maintain an aqueous system by pressurizing the system high enough to keep the water in the liquid phase.

Experimental Methods

The thermochemical reduction experiments were conducted in a 1-L batch reactor (autoclave) with temperature and pressure ratings of 450°C and 5400 psig. Both gas and liquid sampling capabilities are incorporated in the reactor, enabling samples to be collected and analyzed throughout the experimental run. The reactor is shown in Figure 1. The components analyzed in this system were NO_3^- , NO_2^- , N_2O , N_2 , and NH_3 .

Experimental runs (A through F) were conducted using ~3 wt% NO_3^- solutions mixed with a reducing agent (A. ammonia, B. formate, C. urea, D. glucose, E. methane, F. hydrogen) in a buffered aqueous solution. Strongly basic solutions were prepared with a $\text{NaOH-Na}_3\text{PO}_4$ buffer; weakly basic solutions

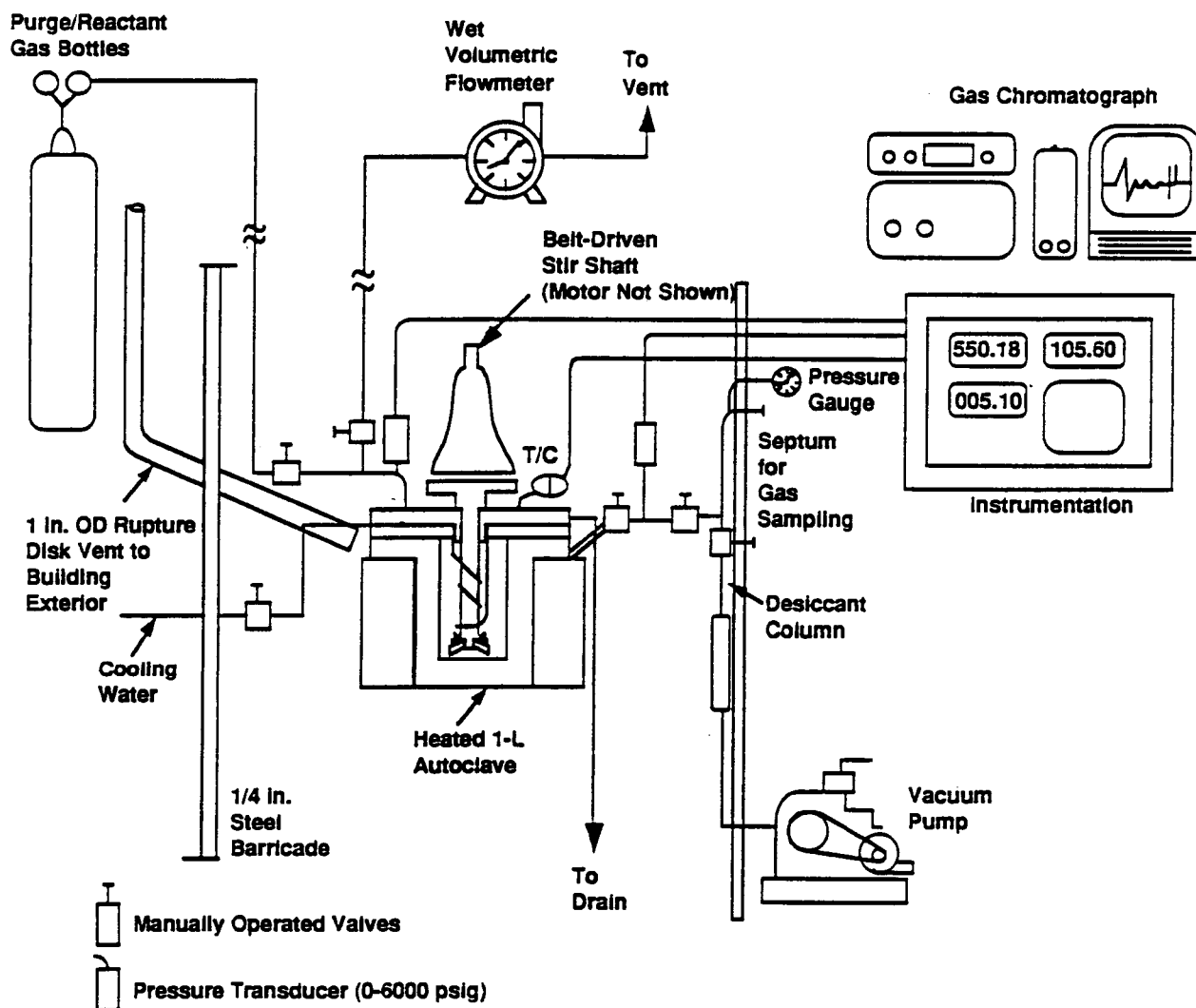


Figure 1. Schematic Diagram of the Batch Reactor System

were prepared with a NaOH-NH₄H₂PO₄ buffer, while H₃PO₄ was used to prepare acidic solutions. The initial pH was measured, and the reactants were charged to the reactor, which was then flushed and pressurized with helium to 100 psig to provide a cushion gas. In those instances where a reactant gas, e.g., CH₄ or H₂, was employed, it was used in place of helium. The reactor was then heated to reaction temperature and allowed to react for a fixed period of time. Rapid stirring of reactants was maintained during heatup and reaction. Gas samples were drawn and analyzed at predetermined intervals throughout the run.

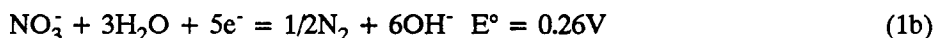
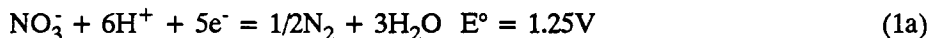
Following completion of each run, the reactor was rapidly quenched to room temperature with water via an immersed cooling coil. A final gas sample was taken, and the gas volume measured by venting through a wet test meter. The contents of the reactor were then removed and weighed to permit overall material balances to be determined; the product was removed and stored in a tightly sealed glass vial in the refrigerator for subsequent analysis for nitrate, nitrite, and ammonia.

Gas analyses were performed with a Model 158A Carle gas chromatograph equipped with an 8-ft 80% Porapak N - 20% Porapak Q 50/80 mesh column; an 8-ft molecular sieve 13X 80/100 mesh column; a 6-ft 8% OV-101 on Chromosorb W 80/100 mesh column; a thermal conductivity detector; and helium and nitrogen carrier gases with flow rates of 26 cm³/min and 55 cm³/min, respectively. Analyses were performed at a column temperature of 65°C. This configuration allowed the measurement of hydrogen, nitrogen, nitrous oxide, carbon monoxide, carbon dioxide, and C1 through C5 hydrocarbons. Nitric oxide, nitrogen dioxide, and ammonia could not be reliably analyzed in the gas phase with this gas chromatographic setup. The ammonia peak was broad and lacked quantitative reproducibility. Both NO₂ and NO are reactive compounds that are scavenged by trace quantities of air in the system or introduced during sampling. The NO₂ furthermore is irreversibly adsorbed on many types of column packing.

Chemical analysis for nitrogen compounds in the aqueous phase employed the Hach Spectrophotometric methods Nitraver 5 and Nitraver 3 for NO₃⁻ and NO₂⁻, respectively. An Orion Model 95-12 ion selective NH₄⁺ electrode with a Beckman Model 3500 digital pH/mv meter was used for NH₃ analysis.

Results and Discussion

The richness of nitrogen redox chemistry in acid and base is illustrated by the standard oxidation potential diagrams shown in Figure 2 (Latimer 1952). While the half reaction of the reduction of nitrate to nitrite is favorable at any pH, the standard free energy change in acid (144 kcal), Equation (1a), is much more than that in base (30 kcal), Equation (1b). Reduction of nitrate to nitrogen is a five-electron process. Examination of Figure 2 reveals that in the reduction of nitrate to nitrogen, each one-electron reduction has a favorable free energy change in acidic media (ΔG is negative). On the other hand, in basic solution, two of the one-electron reductions, NO_3^- to N_2O_4 and NO_2^- to NO , have unfavorable free energy changes (ΔG is positive).



