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THE INTERACTIONS OF HYDRAZINE, FERROUS SULFAMATE, SODIUM NITRITE, AND NITRIC ACID IN NUCLEAR FUEL PROCESSING SOLUTIONS

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Abstract

Hydrazine and ferrous sulfamate are used as reductants in a variety of nuclear fuel processing solutions. An oxidant, normally sodium nitrite, must frequently be added to these nitric acid solutions before additional processing can proceed. The interactions of these four chemicals have been studied under a wide variety of conditions using a 2^p factorial experimental design to determine relative reaction rates for desired reactions and side reactions. Evidence for a hydrazine-stabilized, sulfamic acid — nitrous acid intermediate was obtained; this intermediate can hydrolyze to ammonia or decompose to nitrogen. The oxidation of Fe^{2+} by NO_2^- was shown to proceed at about the same rate as the scavenging of NO_2^- by sulfamic acid. Various side reactions are discussed.

Introduction

Solutions of ferrous sulfamate in nitric acid and of ferrous sulfamate and hydrazine in nitric acid are commonly used in the chemical reprocessing of nuclear fuels to control the valence states of various actinide elements [1, 2]. The function of both sulfamate and hydrazine is to scavenge the radiolytically produced oxidizing agents such as H_2O_2 and NO_2^-. In some cases it is necessary to oxidize the Fe^{2+} reductant, usually with $NaNO_2$ or heat, before the next processing step can occur. At the Savannah River Plant (SRP), waste streams from the processes which use either $Fe(NH_2SO_3)_2$ or $Fe(NH_2SO_3)_2$ - NH_2NH_2 solutions are evaporated to strip most of the nitric acid before the waste is neutralized and transferred to mild-steel waste storage tanks.

A number of studies have been made on the reactions of sulfamate ion with nitrite ion [1, 3-6], on the hydrolysis of sulfamate [7-11], on the oxidation of hydrazine by nitrite [1, 5], on the radiolytic instability of ferrous sulfamate [12], and on the reactions of sulfamic acid with nitric acid [13]. However, these studies do not adequately define the interactions of these reagents under process conditions. Additional experiments were performed employing 2^p factorial experimental designs so that the maximum number of process conditions could be studied in a reasonable amount of time.

Discussion

EXPERIMENTAL PROCEDURE

All chemicals used for the experiments were reagent grade with the exception of ferrous sulfamate. All were used without further purification. Technical-grade ferrous sulfamate obtained from Turco Products was used for some experiments; for other experiments, the ferrous sulfamate was prepared from reagent-grade iron wire and reagent-grade sulfamic acid. Solutions were prepared with distilled water. Ammonia concentrations were determined with a specific ion electrode using the method of standard addition. The redox potential (E_h) relative to the normal hydrogen electrode was measured with a platinum combination redox specific ion electrode. Iron(II) and total Fe concentrations were determined by the o-phenanthroline method; sulfamate concentrations were determined by removing Fe on an ion exchange column and titrating the sulfamate with standard $NaNO_2$.

EXPERIMENT DESIGN

Two-level factorial experimental designs [14] permit estimation of the effects of several factors simultaneously. This is accomplished by making experimental runs at all combinations of the p-factors, with ℓ levels per factor. These two-level factorial experiments are easy to design and analyze, are readily adaptable to both continuous and discrete factors, and provide adequate prediction models for factor relationships that have no strong curvature (maximum or minimum) in the experimental region. For continuous variables the higher value is coded "+" and the lower value coded "-." The coding for a 2^4 factorial design is given in table 1.

Use of these designs permits estimation of factor effects more precisely than one-at-a-time testing because of the hidden replication included. Systematic error is kept at a minimum by replication of design points and randomization of the trials before running.

These designs do not give an estimate of curvature of responses on the experimental region. However, an estimate of the overall curvature can be obtained by running points at a middle value of all factors. The severity of the curvature is estimated by the difference between the average of the design points and the average of the center points.

If a computed factor effect is larger (in absolute value) than the "minimum significant factor effect," the experimenter can safely conclude that the true effect is nonzero. Similarly, if the curvature effect is larger than the "minimum significant curvature effect," the experimenter can safely conclude that nonzero curvature is associated with at least one variable.

The computed factor effects represent the difference between response at the high and low levels of the factor. If the factor effect is divided by the difference of the high and low levels of the factors, the results will be the change in the response for a unit change in the factor.

