Hanford Ferrocyanide Waste Chemistry and Reactivity Preliminary Catalyst and Initiator Screening Studies

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HANFORD FERROCYANIDE WASTE CHEMISTRY AND
REACTIVITY PRELIMINARY CATALYST AND
INITIATOR SCREENING STUDIES

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SUMMARY

During the 1950s, ferrocyanide was used to scavenge radiocesium from
aqueous nitrate-containing Hanford wastes. During the production of defense
materials and while these wastes were stored in high-level waste tanks at the
Hanford Site, some of these wastes were likely mixed with other waste con-
stituents and materials. Recently, Pacific Northwest Laboratory (PNL) was
commissioned by Westinghouse Hanford Company (WHC) to investigate the chemical
reactivity of these ferrocyanide-bearing wastes. Because of known or poten-
tial thermal reactivity hazards associated with ferrocyanide- and nitrate-
bearing wastes, and because of the potential for different materials to act as
catalysts or initiators of the reactions about which there is concern, we at
PNL have begun investigating the effects of the other potential waste constit-
uents. This report presents the results of a preliminary screening study to
identify classes of materials that might be in the Hanford high-level waste
tanks and that could accelerate or reduce the starting temperature of the
reaction(s) of concern. We plan to use the results of this study to determine
which materials or class of materials merit additional research.

Our preliminary study employed a statistically based experimental design
and PNL's time-to-explosion (TTX) test to investigate the effects of
tetrasodium ethylenediaminetetraacetate (EDTA) and the hydroxides of iron,
chromium (III), and nickel on the reaction between sodium nickel ferrocyanide
and equimolar sodium nitrate and nitrite. These selected potential catalysts
and initiators were tested individually and in their possible combinations
(also termed treatments), each at 0.03 mole per mole of ferrocyanide in a
mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and
nitrite. The amount of nitrate and nitrite in the tested mixtures was 1.1
times the stoichiometric amount needed for the most energetic reactions.

The test results suggest that many of the treatments lowered the TTX at
each of the test temperatures; however, only a few treatments lowered the TTX
sufficiently to cause a statistically significant effect at the 95% confidence
level. At 380°C, these treatments were EDTA alone; the combination of EDTA,

iron hydroxide, and chromium hydroxide; and the combination of all the materials. At 350°C, the combination of EDTA and iron hydroxide caused a statistically significant reduction. Note that EDTA was present in each of these mixtures. At 320° and 296°C, no treatment significantly reduced the TTX, nor did any of the treatments reduce the minimum observed explosion temperature of 293 ± 3°C. We hypothesize that possibly oxidation of the EDTA first provided additional heat to the system, or that EDTA complexed with the sodium nickel ferrocyanide to destabilize the compound and increase the susceptibility to oxidation by nitrate or nitrite.

This screening study suggests that materials such as EDTA or other organic complexants will have the greatest catalytic or initiating effect on the reaction between sodium nickel ferrocyanide and nitrate and/or nitrite, though there are indications that the transition metal hydroxides work in conjunction with EDTA or could enhance EDTA's effect. At a minimum, future studies should focus on EDTA and probably should include one or two of the transition metal hydroxides we tested; other organic complexants should also be evaluated.

CONTENTS

FIGURES

TABLES

1.0 INTRODUCTION

1.1 SOURCE AND NATURE OF HANFORD FERROCYANIDE-BEARING WASTES

At the Hanford Site during the 1950s, radiocesium was scavenged from aqueous radioactive wastes containing nitrate by precipitating alkali nickel ferrocyanides. In some cases, the aqueous wastes contained large quantities of dissolved solids that precipitated during the decontamination treatments, potentially mixing with the ferrocyanide solids. In other cases, the process likely resulted in ferrocyanide solids free of other insoluble solids. The radiocesium scavenging campaigns were often coupled with other processes to scavenge other radionuclides, thus producing solid wastes containing other radionuclides and chemicals.

The ferrocyanide wastes have been stored in Hanford's single-shell tanks (SSTs) for over 30 years. During that time, these wastes were heated to evaporate excess solution, and concentrated and hot wastes were added to the ferrocyanide-containing tanks. The ferrocyanide wastes were moved to other tanks and exposed to high levels of radiation and to pH levels above 7. All of these normal tank management activities and environmental exposures have potentially caused different materials to be added to the original ferrocyanide-bearing wastes. These additional materials include organic complexants (Klem 1990), transition metal hydroxides, sulfides, calcium or strontium phosphates, chlorides, fission product oxides or hydroxides (Scheele et al. 1992). The organic complexants and sulfides are themselves susceptible to rapid oxidation by nitrates and nitrites and could act as initiators or catalysts for the ferrocyanide reaction with nitrate and nitrite. Transition metals, which will be in the wastes as results of fission or corrosion, are known to act as catalysts for some reactions.