The standard redox potential for the NO_3^-/N_2 couple predicts that any reducing agent with an $E^\circ > -1.25\text{ V}$ in acidic solution and $E^\circ > -0.26\text{ V}$ in basic solution should provide favorable free energy change for the redox reaction. The standard oxidation potentials for the investigated reducing reagents are listed in Table 1 for both acidic (E_a° , pH = 0) and basic (E_b° , pH = 14) solutions.

Results from 16 experimental runs are summarized in Table 2. Complete experimental data for each run are given in the appendix. The pH values listed in Table 2 are those determined experimentally at the beginning (pH_i) and end (pH_f) of the runs. The temperature, pressure, and time refer to those experimental parameters at run conditions. Time zero corresponds to the time the reactor reached the indicated reaction temperature. The heatup time to reaction temperature is about 0.5 h for the low-temperature (<250°K) runs and about 1.0 h for the high-temperature (300°C to 350°C) runs. With the exception of Runs A-1 through A-3, the reactant ratios were selected so that an excess of reducing agent was present to force the reaction to completion.

With the exception of Runs E-1 and F-1, the percent nitrate conversion reported in Table 2 is based on the amount of nitrate (NO_3^-) consumed during the reaction, which in turn was determined from the difference between the amount charged initially and that found in the recovered product by the previously described spectrophotometric method. In Runs E-1 and F-1 the conversion is based on the amount of nitrogen (N_2) observed in the reaction products.

Table 3 contains the total quantities of nitrogen compounds expressed in g-moles in the gaseous and liquid phase at the beginning and conclusion of each of the experimental runs. The initial amounts are based on quantities of reagents used in the experimental runs determined by the weight of liquid and solid reagents and the volume of gaseous materials. The fixed final amounts of materials are based on analyses performed and material balance considerations. In most cases, mass balances were not good.

Large amounts of nitrous oxide, (N_2O) and N_2 were produced from the ammonia-nitrate system under acidic reaction conditions, while N_2O was nondetectable in the final reaction product from the formate-nitrate system under both acidic and basic conditions. Nitrogen oxides constitute an undesirable byproduct.

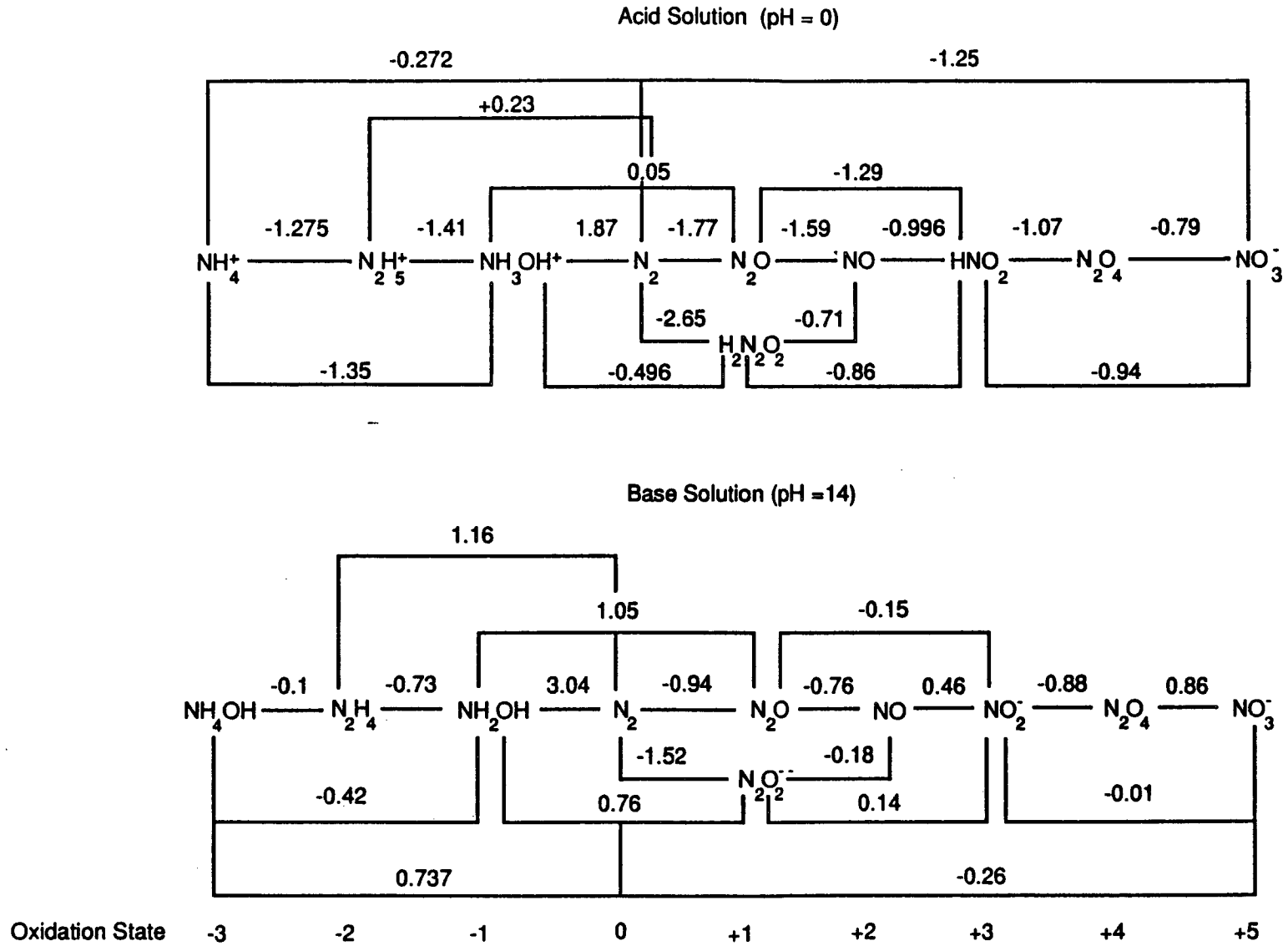


Figure 2. Oxidation Potential Diagrams for Nitrogen (adapted by permission from Latimer 1952)

Table 1. Oxidation Potentials for Reducing Reagents (data compiled from Latimer 1952)

Couple	E_a° , volts	E_b° , volts
$\text{CO}(\text{NH}_2)_2/\text{CO}_2, \text{N}_2$	-0.10	0.70
NH_3/N_2	-0.27	0.74
$\text{HCO}_2\text{H}/\text{CO}_2$	0.20	1.01
CH_4/CO_2	-0.16	0.66
H_2/H^+	0.0	0.83
$\text{C}_6\text{H}_{12}\text{O}_6/\text{CO}_2$	0.03	0.86

E_a° , standard oxidation potential at pH = 0.

E_b° , standard oxidation potential at pH = 14.

Table 2. Summary of Nitrate Reduction Experiments

Run No.	Reactants mole:mole	pH _i	pH _f	Temp., °C	Press. at Temp., psig	Time at Temp., h	Nitrate Conv., %
A-1	$\text{NH}_3:\text{NO}_3^-$	12.5	12.7	250	617	3.75	0
A-2	$\text{NH}_3:\text{NO}_3^-$	12.5	NM	300	1220	3.00	2
A-3	$\text{NH}_3:\text{NO}_3^-$	12.5	12.8	350	2278	6.00	9
A-4	2.4 $\text{NH}_3:\text{NO}_3^-$	7.8	6.9	350	2484	2.00	1
A-5	2.4 $\text{NH}_3:\text{NO}_3^-$	4	2.6	350	2558	2.00	100
A-6	2.4 $\text{NH}_3:\text{NO}_3^-$	4	4.5	250	588	2.00	13
A-7	2.4 $\text{NH}_3:\text{NO}_3^-$	3.9	5.5	300	1264	2.00	51
A-8	2.3 $\text{NH}_3:\text{NO}_3^-$	4	2.8	350	2558	2.00	100
B-1	3.0 $\text{HCO}_2^-:\text{NO}_3^-$	3.9	7.5	350	2852	2.00	100
B-2	3.0 $\text{HCO}_2^-:\text{NO}_3^-$	13.2	9.7	325	1970	2.00	99
B-3	3.0 $\text{HCO}_2^-:\text{NO}_3^-$	13.2	9.8	305	1294	2.00	74
C-1	0.7 Urea: NO_3^-	12.7	10.1	345	2058	2.00	20
D-1	0.4 Glucose: NO_3^-	13 ^(a)	8.2	350	2323	2.00	48
E-1	1.4 $\text{CH}_4:\text{NO}_3^-$	13.2	9.9	350	2572	2.00	6
F-1	3.7 $\text{H}_2:\text{NO}_3^-$	13.2	NM	360	3102	2.00	18

NM = not measured.