The model underlying the two-level factorial is of the form

$$
\begin{aligned}
y = {} & b_o + b_1x_1 + b_2x_2 + \ldots\ b_px_p + \\
& b_{12}x_1x_2 + b_{13}x_1x_3 + \ldots + b_{p-1,p}x_{p-1}x_p + \\
& \text{higher order interactions}
\end{aligned}
$$

where

y = predicted response for Fe^{2+}, $NH_2SO_3^-$, or NH_3

$x_j = \dfrac{\text{factor level} - (\text{Hi} + \text{Lo})/2}{(\text{Hi} - \text{Lo})/2}$, j^{th} factor

b_j = 1/2 (factor effect for x_j)

$b_{jj'}$ = 1/2 (interaction effect for $x_j, x_{j'}$)

Concentrations of the four components [HNO_3, $NaNO_2$, $Fe(NH_2SO_3)_2$, and NH_2NH_2] were varied over the ranges found in the 12 to 15 processes in which they are commonly used. Most of these processes use only $Fe(NH_2SO_3)_2$ as the reductant instead of both $Fe(NH_2SO_3)_2$ and NH_2NH_2. Also, those processes using both $Fe(NH_2SO_3)_2$ and NH_2NH_2 contain gross amounts of Al^{3+}, whereas most of the processes using only $Fe(NH_2SO_3)_2$ usually contain only traces of Al^{3+}. Therefore, two basic experimental designs were used: one containing $Fe(NH_2SO_3)_2$ and HNO_3 and the other containing $Fe(NH_2SO_3)_2$, Al^{3+}, NH_2NH_2, and HNO_3.

For the $Fe(NH_2SO_3)_2$ - HNO_3 test series, a 2^5 factorial design was set up which varied the concentrations of $Fe(NH_2SO_3)_2$, $NaNO_2$, and HNO_3. A reflux step was the fifth variable, and the time between the addition of all chemicals and the beginning of the refluxing was the fourth variable. For the series containing $Fe(NH_2SO_3)_2$ and NH_2NH_2, a 2^4 factorial experimental design was set up which varied the concentrations of NH_2NH_2, $Fe(NH_2SO_3)_2$, and $NaNO_2$ with a reflux step being the fourth variable; Al^{3+} and HNO_3 were kept constant. The extreme values for both series are given in table 2.

RESULTS

Analytical data for the experiments with $Fe(NH_2SO_3)_2$ at ambient temperature (ambient temperature portion of the 2^5 design) are given in table 3. A summary of the statistical data is given in table 4. The model indeed shows that the major source of Fe^{2+}, $NH_2SO_3^-$, and NH_4^+ is $Fe(NH_2SO_3)_2$. The major reactions are:

$$4H^+ + 4Fe^{2+} + 2HNO_2 \rightarrow 4Fe^{3+} + N_2O + 3H_2O \text{ [15]} \qquad (1)$$

$$NH_2SO_3H + HNO_2 \rightarrow H_2SO_4 + N_2 + H_2O \text{ [13]} \qquad (2)$$

The most important remaining reactions are:

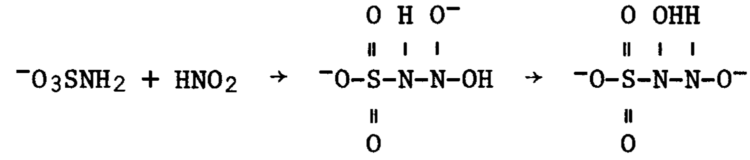
$$2NO_2^- + 2H^+ \rightarrow H_2O + NO + NO_2 \text{ [15]} \qquad (3)$$

$$4H^+ + 6Fe^{2+} + 2HNO_3 \rightarrow 6Fe^{3+} + 2NO + 4H_2O \text{ [14]} \qquad (4)$$

$$NH_2SO_3H + H_2O \rightarrow NH_4^+ + HSO_4^- \text{ [13]} \qquad (5)$$

Therefore, this predictive model works. Data for the full-scale 2^5 experiments with $Fe(NH_2SO_3)_2$ solutions are given in tables 5 and 6, and the data for NH_2NH_2 - $Fe(NH_2SO_3)_2$ solutions are given in tables 7 and 8.

In agreement with Biddle and Miles [5], and with Groh and Russell [6], both sets of experiments show that sulfamate reacts with NO_2^- to form an intermediate. Biddle and Miles obtained spectral evidence for an intermediate, with an absorption band centered at 415 nm which was present in the solution 30 msec after mixing NO_2^- and $NH_2SO_3^-$ and decreased steadily thereafter. Groh and Russell isolated an intermediate from the reaction at very high concentrations between metal sulfamates and potassium nitrite. This set of experiments indicates that the average lifetime of the intermediate is much greater than 5 minutes. If the average lifetime were less than 5 minutes, our experiments would not have detected the intermediate. It is therefore suggested that the intermediate of Biddle and Miles forms (Intermediate A) and then rearranges to form the intermediate of Groh and Russell (Intermediate B).