Because of concerns about the safe storage of these wastes (Burger 1984; Peach 1991), Westinghouse Hanford Company (WHC, the operating contractor for the Hanford Site) has chartered Pacific Northwest Laboratory (PNL)[a] to

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investigate the reactivity and explosivity of ferrocyanide wastes. As part of these reactivity studies, we at PNL are investigating the effects of waste constituents that could have been mixed with the precipitated ferrocyanides. Our objective in this study is to identify candidate waste constituents that may act as catalysts or initiators; to do so, we performed a preliminary study to screen selected classes of materials that might be in the Hanford high-level waste (HLW) tanks. We plan to use the results of this preliminary study to determine which materials or class of materials merit additional study. This report specifically discusses the results of our preliminary screening studies using the PNL time-to-explosion (TTX) test coupled with statistically based analytical methods to identify the material or combination of materials that cause a reduction in the TTX.

1.2 SELECTION OF CATALYSTS AND INITIATORS FOR TESTING

In our previous studies to determine the effects of potential catalysts and initiators on the thermal reaction between cesium nickel ferrocyanide and equimolar sodium nitrate and nitrite, we used the TTX test to investigate tetrasodium ethylenediaminetetraacetate (EDTA), a mixture of tributyl phosphate and normal paraffin hydrocarbon (TBP/NPH), ferric hydroxide, nickel hydroxide, ammonium nitrate, and sodium hydroxide at the 5 mol% level in the oxidant. Ferric hydroxide, nickel hydroxide, and EDTA reduced the explosion times and the minimum explosion temperatures. EDTA had the greatest effect, causing a reduction in the minimum explosion temperature from 350° to 280°C. The other compounds had minimal effects (Burger and Scheele 1991).

Based on our previous results and on our discussion with M. J. Klem of WHC regarding other materials that are likely to be or have been observed in the SST wastes, we selected EDTA, and ferric, nickel, and chromium (III) hydroxides (abbreviated E, F, N, and C, respectively) for our preliminary studies to determine catalysts and initiators for the reaction between sodium nickel ferrocyanide and sodium nitrate and nitrite. We also decided to use a catalyst and/or initiator ratio of 0.03 mole per mole of sodium nickel ferrocyanide.

2.0 EXPERIMENTAL

The effects of four potential catalysts or initiators on the reactions of sodium nickel ferrocyanide with an equimolar mix of sodium nitrate and sodium nitrite were studied using a modified Henkin test. All the materials used in these studies were prepared at PNL except for the EDTA, which was purchased from a commercial vendor. This section of the report contains a description of the preparation of the materials, test methods, and the experimental design.

2.1 PREPARATION OF MATERIALS

The scavenging of radiocesium from the aqueous Hanford wastes was accomplished by adding $K_4Fe(CN)_6$ (or the sodium analog) to the aqueous waste, adjusting the pH to about 9, and adding $NiSO_4$ at a concentration equal to the ferrocyanide. The ferrocyanide compound used in the studies described in this report was prepared in a similar manner and washed to remove the soluble salts to provide a relatively pure sodium nickel ferrocyanide.

To prepare the sodium nickel ferrocyanide for this study, sodium ferrocyanide $[(Na_4Fe(CN)_6 \cdot 10\ H_2O)]$ (0.17 $\underline{M}$) was dissolved in an aqueous solution with a high ionic strength (1.7 $\underline{M}$ $NaNO_3$). This solution was agitated and heated to 80°C, followed by the addition of $Ni(NO_3)_2$ (0.15 $\underline{M}$). The solution was agitated for 1 h at 70°C and allowed to settle overnight at 60°C. Only minimal settling occurred; therefore, the sample was centrifuged (ambient temperature), and the supernate was decanted. To produce a relatively pure sodium nickel ferrocyanide, the majority of the centrifuged solids were washed with water several times. In addition, a final wash was performed with a 0.03 $\underline{M}$ Na_2SO_4 solution at pH 10. The washed solids were centrifuged, dried in a vacuum oven at 160°C and low vacuum (<20 mm Hg), and ground with a mortar and pestle to -200 mesh.