(a) Estimated.

Table 3. Summary of Nitrate Reduction Specificity

Run No.	Initial, g-moles		Final, g-moles					Unaccounted ^(c)
	NO ₃ ⁻	NH ₃	NO ₃ ⁻	NO ₂ ⁻	N ₂ O	N ₂	NH ₃	
A-1	0.205	0.205	0.213	t	0.00	0.0043	0.193	-0.005
A-2	0.205	0.205	0.202	0.0007	0.00	0.0002	0.181	0.026
A-3	0.205	0.205	0.185	0.0039	0.00	0.0004	0.143	0.077
A-4	0.205	0.501	0.203	0.00	0.028	0.148	0.337	-0.186
A-5	0.205	0.499	0.0008	(a)	0.045	0.199	0.197	0.012
A-6	0.205	0.499	0.177	0.00	0.00	0.0046	0.677	-0.159
A-7	0.205	0.499	0.101	0.00	0.001	0.068	0.357	0.108
A-8	0.205	0.499	t	0.00	0.062	0.192	0.204	-0.007
B-1	0.205	0.00	t	0.00	0.0002	0.102	0.00	0.001
B-2	0.205	0.00	0.002	(a)	0.0002	0.046	0.00	0.111
B-3	0.208	0.00	0.054	(a)	0.0027	0.034	0.00	0.081
C-1	0.205	0.205 ^(b)	0.166	0.00	t	0.0064	0.318	-0.087
D-1	0.205	0.00	0.099	(a)	0.00	0.0050	0.00	0.097
E-1	0.205	0.00	(a)	(a)	t	0.0061	0.00	0.193
F-1	0.205	0.00	(a)	(a)	0.0002	0.018	0.00	0.169

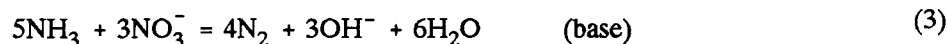
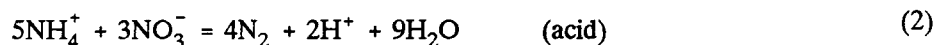
(a) Not determined.

(b) There is an additional 5.02 g NH₃ available if the urea is completely hydrolyzed.

(c) Unaccounted nitrogen, moles initial nitrogen less moles final nitrogen.

t = trace ≤ 0.01 g.

under acidic (pH ≈ 4) and basic (pH ≈ 13) conditions. The stoichiometry of the reduction reaction is given in Equations (2) and (3) for acidic and basic conditions, respectively.



As shown in Table 2, the NO₃⁻ reduction in basic solutions was found to be a very sluggish reaction. At pH = 13 the NO₃⁻ conversion was 0% (Run A-1) after reacting for 3.75 h at 250°C and only 9% (Run A-3) after 6 h at 350°C. Even at near-neutral conditions (pH = 7.8) the NO₃⁻ conversion was only

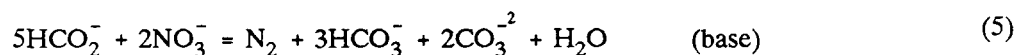
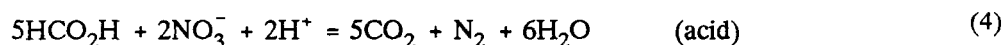
1% after 2 h at 350°C (Run A-4). The slowness of nitrate reduction with ammonia in basic media may be due to the large activation barrier in the formation of N_2O_4 and NO as intermediate products although the mechanism of the reaction is unknown. Also, the limited solubility of ammonia under basic conditions may have contributed to the poor nitrate conversion.

In acidic solution at pH = 4 the reduction with ammonia was comparatively facile as shown in Run A-5, where 100% NO_3^- conversion was achieved in 2 h at 350°C. Further experiments at pH = 4 (A-6 through A-8) revealed the effect of temperature on the conversion. Experimental NO_3^- conversions were 13% at 250°C, 51% at 300°C, and 100% at 350°C. These results are plotted in Figure 3.

The attainable reproducibility of the experimental runs is revealed by a comparison between Runs A-5 and A-8. These runs, insofar as possible, were conducted under identical conditions. Total nitrogen material balances as shown in the appendix reveal 9.86 g N charged and 9.61 g N recovered in Run A-5 and 9.40 g N charged and 9.99 g N recovered in A-8. Both runs reveal 100% nitrate conversion. Table 3 indicates that the major nitrogen products were N_2 and N_2O , although, as previously pointed out, the analysis for other gaseous nitrogen compounds (NO and NO_2) was unreliable. The reactivity order of the nitrogen oxides, $N_2O < NO_2 < NO$, is consistent with the products observed. NO reacts instantly with air.

Figure 4 shows the time-dependent production of N_2 and N_2O and the concomitant decrease of the cushion gas concentration with reaction time for a pH 4 reduction at 350°C. The production of N_2 and N_2O starts slowly, followed by a rapid increase in yield and finally slows again toward the end of the reaction. The slowing of the reaction in the final stages is consistent with mass action effects, where the decrease in the concentration of reactants and the increase in concentration of products retard the forward reaction. The slow initial stage of the reaction, or induction period is seen in both acidic and basic solutions and has been observed by other investigators (Cecille and Kelm 1986; Longstaff and Singer 1954; Kubota et al. 1979; Germain et al. 1974). While the induction period in acid is reported to be affected by temperature, concentration of reactants, and reactor walls, it is primarily a function of nitrous acid in the system where HCHO, HCO_2H , and possibly other reducing agents are employed. The addition of sodium nitrite can shorten or even eliminate the induction period in the HCHO/ HNO_3 and HCO_2H/HNO_3 systems (Kubota et al. 1979).

The B series of runs employed formate as the reducing agent. The stoichiometric reactions for both acidic and basic conditions are given below.



In contrast to reduction with ammonia, formate produced high nitrate conversions in both acidic and basic solutions. At an initial pH of 13, nitrate conversions of 74% and 99% were obtained by reaction for 2 h at 305°C and 325°C, respectively. At an initial pH of 4, a nitrate conversion of 100% was obtained by reacting 2 h at 350°C. The product gas composition as a function of reaction time for the latter run (No. B-1) is shown in Figure 5. Initially, CO, H_2 , and CO_2 are the predominant gaseous products. As the reaction proceeds, the carbon monoxide-shift reaction producing CO_2 and H_2 peaks, and the rate of nitrogen production increases.