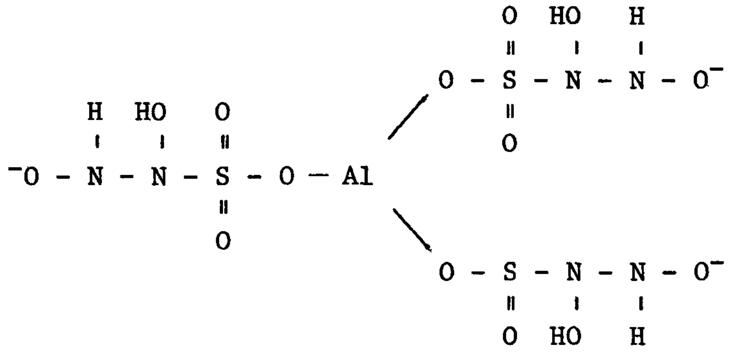
$$^{-}O_3SNH_2 + HNO_2 \rightarrow {}^{-}O\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}\overset{\overset{H}{|}}{N}\text{-}\overset{\overset{O^{-}}{|}}{N}\text{-}OH \rightarrow {}^{-}O\text{-}\underset{\underset{O}{\|}}{\overset{\overset{O}{\|}}{S}}\text{-}\overset{\overset{OH}{|}}{N}\text{-}\overset{\overset{H}{|}}{N}\text{-}O^{-} \qquad (6)$$

Intermediate A Intermediate B

Our experiments show that Intermediate B can either decompose to $N_2(g)$ and SO_4^{2-} or can be hydrolyzed to NH_4^+ and SO_4^{2-}.

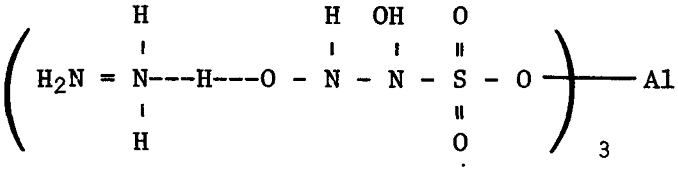
The experiments with NH_2NH_2 as a variable and Al^{3+} at a constant 0.09M showed the same indications about $NH_2SO_3^-$ as above, and show that NH_2NH_2 is oxidized by NO_2^-. In solutions containing both NH_2NH_2 and $NH_2SO_3^-$, the NO_2^- - $NH_2SO_3^-$ intermediate appears to be stabilized by NH_2NH_2 toward hydrolysis to NH_4^+ and SO_4^{2-}.

The sulfamate-nitrite intermediate is formed first. This intermediate is further stabilized as an aluminum complex [6].