Chemical analyses of the sodium nickel ferrocyanide sample were performed to determine the composition of the sample. The chemical analyses performed included inductively coupled argon plasma atomic emission spectroscopy (ICP/AES) to measure elemental content, ion chromatography (IC) to

measure anion content, x-ray diffraction spectroscopy (XRD) to identify specific chemical species, total cyanide, total carbon, and scanning thermogravimetric analysis (STG). The composition of this sample as determined by these methods was nominally $Na_2NiFe(CN)_6 \cdot 3\ H_2O$.

Three of the catalysts [iron (III), nickel (II), and chromium (III) hydroxides] were prepared from 3 $\underline{M}$ solutions of $Fe(NO_3)_3$, $Ni(NO_3)_2$, and $Cr(NO_3)_3$. These solutions were titrated with NaOH to pH 13 to precipitate the metals as hydroxide salts or as hydrous oxides. The precipitate was centrifuged and the supernate discarded. Chemical analyses of these salts indicated that their nominal compositions were $Cr(OH)_3 \cdot H_2O$, $FeO(OH) \cdot 2\ H_2O$, and $Ni(OH)_2$. EDTA, the fourth suspect catalyst and/or initiator, was purchased from a commercial chemical supply company as the tetrasodium salt (98% purity).

The oxidant was prepared by mixing reagent grade $NaNO_2$ and $NaNO_3$ at a mole ratio of 1:1. The mix was placed in a 350°C oven for 2 h. The molten salt was cooled to room temperature, and the resulting solid was ground to -200 mesh. The solids were placed in a 60°C oven for 2 h and then stored in a desiccator.

The samples used for the TTX testing were prepared by mixing the catalyst/initiator (C/I) with the oxidant, then mixing the sodium nickel ferrocyanide with the oxidant and C/I mixture, using a slight excess of oxidant; i.e., 1.1 times the stoichiometric amount for the most energetic postulated reactions requiring 6 moles of $NaNO_3$ or 10 moles of $NaNO_2$ per mole of ferrocyanide (Scheele et al. 1992). The composition of each of the sixteen different C/I test samples was selected to allow use of statistically based analytical methods to identify significant factors; the experimental design is discussed in more detail later in Section 2.3. The amount of each of the C/Is was equivalent to 3 mol% of the ferrocyanide. The concentration for each of the components in these samples is given in Table 1.

2.2 TEST METHODS

We used the PNL TTX test (Burger and Scheele 1991) to investigate the effects of selected potential catalysts and/or initiators on the reactivity

2.2

TABLE 1. Composition of Tested Samples

Treatment	$Na_2NiFe(CN)_6$	Concentration, Mole Per Mole Ferrocyanide					
		$NaNO_3$	$NaNO_2$	Cr[a]	Fe[a]	Ni[a]	$EDTA$[b]
Control	1	4.12	4.12	0	0	0	0
E	1	4.12	4.12	0	0	0	0.033
N	1	4.12	4.12	0	0	0.033	0
E*N	1	4.12	4.12	0	0	0.033	0.033
F	1	4.12	4.12	0	0.033	0	0
E*F	1	4.12	4.12	0	0.033	0	0.033
N*F	1	4.12	4.12	0	0.033	0.033	0
E*N*F	1	4.12	4.12	0	0.033	0.033	0.033
C	1	4.12	4.12	0.033	0	0	0
C*E	1	4.12	4.12	0.033	0	0	0.033
N*C	1	4.12	4.12	0.033	0	0.033	0
E*N*C	1	4.12	4.12	0.033	0	0.033	0.033
F*C	1	4.12	4.12	0.033	0.033	0	0
E*F*C	1	4.12	4.12	0.033	0.033	0	0.033
N*F*C	1	4.12	4.12	0.033	0.033	0.033	0
E*N*F*C	1	4.12	4.12	0.033	0.033	0.033	0.033

(a) Precipitated from pH 13 solution as hydroxide or hydrous oxide.
(b) Tetrasodium ethylenediamineacetate.

and explosivity of mixtures of sodium nickel ferrocyanide and sodium nitrate
and nitrite. This section provides a brief description of the TTX test.