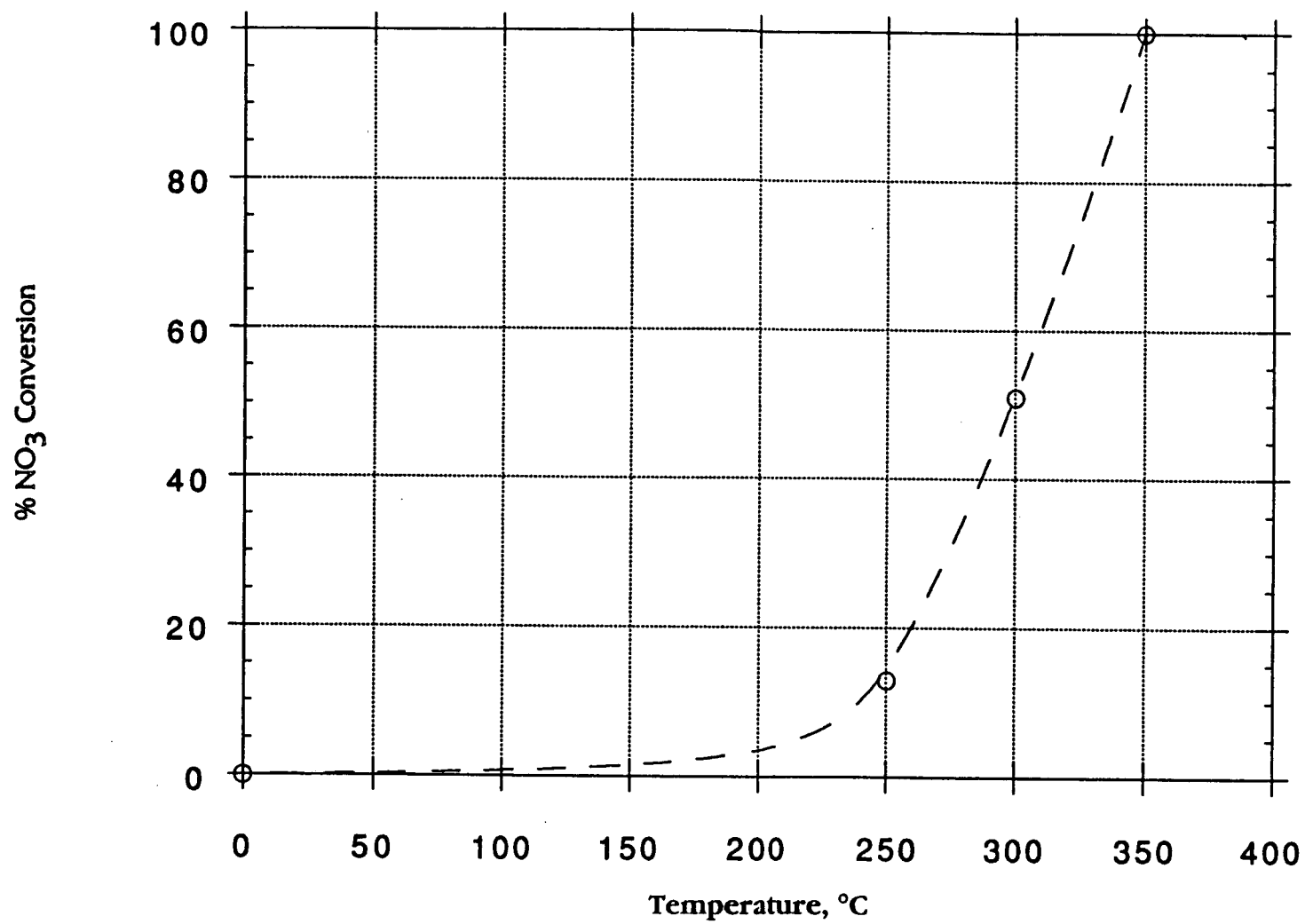


Figure 3. NO_3 Reduction with NH_4^+ at pH 4 Reaction Time, 2 h

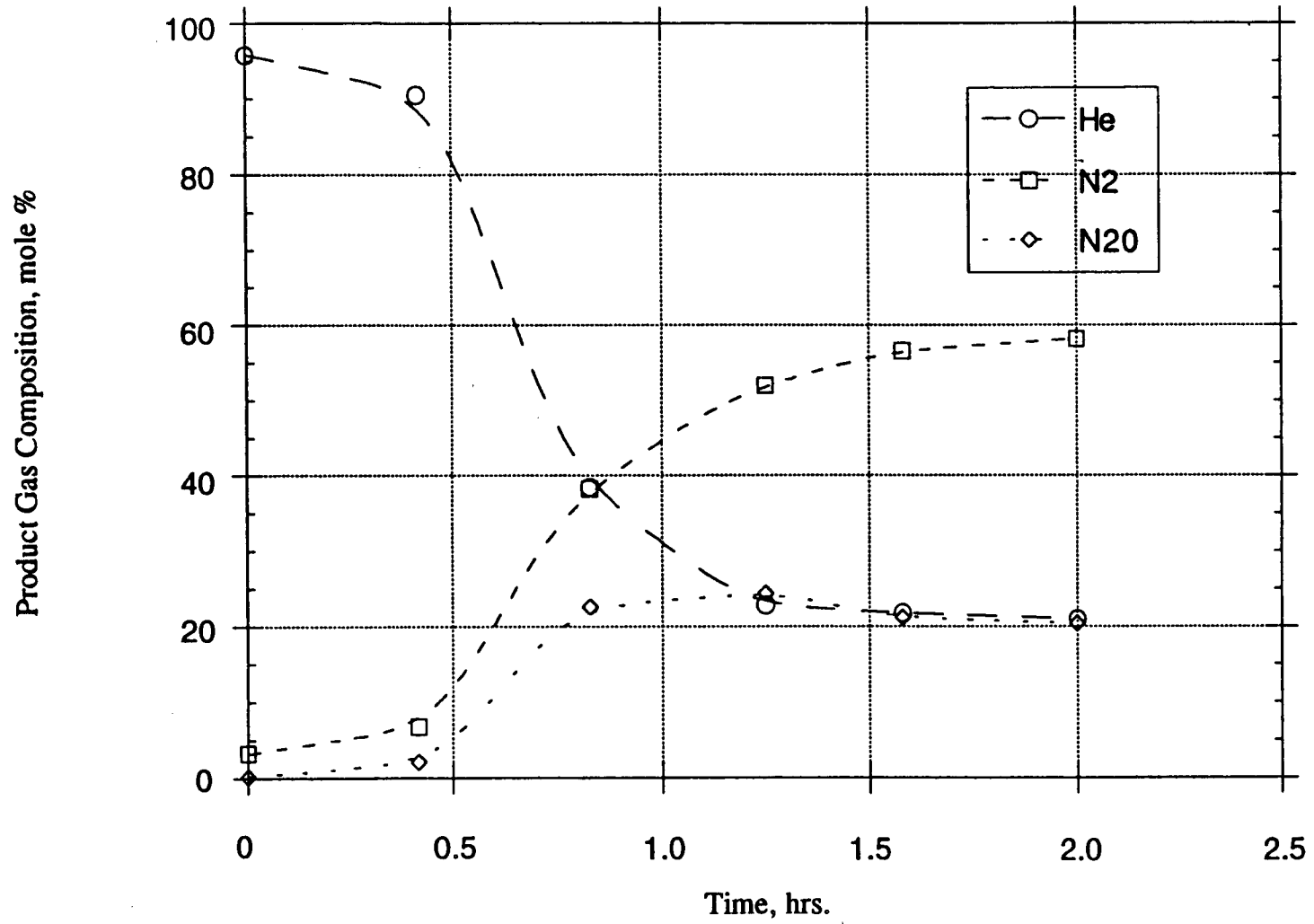


Figure 4. Time Dependent Gas Composition for NO₃ Reduction with NH₄⁺ at pH 4 and 350°C (Run A-8)