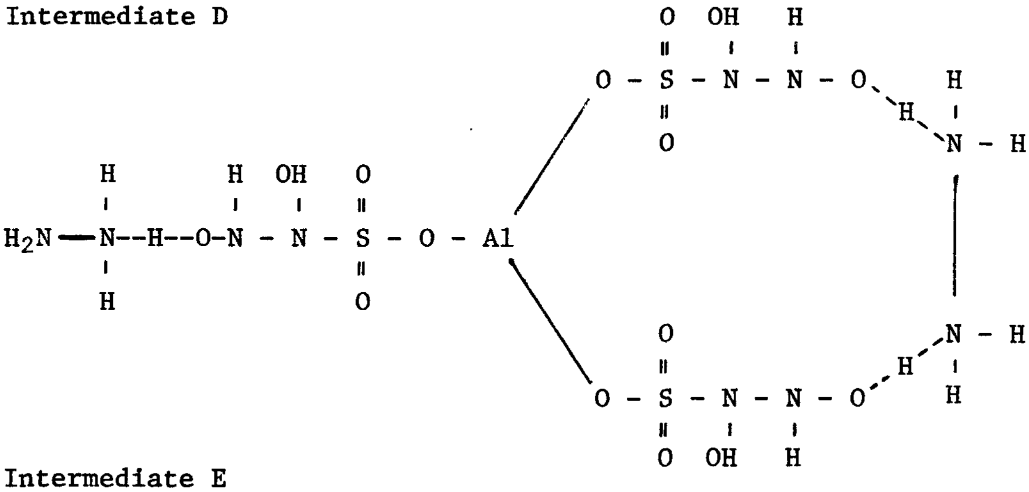


Intermediate C

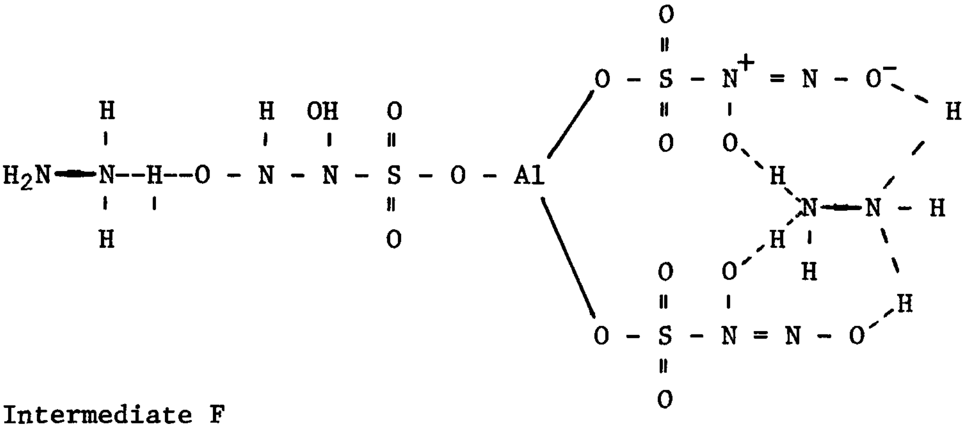
This complex, which has been isolated as a potassium salt [6], yields ample opportunity for hydrogen bonding. It is this hydrogen bonding ability that probably accounts for the further increase in the stability of the NO_2^- - $NH_2SO_3^-$ intermediate in the presence of Al^{3+} and hydrazine. The following are proposed as possible structures for the NO_2^-, $H_2NSO_3^-$, N_2H_4, Al^{3+} complex.



Intermediate D



Intermediate E



Intermediate F

With this complex, it is also possible to decompose either to $N_2(g)$, SO_4^{2-}, and Al^{3+} or to hydrolyze to NH_4^+, SO_4^{2-}, and Al^{3+}.

The final set of experiments were designed to separate the Fe^{2+} and $NH_2SO_3^-$ reactions with NO_2^- and HNO_3. This was done by the more traditional method of varying only one component at a time. These experiments show that the formation of the NO_2^- - $NH_2SO_3^-$ intermediate is faster than the oxidation of Fe^{2+} by $NO2^-$ (figure 1). They further show that a small excess of $NO2^-$ beyond the complexation of sulfamate is not sufficient to catalyze the oxidation of Fe^{2+} by HNO_3. Until about 80% of the $NH_2SO_3^-$ is consumed, the reaction appears to be:

$$14NH_2SO_3H + 4\ Fe^{2+} + 16\ HNO_2 + 4H^+ \rightarrow$$
$$4Fe^{3+} + N_2O(g) + 14N_2(g) + 14H_2SO_4 + 17H_2O \qquad (7)$$

Beyond about 80% consumption of the $NH_2SO_3^-$, the reaction appears to be:

$$2NH_2SO_3H + 4\ Fe^{2+} + 4HNO_2 + 4H^+ \rightarrow$$
$$4Fe^{3+} + N_2O(g) + 2\ H_2SO_4 + 2N_2(g) + 5H_2O \qquad (8)$$

At 1.0M HNO_3, the reaction

$$2NO_2^- + 2H^+ \rightarrow H_2O + NO + NO_2 \text{ [15]} \qquad (3)$$

is of little importance. However, as the HNO_3 concentration increases, it consumes a larger portion of the NO_2^- added.

The interactions of Fe^{2+}, $NH_2SO_3^-$, $NH_2NH_3^+$, HNO_2, and HNO_3 can be summarized as follows.

1) At or near room temperature and with $HNO_3 \leq 1.0M$, the major reactions occurring are:

$$HNO_2 + NH_2SO_3H \xrightarrow{\text{fast}} \text{Intermediate A} \xrightarrow{\text{fast}} \qquad (9)$$
$$\text{Intermediate B} \xrightarrow{\text{slow}} N_2(g) + H_2SO_4$$

$$4H^+ + 4\ Fe^{2+} + 2HNO_2 \xrightarrow{\text{fast}} N_2O + 4Fe^{3+} + 3H_2O \text{ [15]} \qquad (10)$$

If Al^{3+} and hydrazine are also in these solutions, the following reactions occur:

$$\text{Intermediate B} + Al^{3+} \xrightarrow{\text{fast}} \text{Intermediate C} \xrightarrow[\text{fast}]{NH_2NH_2}, \text{Intermediate D, E, or F} \qquad (11)$$

$$\text{Intermediate D, E, F} \xrightarrow[NO_2^-]{\text{slow}} N_2 + H_2SO_4 + Al^{3+} \qquad (12)$$

$HNO_2 + N_2H_4 \rightarrow HN_3 + 2H_2O$ (13)

$HNO_2 + HN_3 \rightarrow N_2O + N_2 + H_2O$ (14)

$2Fe^{2+} + HNO_3 + 2H^+ \rightarrow HNO_2 + 2\ Fe^{3+} + H_2O$ (15)

$3N_2H_4 \rightarrow 2NH_3 + 2N_2 + 3H_2$ (16)

$2N_2H_5^+ + 2Fe^{3+} \rightarrow 2Fe^{2+} + N_2 + 2NH_4^+ + 2H^+$ (17)

$2NO_2^- + 2H^+ \rightarrow H_2O + NO + NO_2$ (3)

$NH_2SO_3H + H_2O \rightarrow NH_4^+ + HSO_4^-$ (5)

Intermediate B + $H_2O \rightarrow NH_4^+ + HSO_4^-$ (18)

2) At or near room temperature and with $HNO_3 > 3.0M$, the destruction of NO_2^- by HNO_3, reaction (3), becomes as rapid or more rapid than the oxidation of Fe^{2+}, NH_2SO_3H, and NH_2NH_2.