The PNL TTX test provides a rough method of measuring kinetic effects
and determining relative explosivities of materials. Therefore, the test was
chosen to investigate the effects of selected C/Is on the explosivity of mix-
tures of $Na_2NiFe(CN)_6$, nitrate, nitrites, and catalysts and initiators. In
this test method, the TTX was measured as a function of temperature for small,
60- to 70-mg quantities of the various mixtures (the amount of ferrocyanide
remained constant). By measuring the time required for an explosion to occur
at several temperatures, it was possible to extrapolate the plot of time

2.3

versus temperature to the minimum explosion temperature, or critical tempera-
ture, T_c, for that particular configuration and size.

For the TTX testing, a 5-mm-diameter test tube (a thin wall NMR tube)
containing about 70 mg of sample was placed into a fitted 2.75-cm-deep hole in
a stainless steel right cylinder measuring 3.6-cm diameter by 4-cm tall.
Another hole, adjacent to the first, was provided for a thermocouple. The
cylinder, surrounded by an insulating block, was placed on a hot plate and
heated to and maintained at the desired temperature by a temperature
controller.

The sample was placed in the heated cylinder, and the time from inser-
tion to explosion was measured and recorded along with any visual observa-
tions. An explosion was defined : either a loud noise or a flash of light;
often both occurred. If no pronounced chemical reaction occurred within nomi-
nally 30 min, the test was stopped. The test performed using the standard TTX
procedure can be considered as a modified Henkin test (Henkin and McGill 1952;
Caldwell et al. 1984; Faubian 1984).

In the TTX test, the TTX should be dependent on the temperature as would
be predicted by the Arrhenius equation if a single reaction mechanism occurs.
Often an explosion occurred after a period of a few seconds, but occasionally
some occurred after 25 min. Only one test, at 296°C, did not explode after
30 min. The absence of an explosion did not mean an exothermic reaction did
not occur. Gases that were normally evolved during the testing of ferrocya-
nide and nitrate and/or nitrite mixtures included oxides of nitrogen (identi-
fied by the characteristic brown color of NO_2 produced either just above the
reaction mixture or slightly higher after the NO had an opportunity to react
with air), and often the contents of the tube were splattered at lower
temperatures.

2.3 EXPERIMENTAL DESIGN

To identify the materials or combination of materials that acted as
catalysts or initiators, we selected an experimental design that would allow
us to use statistically based analytical methods. The design of this C/I
study was based on partial replication of a full factorial experiment in a

2.4

randomized block design. The factors investigated were the four C/Is at two concentration levels, 0 and 0.03 mole per mole of ferrocyanide, and the temperature of the experimental apparatus. The compositions of the 15 C/I treatment and control test mixtures resulting from this experimental design are presented in Table 1.

Each of the treatments was tested at four different temperatures (nominal levels of 296°, 320°, 350°, and 380°C) using four distinct apparatus to allow the four tests to run concurrently. This design produced 64 distinct treatments when the 16 C/I mixtures were tested at each of the four temperatures.

Each of the 15 possible C/I treatments plus the control were randomly sequenced with replication of some of the treatments. The randomization scheme allocated the treatments to the 33 tests performed on the first day so that:

- each C/I treatment with a single C/I was tested at three temperatures (12 tests)

- three of the mixtures with two C/Is were tested at two temperatures, and three were tested at one (9 tests)

- the mixtures with three C/Is were tested at one temperature (4 tests)

- the mixture with all four C/Is was tested at two temperatures, (2 tests)

- the control, $Na_2NiFe(CN)_6$ sans C/I, was tested at three temperatures; once at 380°C, twice at 320°C, and three times at 350°C (6 tests).

Each experimental apparatus was held at its assigned temperature throughout the 33 tests performed on the first day. The same order for the C/I treatments was maintained in all four sets of 33 tests with the temperatures randomly assigned to the individual experimental apparatus. A total of 132 tests were performed during the four days of study.

The expected marked differences in the TTX at the various temperatures should make irrelevant any lack of independence that may have resulted from following the same testing sequence of the C/I in each subset of 33 tests.

2.5

3.0 RESULTS OF SCREENING STUDY

This section presents and discusses the results of our first screening study to identify catalysts and/or initiators for the thermal reaction between ferrocyanide and nitrate and nitrite. In this study we used the PNL TTX test and designed the experiments such that statistical methods could be used to determine whether EDTA (E), $Ni(OH)_2$ (N), Fe_2O_3 (F), or $Cr(OH)_3$ (C), and all their possible combinations reduced the TTX at four discrete temperatures, ranging from 295° to 380°C, of a mixture of $Na_2NiFe(CN)_6$ and a stoichiometric amount of equimolar sodium $NaNO_3$ and $NaNO_2$.