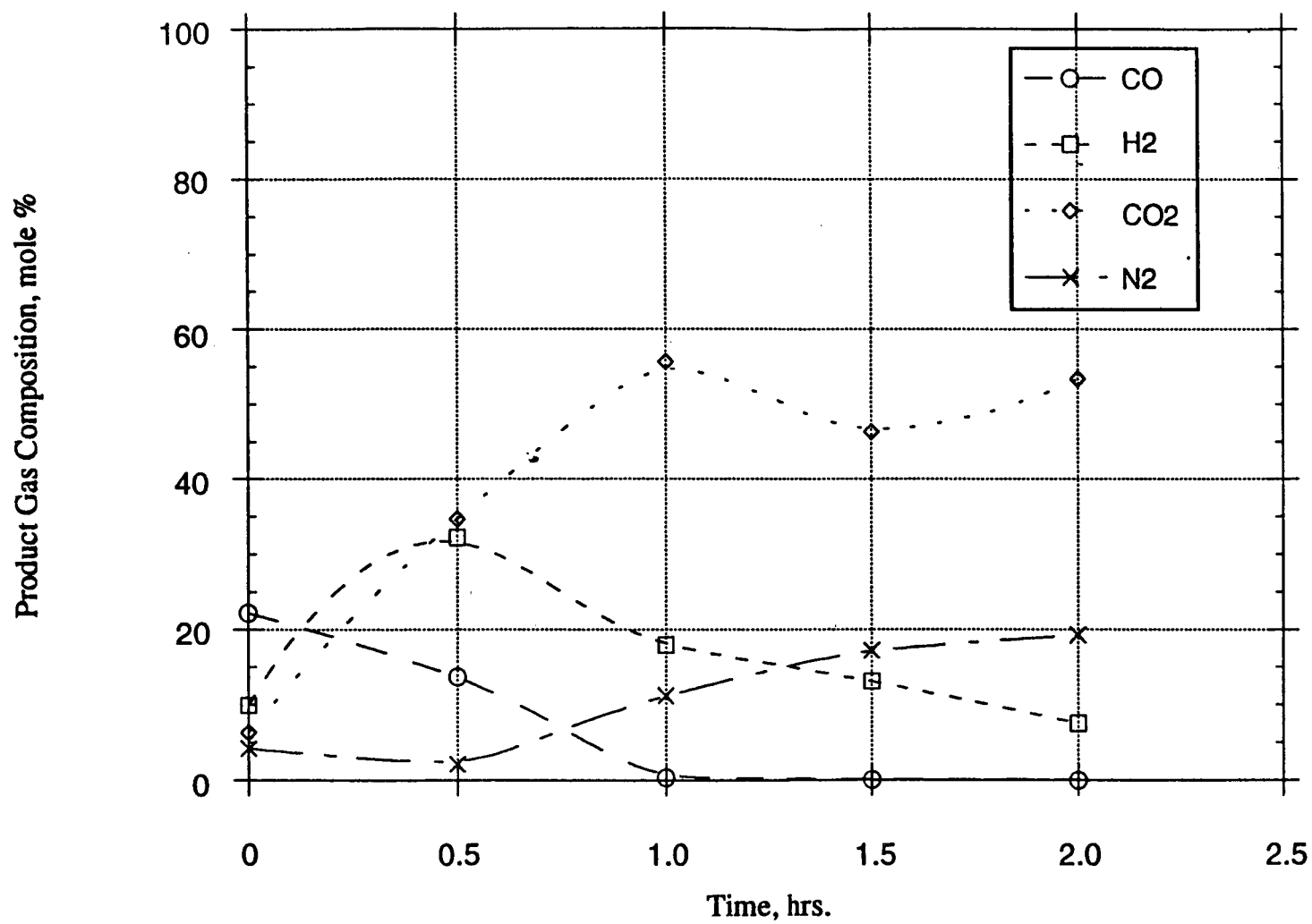
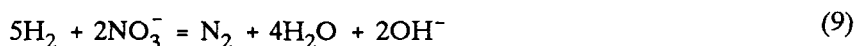
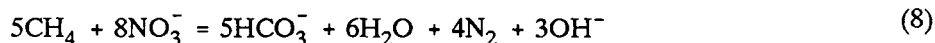
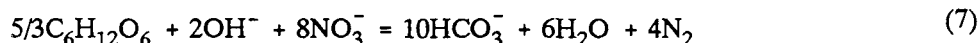
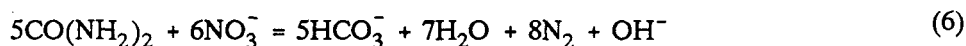


Figure 5. Time Dependent Gas Composition for NO_3^- Reduction with HCO_2^- at pH 4 and 350°C

The only appearance of NO_x 's was N_2O at time zero where the concentration was 0.5%. The implication is that since measurable quantities of the product gases from the reduction are present at time zero, it is apparent that some reaction of the formate occurred in the 30 to 45 min required to bring the reactants from ambient to reaction temperature (350°C). At this temperature, some thermal decomposition of formate into hydrogen and carbon monoxide would be expected. Figure 5 shows very little N_2 forming during this period, and, in fact, the N_2 production rate remains low until about 0.5 h into the reaction. A similar induction period was observed when ammonia was the reducing agent (Figure 4). The major difference observed between using ammonia and formate as reducing agents under acidic conditions is the amount of N_2O formed. With formate there was no N_2O in the final product gases under acidic conditions; with ammonia as the reducing agent, N_2O was present throughout the 2-h run and accounted for 24 mol % of the product gases.

As a final observation in the B series of runs, the reduction of NO_3^- by formate has a neutralizing influence on the reaction media, amounting to about 3.5 pH units when starting from either pH 13 or pH 4. This change in pH in the absence of adequate buffering capacity by the reacting solution is predicted by Equations (4) and (5).

The C, D, E, and F series of runs employed urea, glucose, methane, and hydrogen, respectively, as reducing agents under basic conditions. The reaction stoichiometry under basic conditions is given in the following reactions.



The nitrate reduction results using urea are summarized in Table 3 under Run C-1. Twenty percent nitrate conversion was achieved after 2 h reaction at 345°C and initial pH of 12.7. Carbon dioxide and small amounts of N_2O were observed in the reaction products. Nitrogen gas was continuing to be produced when the run was terminated. No hydrogen or carbon monoxide was observed in the product gas, contrary to Runs B-1 through B-3, where a carbon-based reducing agent (formate) was also used.

Glucose proved to be a more effective reducing agent than urea. Under basic (pH = 13) conditions 48% nitrate conversion was achieved after reacting 2 h at 350°C . The gas chromatography data contained in the appendix (Run D-1) shows N_2O present only at low concentration at the beginning of the run. The amount of nitrogen produced increased throughout the run. There were also carbon-based gaseous species such as carbon monoxide and carbon dioxide, as well as hydrogen, which would be expected products of the water gas shift reaction under these experimental conditions.

For Runs E-1 and F-1, where methane and hydrogen were employed as reducing agents, the nitrate conversion is based on product gas analysis. Methane produced a 6% nitrate conversion to nitrogen, while hydrogen produced an 18% conversion to nitrogen. Only trace amounts of N_2O were observed in the gaseous products for both reducing agents.

The effectiveness of nitrate destruction in basic solution roughly correlates with the standard oxidation potential of the reducing agent (Table 1, Figure 6). The best reducing agents (highest oxidation potential) are most active for NO_3^- reduction following the order: formate > glucose > urea > hydrogen > ammonia \approx methane. The lower-than-expected activity for hydrogen and ammonia could in part be due to the low solubility of these reducing agents in the reaction medium.