3) If solutions at or near 1.0M HNO_3 are heated to about 50°C for a short time (up to one-half hour) without adding $NaNO_2$, Fe^{2+} is oxidized to Fe^{3+}. The first reaction appears to be reaction (15) with the HNO_2 consumed by reaction (10) as very little, if any, NH_2SO_3H and NH_2NH_2 are consumed.

4) If solutions containing 1M HNO_3 and $Fe(NH_2SO_3)_2$ are heated to boiling, the Fe^{2+} will be consumed by reactions (15) and (10); about 95% of the NH_2SO_3H will hydrolyze by reaction (5) and the other 5% of the NH_2SO_3H will be consumed by reaction (9).

5) If solutions containing 8M HNO_3 and $Fe(NH_2SO_3)_2$ are heated to boiling, the Fe^{2+} will be consumed by reactions (15) and (10). About 40 to 50% of the $NH_2SO_3^-$ will hydrolyze by reaction (5) and the remainder will be oxidized by reaction (9).

6) If solutions containing hydrazine and 1M to 8M HNO_3 are heated to boiling, about 40 to 50% of the NH_2NH_2 will undergo self-oxidation -- reduction by reaction (16). The remainder will be oxidized by the reactions (13) and (14) at low acid or at high acid by the reaction:

$$4N_2H_4 + O_2 \rightarrow 2N_2 + 4NH_3 + 2H_2O. \quad (19)$$

7) If $NaNO_2$ is added to solutions containing about 8M HNO_3 and Fe^{2+}, NH_2SO_3H, and NH_2NH_2, and the solution then brought to a boil, the nitrite is consumed by reactions (9), (10), (3), (13), and (14). The Intermediate B formed by reaction (9) reacts with Al^{3+} according to reaction (11) to form Intermediate C which then reacts with NH_2NH_2 to form either Intermediate D, E, or F. If heating of the Al-sulfamate-nitrite complex begins too soon, the complex hydrolyzes by reaction (20), following, instead of decomposing by reaction (12).

$$\text{Intermediate D, E, F} + H_2O \xrightarrow{\text{heat}} NH_4^+ + HSO_4^- + Al^{3+} + NO_x(?) \quad (20)$$

Conclusions

Minor side reactions of oxidants and reductants used in valence adjustments steps of plant-scale processes can add significantly to the waste volume which must be stored. A better understanding of how to control and minimize these side reactions has led to more effective use of oxidants in nuclear fuel processing solutions at Savannah River.

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TABLE 1
TWO-LEVEL FACTORIAL EXPERIMENTAL DESIGN

	Factors			
Trial	X1	X2	X3	X4
1	-	-	-	-
2	+	-	-	-
3	-	+	-	-
4	+	+	-	-
5	-	-	+	-
6	+	-	+	-
7	-	+	+	-
8	+	+	+	-
9	-	-	-	+
10	+	-	-	+
11	-	+	-	+
12	+	+	-	+
13	-	-	+	+
14	+	-	+	+
15	-	+	+	+
16	+	+	+	+

TABLE 2
VARIABLE EXTREMES FOR 2^p EXPERIMENTAL DESIGNS

	Experiments			
	FS[a]		FS - NH_2NH_2	
Variable	High	Low	High	Low
HNO_3, M	5.0	1.0	7.75	7.75
FS, M	0.0	0.1	0.1	0.0
NH_2NH_2, M	0.0	0.0	0.1	0.0
$NaNO_2$, M	0.4	0.0	0.4	0.01
Reflux	Yes	No	Yes	No
Time	48 hr	5 min	35 min	25 min

[a] FS = Ferrous sulfamate.

TABLE 3
RAW ANALYTICAL DATA FOR THE SYSTEM FS[a] - $NaNO_2$ - HNO_3 AT AMBIENT TEMPERATURE

2^3 Factorial Design Points	Fe^{2+}, M		$NH_2SO_3^-$, M		NH_3, ppm	
	Mean[b]	Variance	Mean	Variance	Mean	Variance
1	0.0000	0.0000	0.0000	0.0000	1.18	0.499
2	0.0000	0.0000	0.0000	0.0000	1.28	0.608
3	0.0872	3.572×10^{-6}	0.1675	2.25×10^{-4}	38.75	8.302
4	0.0228	1.6240×10^{-5}	0.1425	2.25×10^{-4}	41.00	11.747
5	0.00000	0.0000	0.0000	0.0000	1.08	0.359
6	0.0000	0.0000	0.0000	0.0000	0.90	0.735
7	0.0000	0.0000	0.0000	0.0000	39.25	17.056
8	0.0000	0.0000	0.0000	0.0000	40.25	20.614
9	0.0000	0.0000	0.0000	0.0000	20.75	5.679

[a] FS = Ferrous sulfamate.