The full set of test data is presented in Appendix A. Table A.1 lists the treatments in their natural order, along with their resulting TTX in seconds at each temperature. No statistical analysis was performed to determine whether the testing order (test number) and the experimental apparatus affected the TTX.

In addition to using statistical analytical methods, we conducted a very small study to determine the minimum explosion temperature for the different treatments using the sample size and geometry of our TTX test. In this study the treatments did not change the explosion temperature relative to the control. The minimum explosion temperature for this geometry and sample size was 293° ± 3°C independent of treatment.

3.1 PRELIMINARY DISCUSSION OF RESULTS

In early TTX testing, Burger and Scheele (1991) found a bilinear relationship between the natural log of the TTX, ln(TTX), and the inverse of the absolute temperature (1/T). If the explosive reaction is a single reaction that follows expected Arrhenius kinetic behavior, a linear relationship between ln(TTX) and 1/T should be observed instead of the bilinear relationship observed in Figure 1, which presents a plot of ln(TTX) versus 1/T for the control mixture and is typical of most of the other mixtures.

A bilinear relationship is one that is linear with one slope over part of the range and another slope over the other part of the range. The intersection of the two lines is referred to as the inflection point. The

3.1
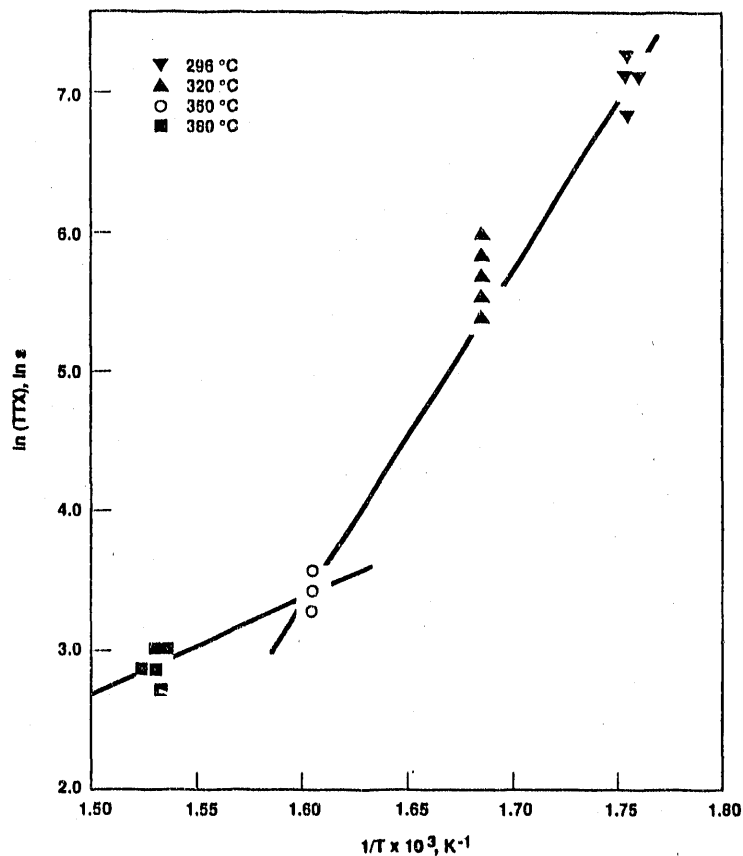
FIGURE 1. Arrhenius-Type Plot for ln(TTX) versus Reciprocal Temperature for a Mixture of Sodium Nickel Ferrocyanide and Equimolar Sodium Nitrate and Nitrite (control)

inflection point in Figure 1 is near 1/T of 1.6 X 10^{-3} or at a temperature of 350°C, which is near that observed for most treatments. An inflection point could be caused by a change in chemical mechanism for the explosion, or it might be explained by the relative time for heat transfer into the sample compared to the TTX.

The hypothesis of a change in chemical mechanism is supported by the differential scanning calorimetry (DSC) analysis of the control mixture presented in Figure 2. According to this figure, several discrete reactions occur as the sample is heated to increasing temperatures or the oxidation of sodium nickel ferrocyanide by sodium nitrate and nitrite is a multistep

3.2

+10

Endothermic ↑

0

Heat Flow, mW

Exothermic ↓

-10

-20

60 110 160 210 260 310 360 410 460 510 560

Temperature, °C

Scanning Rate: 5.0 °C/min
Total Sample Wt: 5.2 mg:
    1.9 mg $Na_2NiFe(CN)_6 \cdot XH_2O$
    3.3 mg $NaNO_3/NaNO_2$