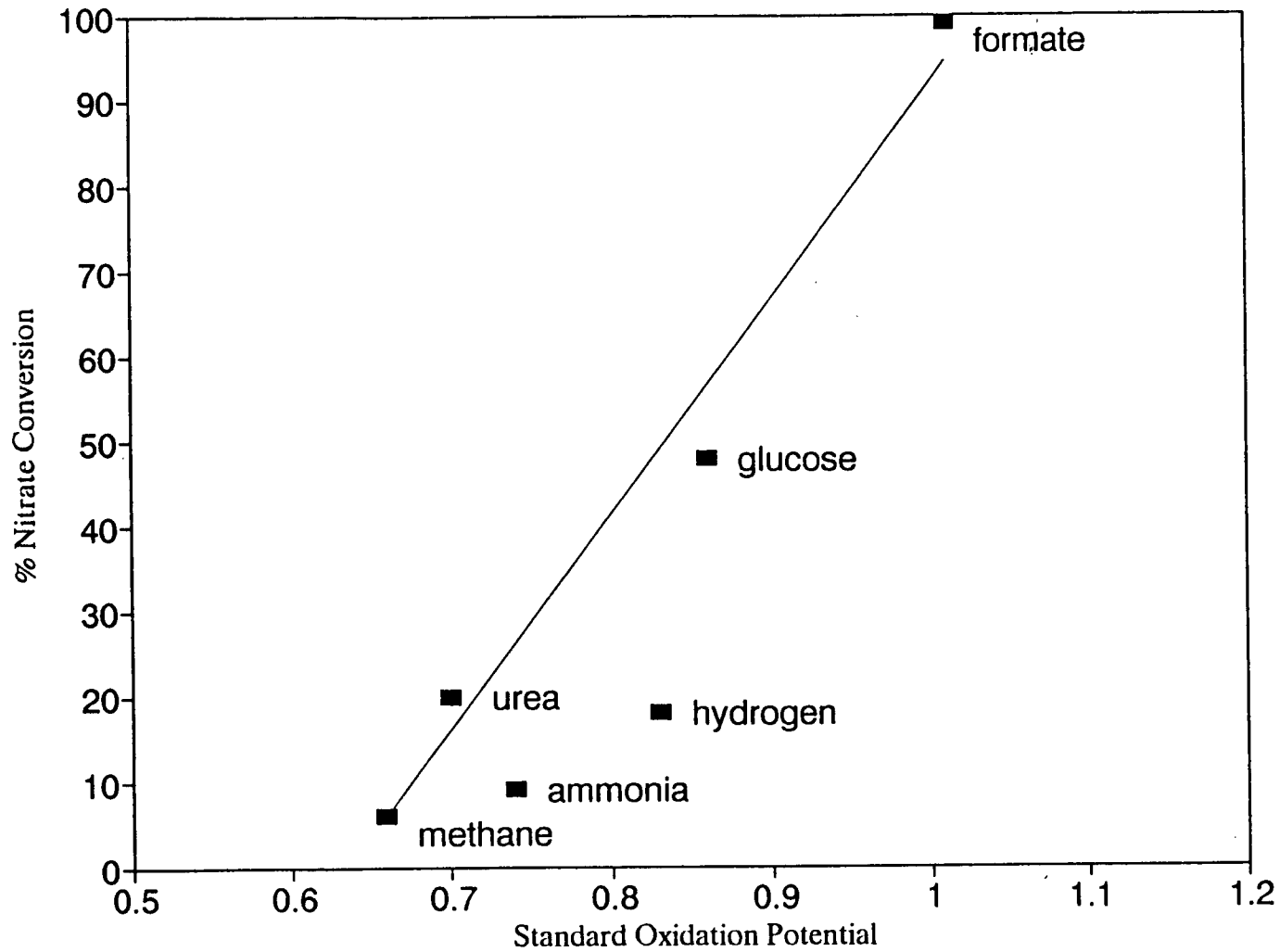


Figure 6. Nitrate Conversion in Basic Solution vs. Oxidation Potential

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Appendix
Experimental Data

Nitrogen Material Balance Run No. A-1							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	13.2000	-0.50	-0.01	2.87	2.98
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0028	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂	28.01	0.0000	0.1150	-0.12	0.00	0.00	0.12
NH ₃ (g)	17.03	0.0000	0.0152	-0.02	0.00	0.00	0.01
NH ₄ ⁺	18.04	3.6960	3.46	0.24	0.01	2.87	2.69
Total N						5.74	5.79

Gas Chromatography Data Run No. A-1							
Sample	Initial	1	2	3	4	5	Final
t, °C	20	250	249	252	250	251	23
atm, gauge	7	41	41	44	42	43	6
hr		0	1	2	3	3.75	
Comp., mole %							
He	99.99	93.47	89.37	90.9	95.68	96.17	95.61
H ₂	0	0	0	0	0	0	0
N ₂	2.09	6.62	6.35	6.07	0.86	0.64	2.81
O ₂	0.773	1.75	1.65	1.67	0.29	0.06	0.97
CH ₄	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
N ₂ O	0	0	0	0	0	0	0
NH ₃	0	0	0	0	0	0	0
Backflush	3.67	2.27	1.09		3.17	3.14	
		104.11	98.46	98.64	100	100.01	100

Nitrogen Material Balance Run No. A-2							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	12.5000	0.20	0.00	2.87	2.82
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.2588	-0.03	0.00	0.00	0.01
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂	28.01	0.0000	0.0062	-0.01	0.00	0.00	0.01
NH ₃ (g)	17.03	0.0000	0.0015	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	3.6960	3.2470	0.45	0.02	2.87	2.52
Total N						5.74	5.36

Gas Chromatography Data Run No. A-2							
Sample	Initial	1	2	3	4	5	Final
t, °C	22	300	299	299	300	290	23
atm, gauge	6.8	87	86	85	86	73	6
hr		0	0.75	1.5	2.25	3.00	
Comp., m%							
He	96.42	97.34	97.79	97.07	98.31	97.55	38.28
H ₂	0	0	0	0	0	0	0
N ₂	1.31	0.79	0.57	0.58	0.61	0.69	46.01
O ₂	0.43	0.14	0.03	0.08	0.03	0.05	10.34
CH ₄	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
N ₂ O	0	0	0	0	0	0	0
NH ₃	0	0	0	2.26	1.06	1.81	0
Backflush	1.84	1.73	1.61	0	0	0	5.37
	100	100	100	99.99	100.01	100.1	100

Nitrogen Material Balance Run No. A-3							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	11.5000	1.20	0.02	2.87	2.60
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.1767	-0.18	0.00	0.00	0.05
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0000	0.00	0.00	0.00	0.01
N ₂	28.01	0.0000	0.0097	-0.01	0.00	0.00	0.00
NH ₃ (g)	17.03	0.0000	0.0007	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	3.6960	2.580	1.12	0.06	2.87	2.00
Total N						5.74	4.66

Gas Chromatography Data Run No. A-3							
Sample	Initial	1	2	3	4	5	Final
t, °C	23	250	249	252	250	251	23
atm, gauge	6.8	41	41	44	42	43	6
hr		0	1	2	3	3.75	
Comp., m%							
He	99.99	93.47	89.37	90.9	95.68	96.17	95.61
H ₂		0	0	0	0	0	0
N ₂		6.62	6.35	6.07	0.86	0.64	2.81
O ₂	0.06	1.75	1.65	1.67	0.29	0.06	0.97
CH ₄		0	0	0	0	0	0
CO		0	0	0	0	0	0
CO ₂		0	0	0	0	0	0
NO ₂		0	0	0	0	0	0
NO		0	0	0	0	0	0
N ₂ O		0	0	0.19	0.29	0.3	0.07
NH ₃	1.44	0.91	1.05	2.43	0.92	0.82	0
Backflush	3.67	2.27	1.09		3.17	3.14	
		104.11	98.46	98.64	100	100.01	100

Nitrogen Material Balance Run No. A-4							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	12.6000	0.10	0.00	2.87	2.85
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	1.2450	-1.25	-0.03	0.00	0.79
N ₂	28.01	0.0000	4.1470	-4.15	-0.15	0.00	4.15
NH ₃ (g)	17.03	0.0000	0.0604	-0.06	0.00	0.00	0.05
NH ₄ ⁺	18.04	9.0260	6.017	3.01	0.17	7.00	4.67
Total N						9.87	12.50

Gas Chromatography Data Run No. A-4								
Sample	Initial	1	2	3	4	5	6	Final
t, °C	21	345	355	356	347	346	348	19
atm, gauge	6.87	151	178	183	166	166	169	12
hr		0	0.5	0.92	1.33	1.75	2	
Comp., m%								
He	99.99	87.5	79.97	53.91	38.66	34.88	25.62	41.7
H ₂			0.18	0.76	0.65	0.44	0.27	0.23
N ₂		1.9	11.38	35.19	46.74	53	60.04	46.55
O ₂		0.39	0.14	0.12	0.05	0.03	0.06	0.37
CH ₄			0.16	1.29	1.78	0.09	1.36	0.96
CO			0.28	1.2	0.18	0.16	0.03	
CO ₂					2.16	1.62	0.44	0.18
NO ₂								
NO								
N ₂ O			1	4.09	8.16	9.48	12.01	8.9
NH ₃		8.21	6.89	3.44	1.63	0.3	0.16	1.12
		98	100	100	100.01	100	99.99	100.01