[b] Mean of four independent experiments; each solution was analyzed in triplicate.

TABLE 4
RESULTS OF A STATISTICAL DATA ANALYSIS FOR A 2^3 FACTORIAL EXPERIMENTAL DESIGN FOR THE SYSTEM Fe^{2+} - $NH_2SO_3^-$ - NO_2^- - HNO_3 AT AMBIENT TEMPERATURE

Factor	Fe^{2+}, M	$NH_2SO_3^-$, M	NH_3
S_{pooled}[a]	1.150×10^{-3}	5.477×10^{-3}	5.95
[MIN] pooled[b]	0.866×10^{-3}	4.125×10^{-3}	4.31
HNO_3	-1.61×10^{-3}	-6.25×10^{-3}	+0.79
FS[c]	$+32.5 \times 10^{-3}$	$+82.5 \times 10^{-3}$	+38.71
FS - HNO_3	-1.61×10^{-3}	-6.25×10^{-3}	+0.83
NO_2^-	-22.5×10^{-3}	-72.5×10^{-3}	-0.18
HNO_3 - NO_2^-	$+16.1 \times 10^{-3}$	$+6.25 \times 10^{-3}$	-0.38
FS - NO_2^-	-22.5×10^{-3}	-72.5×10^{-3}	+0.44
HNO_3 - FS - NO_2^-	$+16.1 \times 10^{-3}$	$+6.25 \times 10^{-3}$	-0.24
[MINC][d]	1.369×10^{-3}	6.522×10^{-3}	6.82
Curvature[e]	$+6.25 \times 10^{-3}$	31.25×10^{-3}	-0.29

[a] S_{pooled} = standard deviation; S^2_{pooled} = pooled variance.

[b] [MIN] = minimum significant factor effect

[c] FS = ferrous sulfamate, $Fe(NH_2SO_3)_2$.

[d] [MINC] = minimum significant curvature.

[e] Curvature = maxima or minima in the data.

TABLE 5
RAW ANALYTICAL DATA FOR THE SYSTEM FS - $NaNO_2$ - HNO_3

2^5 Factorial Design Points	Fe^{2+}, M		$NH_2SO_3^-$, M		NH_3, ppm	
	Mean	Variance	Mean	Variance	Mean	Variance
1	0.00	0.000	0.000	0.000	0.70	0.020
2	.00	0.000	.000	.000	0.75	0.005
3	.0865	5.00×10^{-7}	.180	0.000	22.00	2.000
4	.0215	4.05×10^{-5}	.155	5×10^{-5}	21.00	18.000
5	0.00	0.000	0.000	0.000	0.70	0.080
6	↓	↓	↓	↓	0.85	0.005
7	↓	↓	↓	↓	27.00	8.000
8	↓	↓	↓	↓	23.50	4.500
9	↓	↓	↓	↓	0.70	0.020
10	0.00	0.000	0.000	0.000	0.85	0.005
11	.0880	8.00×10^{-6}	.155	5×10^{-5}	23.50	0.500
12	.0240	2.00×10^{-6}	.130	8.000	23.50	4.500
13	0.000	0.000	0.000	0.000	0.75	0.005
14	↓	↓	↓	↓	0.65	0.005
15	↓	↓	↓	↓	21.50	4.500
16	↓	↓	↓	↓	19.50	0.500
17	↓	↓	↓	↓	0.75	0.005
18	↓	↓	↓	↓	0.80	0.080
19	↓	↓	↓	↓	2891.50	88620.0
20	↓	↓	↓	↓	3560.00	60552.0
21	↓	↓	↓	↓	0.90	0.020
22	↓	↓	↓	↓	0.65	0.045
23	↓	↓	↓	↓	43.50	0.500
24	↓	↓	↓	↓	30.50	4.500
25	↓	↓	↓	↓	0.80	0.000
26	↓	↓	↓	↓	0.90	0.020
27	↓	↓	↓	↓	2529.00	6050.0
28	↓	↓	↓	↓	2340.00	1458.0
29	↓	↓	↓	↓	0.85	0.005
30	↓	↓	↓	↓	0.55	0.005
31	↓	↓	↓	↓	39.00	2.000
32	↓	↓	↓	↓	22.50	4.500
33	0.000	0.000	0.000	0.000	37.80	24.667