Nitrogen Material Balance Run No. A-5							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	0.0080	12.69	0.20	2.87	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.05
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	1.9980	-2.00	-0.05	0.00	1.27
N ₂	28.01	0.0000	5.5800	-5.58	-0.20	0.00	5.58
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	9.0125	3.5500	5.46	0.30	6.99	2.75
Total N						9.86	9.61

Gas Chromatography Data Run No. A-5								
Sample	Initial	1	2	3	4	5	6	Final
t, °C	21	345	361	355	351	351	350	19
atm, gauge	6.73	149	199	183	173	172	169	14
hr		0	0.42	0.67	1.25	1.58	2	
Comp., m%								
He	99.99	95.73	93.87	40.02	30.6	18.64	22.75	34.97
H ₂		0	0	0	0	0	0.24	0.27
N ₂		2.42	4.45	48.56	54.28	65.61	63.04	51.88
O ₂		0.44	0.39	0.1	0.07	0.21	0.12	0.8
CH ₄		0	0	0	0	0	0	0
CO		0	0	0	0	0	0	0
CO ₂		0.32	0.32	0.26	0.4	0.33	0.25	0.25
NO ₂		0	0	0	0	0	0	0
NO		0	0	0	0	0	0	0
N ₂ O		0.69	0.96	11.05	14.65	15.22	13.61	11.83
NH ₃		0.4	0	0	0	0	0	0
		100	99.99	99.99	100	100.01	100.01	100

Nitrogen Material Balance Run No. A-6							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	11.0000	1.70	0.03	2.87	2.48
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂	28.01	0.0000	0.1340	-0.13	0.00	0.00	0.13
NH ₃ (g)	17.03	0.0000	0.0257	-0.03	0.00	0.00	0.02
NH ₄ ⁺	18.04	9.0125	12.1750	-3.16	-0.18	6.99	9.45
Total N						9.86	12.09

Gas Chromatography Data Run No. A-6							
Sample	Initial	1	2	3	4	5	Final
t, °C	21	240	250	255	255	253	18
atm, gauge	6.87	33	41	43	43	42	6
hr		0	0.5	1	1.5	2	
Comp., m%							
He	99.99	92.39	96.22	96.86	98.08	94.44	94.46
H ₂		0.78	0	0	0.18	0.21	0.16
N ₂		4.41	2.29	2.06	1.4	3.92	3.46
O ₂		0.92	0.47	0.41	0.13	0.59	0.38
CH ₄		0	0	0	0	0	0
CO		0	0	0	0	0	0
CO ₂		1.49	1.02	0.67	0.21	0.84	0.44
NO ₂		0	0	0	0	0	0
NO		0	0	0	0	0	0
N ₂ O		0	0	0	0	0	0
NH ₃		0	0	0	0	0	1.09
		99.99	100	100	100	100	99.99

Nitrogen Material Balance Run No. A-7							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	6.2400	6.46	0.10	2.87	1.41
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0532	-0.05	0.00	0.00	0.03
N ₂	28.01	0.0000	1.733	-1.73	-0.06	0.00	1.73
NH ₃ (g)	17.03	0.0000	0.000	0.00	0.00	0.00	0.02
NH ₄ ⁺	18.04	9.0125	6.4300	2.58	0.14	6.99	4.99
Total N						9.86	8.17

Gas Chromatography Data Run No. A-7							
Sample	Initial	1	2	3	4	5	Final
t, °C	21	295	301	300	302	300	18
atm, gauge	6.87	79	88	87	89	88	9
hr		0	0.5	1	1.5	2	
Comp., m%							
He	99.99	96.55	92.68	75.43	66.7	63.09	64.21
H ₂		0	3.14	7.41	7.33	6.97	4.9
N ₂		2.43	3.28	15.8	24.48	28.97	29.92
O ₂		0.6	0.15	0.52	0.56	0.19	0.61
CH ₄		0	0	0	0	0	0
CO		0	0	0	0	0	0
CO ₂		0.42	0.11	0.48	0.42	0.22	0.06
NO ₂		0	0	0	0	0	0
NO		0	0	0	0	0	0
N ₂ O		0	0.04	0.36	0.5	0.57	0.3
NH ₃		0	0.61	0	0	0	0
		100	100.01	100	99.99	100.01	100

Nitrogen Material Balance Run No. A-8							
Compound	FW	In, g	Out, g	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	0.0013	12.70	0.20	2.87	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	2.7500	-2.75	-0.06	0.00	1.75
N ₂	28.01	0.0000	5.3840	-5.38	-0.19	0.00	5.38
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	8.420	3.6800	4.74	0.26	6.53	2.86
Total N						9.40	9.99

Gas Chromatography Data Run No. A-8								
Sample	Initial	1	2	3	4	5	6	Final
t, °C	20	346	355	346	349	352	350	17
atm, gauge	6.87	151	182	169	177	187	179	14
hr		0	0.42	0.83	1.25	1.58	2	
Comp., m%								
He	99.99	95.9	90.63	38.51	22.85	21.83	21.01	29.72
H ₂		0	0	0	0	0	0	0
N ₂		3.28	6.77	38.24	52.04	56.61	58.2	52.27
O ₂		0.42	0.19	0.39	0.28	0.16	0.24	0.87
CH ₄		0	0	0	0	0	0	0
CO		0	0	0	0	0	0	0
CO ₂		0.21	0.28	0.25	0.21	0.17	0.15	0.14
NO ₂		0	0	0	0	0	0	0
NO		0	0	0	0	0	0	0
N ₂ O		0.2	2.13	22.61	24.4	21.23	20.4	16.99
NH ₃		0	0	0	0.21	0	0	0
		100.01	100	100	99.99	100	100	99.99

Nitrogen Material Balance Run No. B-1							
Compound	FW	In	Out	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	0.0009	12.70	0.20	2.87	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0058	-0.01	0.00	0.00	0.00
N ₂	28.01	0.0000	2.8490	-2.85	-0.10	0.00	2.85
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	0.0000	0.0000	0.00	0.00	0.00	0.00
Total N						2.87	2.85

Gas Chromatography Data Run No. B-1							
Sample	Initial	1	2	3	4	5	Final
t, °C	25	349	354	348	353	353	19
atm, gauge	6.87	187	201	187	197	197	18
hr		0	0.5	1	1.5	2	
Comp., m%							
He	99.99	55.62	16.35	14.25	22.64	19.18	28.02
H ₂	0	9.95	35.21	17.92	13.14	7.53	10.26
N ₂	0	4.26	2.16	11.24	17.23	19.27	20.48
O ₂	0	0.87	0.18	0.47	0.47	0.59	0.36
CH ₄	0	0	0	0	0	0	0
CO	0	22.2	13.72	0.41	0.12	0.05	1.9
CO ₂	0	6.4	34.77	55.7	46.39	53.38	39
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
N ₂ O	0	0.58	0	0	0	0	0
NH ₃	0	0.1	0.6	0	0	0	0
Backflush	0						
		99.98	99.99	99.99	99.99	100	100.02

Nitrogen Material Balance Run No. B-2							
Compound	FW	In	Out	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	0.1330	12.57	0.20	2.87	0.03
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0058	-0.01	0.00	0.00	0.00
N ₂	28.01	0.0000	1.2890	-1.29	-0.05	0.00	1.29
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	0.0000	0.0000	0.00	0.00	0.00	0.00
Total N						2.87	1.32