TABLE 6
RESULTS OF A STATISTICAL DATA ANALYSIS FOR A 2^5 FACTORIAL EXPERIMENTAL DESIGN FOR THE SYSTEM Fe^{2+} - $NH_2OH_3^-$ - NO_2^- - HNO_3

Factor	Fe^{2+}, M	$NH_2SO_3^-$, M	NH_3, ppm
S^2_{pooled} [a]	1.785 × 10^{-3}	2.294 × 10^{-3}	66.923
[MIN][b]	1.890 × 10^{-3}	2.888 × 10^{-3}	55.462
HNO ≡ X1	-8.062 × 10^{-3}	-3.125 × 10^{-3}	+27.709
FS[c] ≡ X2	+13.750 × 10^{-3}	+41.250 × 10^{-3}	+726.584
X1X2	-8.062 × 10^{-3}	-3.125 × 10^{-3}	+27.728
$NaNO_2$ ≡ X3	-13.750 × 10^{-3}	-36.250 × 10^{-3}	-698.990
X1X3	+8.062 × 10^{-3}	+3.125 × 10^{-3}	-32.147
X2X3	-13.750 × 10^{-3}	-36.250 × 10^{-3}	-699.059
X1X2X3	+8.062 × 10^{-3}	+3.125 × 10^{-3}	-32.041
TIME ≡ X4	+0.250 × 10^{-3}	-3.125 × 10^{-3}	-100.034
X1X4	+0.062 × 10^{-3}	0.000	-50.622
X2X4	+0.250 × 10^{-3}	-3.125 × 10^{-3}	-100.028
X1X2X4	+0.062 × 10^{-3}	0.000	-53.647
X3X4	+0.250 × 10^{-3}	+3.125 × 10^{-3}	+97.247
X1X3X4	-0.062 × 10^{-3}	+3.125 × 10^{-3}	+53.378
X2X3X4	-0.250 × 10^{-3}	+3.125 × 10^{-3}	+97.316
X1X2X3X4	-0.062 × 10^{-3}	0.000	+53.434
X5 ≡ Reflux	-13.750 × 10^{-3}	-41.250 × 10^{-3}	+704.672
X1X5	+8.062 × 10^{-3}	+3.125 × 10^{-3}	+28.491
X2X5	-13.750 × 10^{-3}	-41.250 × 10^{-3}	+704.641
X1X2X5	+8.062 × 10^{-3}	+3.125 × 10^{-3}	+28.572
X3X5	+13.750 × 10^{-3}	+36.250 × 10^{-3}	-699.172
X1X3X5	-8.062 × 10^{-3}	-3.125 × 10^{-3}	-31.566
X2X3X5	+13.750 × 10^{-3}	+36.250 × 10^{-3}	-699.141
X1X2X3X5	-8.062 × 10^{-3}	+3.125 × 10^{-3}	-31.497
X4X5	+0.250 × 10^{-3}	+3.125 × 10^{-3}	-99.341
X1X4X5	-0.062 × 10^{-3}	0.000	-53.957
X2X4X5	+0.250 × 10^{-3}	+3.125 × 10^{-3}	-99.347
X1X2X4X5	-0.062 × 10^{-3}	0.000	-53.978
X3X4X5	-0.250 × 10^{-3}	-3.125 × 10^{-3}	+98.996
X1X3X4X5	+0.062 × 10^{-3}	0.000	+53.359
X2X3X4X5	-0.250 × 10^{-3}	-3.125 × 10^{-3}	+98.972
X1X2X3X4X5	+0.062 × 10^{-3}	0.000	+53.328

[a] S_{pooled} = standard deviation; S^2_{pooled} = pooled variance estimate.
[b] [MIN] = minimum significant factor effect.
[c] FS = ferrous sulfamate; $Fe(NH_2SO_3)_2$.

TABLE 7
RAW ANALYTICAL DATA FOR THE SYSTEM
Al^{3+} - NH_2NH_2 - FS - $NaNO_2$ - HNO_3

2^4 Factorial Design Points	NH_3, ppm Mean	Variance
1	13.00	8.00
2	505.00	50.00
3	97.50	312.50
4	625.00	1250.00
5	13.00	0.00
6	415.00	0.00
7	115.00	1250.00
8	600.00	800.00
9	15.0	8.00
10	4692.5	17112.50
11	2187.5	15312.50
12	12530.0	64800.00
13	12.0	0.00
14	413.0	722.00
15	1090.0	200.00
16	6255.0	33800.00
17	3077.5	3612.50

TABLE 8
RESULTS OF A STATISTICAL DATA ANALYSIS FOR A 2^4 FACTORIAL EXPERIMENTAL DESIGN FOR THE SYSTEM
Al^{3+} - NH_2NH_2 - FS - $NaNO_2$ - HNO_3

Factor	Factor Effect Value for NH_3
S_{pooled}	90.50
[MIN]	67.51
X1 ≡ FS	+2811.56
X2 ≡ NH_2NH_2	+2177.69
X1X2	+1318.44
X3 ≡ $NaNO_2$	-1469.06
X1X3	-1198.31
X2X3	-375.94
X1X2X3	-106.69
X4 ≡ Reflux	+3101.44
X1X4	+2334.94
X2X4	+2054.81
X1X2X4	+1288.81
X3X4	-1444.69
X1X3X4	-1165.19
X2X3X4	-396.56
X1X2X3X4	-118.56
[MINC]	143.218
Curvature	-1763.844

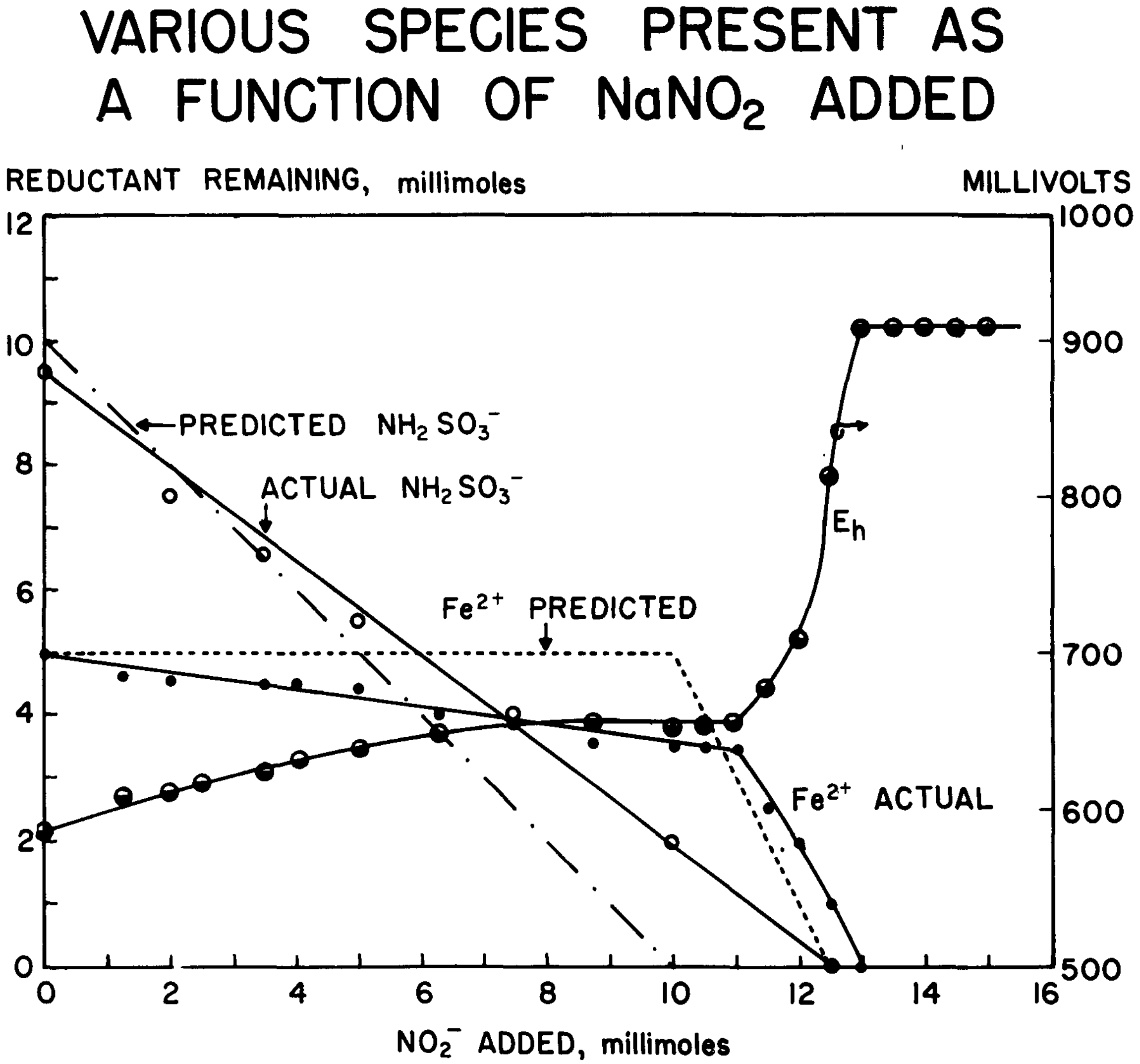

FIGURE 1. VARIOUS SPECIES PRESENT AS A FUNCTION OF NaNO$_2$ ADDED.