Gas Chromatography Data Run No. B-2							
Sample	Initial	1	2	3	4	5	Final
t, °C	27	350	345	268	308	334	18
atm, gauge	68.7	169	167	75	104	142	18
hr		0	0.5	1.08	1.67	2.67	
Comp., m%							
He	99.99	91.4	31.13	22.02	23.31	23.25	31.36
H ₂		4.29	61.34	58.7	55.34	55.29	58.38
N ₂	0	1.61	3.19	12.7	15.05	12.22	9.81
O ₂	0	0.24	0.11	1.62	1.81	1.39	0.09
CH ₄	0	0	0	0	0	0	0
CO	0	0.06	0.2	0.05	0	0	0.04
CO ₂	0	2.29	0.56	4.56	4.46	7.86	0.28
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
N ₂ O	0	0.12	3.46	0.34	0.04	0	0.03
NH ₃	0	0	0	0	0	0	0
Backflush							
		100.01	99.99	99.99	100.01	100.01	99.99

Nitrogen Material Balance Run No. B-3							
Compound	FW	In	Out	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.9000	3.3200	9.58	0.15	2.91	0.75
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.1210	-0.12	0.00	0.00	0.08
N ₂	28.01	0.0000	0.9650	-0.97	-0.03	0.00	0.97
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	0.0000	0.0875	-0.09	0.00	0.00	0.07
Total N						2.91	1.86

Gas Chromatography Data Run No. B-3							
Sample	Initial	1	2	3	4	5	Final
t, °C	22	293	312	315	305	305	18
atm, gauge	6.87	72	94	NR	93	95	15
hr		0	0.5	0.75	1.42	2.08	
Comp., m%							
He	38.39	90.16	92.79	60.26	37.78	NR	38.39
H ₂	51.19	0	3.72	35.99	52.96	NR	51.19
N ₂	8.44	7.02	2.51	2.07	5.14	NR	8.44
O ₂	0	1.08	0.51	0.2	0.18	NR	0.78
CH ₄	0	0	0	0	0	NR	0
CO	0.12	0	0.04	0.05	0.15	NR	0.12
CO ₂	0.41	0	0.14	0.11	0.91	NR	0.41
NO ₂	0	0	0	0	0	NR	0
NO	0	0	0	0	0	NR	0
N ₂ O	0.67	1.64	0.29	1.34	2.88	NR	0.67
NH ₃	0	0	0	0	0	NR	0
Backflush							
		99.9	100	100.02	100	0	100

NR = Not recorded.

Nitrogen Material Balance Run No. C-1							
Compound	FW	In	Out	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	10.3000	2.40	0.04	2.87	2.33
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0021	-0.01	0.00	0.00	0.00
N ₂	28.01	0.0000	0.1780	-0.18	-0.01	0.00	0.18
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	3.6960	5.7200	-2.02	-0.11	2.87	5.72
CO (NH ₂) ₂	60.06	8.8600				4.13	
Total N						9.87	8.23

Gas Chromatography Data Run No. C-1						
Sample	Initial	1	2	3	4	Final
t, °C	18	342	343	343	346	17
atm, gauge	6.53	131	133	133	163	6
hr		0	0.5	1	2	
Comp., m%						
He	99.99	91.18	95.41	96.02	94.62	94.91
H ₂		0	0	0	0	0
N ₂		3.53	1.92	2.47	3.46	4.34
O ₂		0.59	0.28	0.12	0.23	0.47
CH ₄		0	0	0	0	0
CO		0	0	0	0	0
CO ₂		4.7	2.38	1.36	1.65	0.24
NO ₂		0	0	0	0	0
NO		0	0	0	0	0
N ₂ O		0	0	0.03	0.04	0.03
NH ₃		0	0	0	0	0
Backflush						
		100	99.99	100	100	99.99

Nitrogen Material Balance Run No. D-1							
Compound	FW	In	Out	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	6.1100	6.59	0.11	2.87	1.38
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂	28.01	0.0000	0.1450	-0.15	-0.01	0.00	0.15
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	0.0000	0.0000	0.00	0.00	0.00	0.00
Total N						2.87	1.52

Gas Chromatography Data Run No. D-1								
Sample	Initial	1	2	3	4	5	6	Final
t, °C	19	332	359	349	348	350	349	15
atm, gauge	6.73	122	178	163	161	163	161	6
hr		0	0.42	0.83	1.25	1.58	2.08	
Comp., m%								
He		97.92	61.86	30.26	24.41	24.1	24.75	54.19
H ₂		0	16.86	32.56	33.72	30.43	30.43	25.98
N ₂		1.61	1.65	2.22	2.7	2.65	2.9	3.83
O ₂		0.06	0.04	0	0	0		0.1
CH ₄		0	0.22	0.51	0.79	0.9	1.05	1.17
C ₂ H ₂		0	0.08	0.15	0.2	0.22	0.24	0.09
C ₂ H ₆		0	0	0.03	0.05	0.07	0.08	0.25
CO		0.15	0.09	0	0.09	0.07	40.1	0.16
CO ₂		0	18.75	34	37.99	41.25		13.89
NO ₂		0	0.45	0	0	0		0
NO		0	0	0	0	0		0
N ₂ O		0.14	0	0	0	0		0.09
NH ₃		0	0	0	0	0		0
Backflush		0.12	0	0.17	0.05	0.32	0.37	0.34
		100	100	99.99	100	100.01	100	100.09

Nitrogen Material Balance Run No. E-1							
Compound	FW	In	Out	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7600	0.0000	12.76	0.21	2.88	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂	28.01	0.0000	0.1670	-0.17	-0.01	0.00	0.17
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	0.0000	0.0000	0.00	0.00	0.00	0.00
Total N						2.88	0.17

Gas Chromatography Data Run No. E-1							
Sample	Initial	1	2	3	4	5	Final
t, °C	19	348	359	353	352	354	15
atm, gauge	13.61	166	187	174	174	176	13
hr		0	0.42	0.83	1.5	2	
Comp., m%							
He		0	0	0	0	0	0
H ₂		0	0	0	0.22	0.3	0.21
N ₂		1.62	0.8	1.9	2.42	2.2	1.67
O ₂		0.33	0.18	0.44	0.54	0.45	0.23
CH ₄	99.17	98.01	98.9	97.53	96.56	96.63	97.82
C ₂ H ₂		0	0	0	0	0	0
C ₂ H ₆		0	0	0	0	0	0
CO		0	0	0	0	0	0
CO ₂		0	0	0.14	0	0	0
NO ₂		0	0	0	0	0	0
NO		0	0	0	0	0	0
N ₂ O		0.04	0.12	0	0.26	0.42	0.08
NH ₃		0	0	0	0	0	0
		100	100	100.01	100	100	100.01

Nitrogen Material Balance Run No. F-1							
Compound	FW	In	Out	Net, g	Net, M	N In, g	N Out, g
NO ₃	62.00	12.7000	0.0000	12.70	0.20	2.87	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO ₂	46.01	0.0000	0.0000	0.00	0.00	0.00	0.00
NO	30.01	0.0000	0.0000	0.00	0.00	0.00	0.00
N ₂ O	44.01	0.0000	0.0080	-0.01	0.00	0.00	0.00
N ₂	28.01	0.0000	0.5040	-0.50	-0.02	0.00	0.50
NH ₃ (g)	17.03	0.0000	0.0000	0.00	0.00	0.00	0.00
NH ₄ ⁺	18.04	0.0000	0.0000	0.00	0.00	0.00	0.00
Total N						2.87	0.51

Gas Chromatography Data Run No. F-1							
Sample	Initial	1	2	3	4	5	Final
t, °C	19	344	357	359	358	366	23
atm, gauge	29.59	185	213	222	219	216	32
hr		0	0.42	0.92	1.42	2	
Comp., m%							
He	0	0	0	0	0	0	0
H ₂	98.45	99.25	99.18	98.46	98.6	99.14	97.46
N ₂	0.73	0.66	0.75	1.38	1.26	0.76	2.24
O ₂	0.07			0.06	0.05	0	0.11
CH ₄	0.72	0.09	0.06	0.08	0.07	0.08	0.17
C ₂ H ₂	0	0	0	0	0	0	0
C ₂ H ₆	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0
CO ₂	0	0	0	0	0	0	0
NO ₂	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0
N ₂ O	0.03	0	0	0.02	0.02	0.02	0.02
NH ₃	0	0	0	0	0	0	0
Backflush	0						
	100	100	99.99	100	100	100	100

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