39203011.2
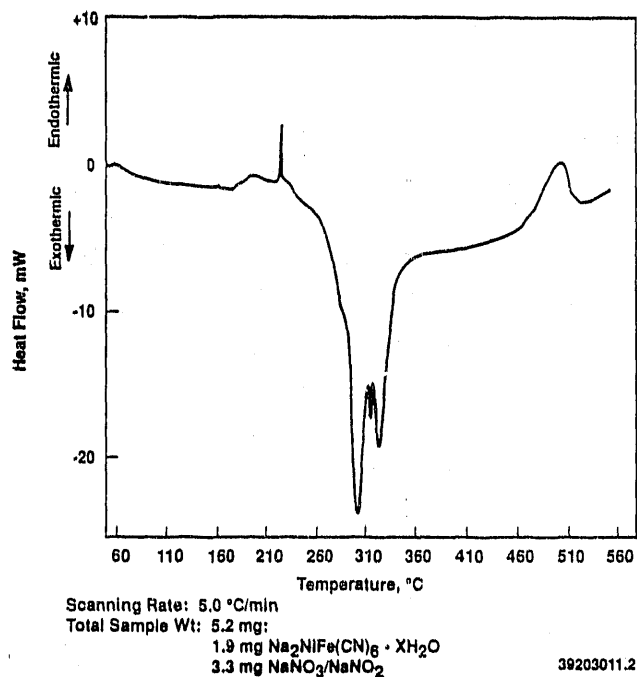
FIGURE 2. DSC Analysis of Reaction(s) Between $Na_2NiFe(CN)_6$ and Equimolar
Sodium Nitrate and Nitrite (control)

reaction. Our STG results (Figure 3) and our initial mass spectral analysis
of the released mass 28 gases from the control shown in Figure 4 (Scheele
et al. 1992) also indicate there are discrete temperature regimes for produc-
tion of product gases. These observations suggest that a singular reaction
will not predominate throughout the entire temperature range used in the TTX
testing.

A second possible explanation for the data at 380°C to have exhibited
different behavior than the rest of the data in Figure 1 could involve the
physical heating of the reaction material. There is a time lag between the
moment a sample tube is placed within the heated block and the time the
reactants have equilibrated at the block temperature. At the very short TTXs
measured for the 380°C data, this time lag could represent a very significant
fraction of the TTX value.

In earlier studies using $Cs_2NiFe(CN)_6$ to determine a time-temperature
profile, we inserted a micro thermocouple into the test mixture and monitored
temperature and time using a strip chart recorder. We encountered problems

3.3
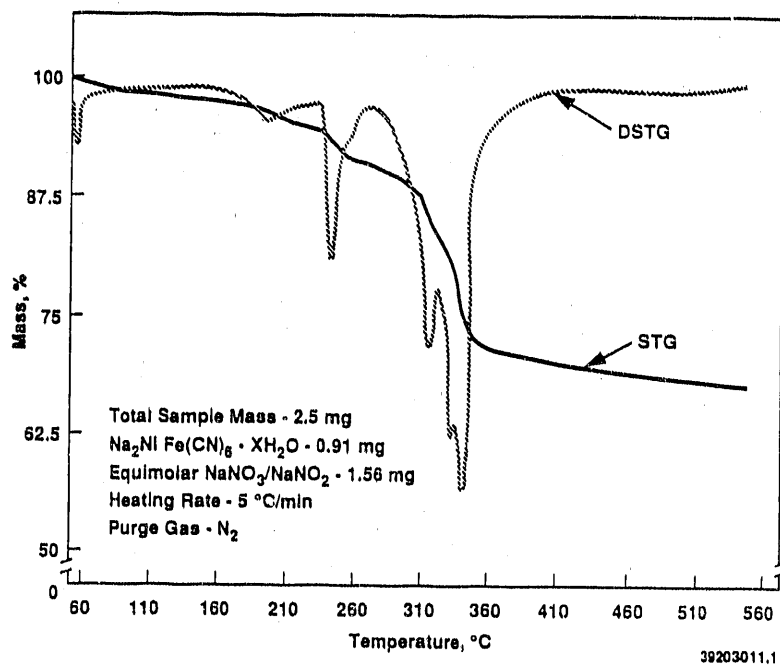
FIGURE 3. STG Analyses of Reaction(s) Between $Na_2NiFe(CN)_6$ and Equimolar Sodium Nitrate and Nitrite (control)

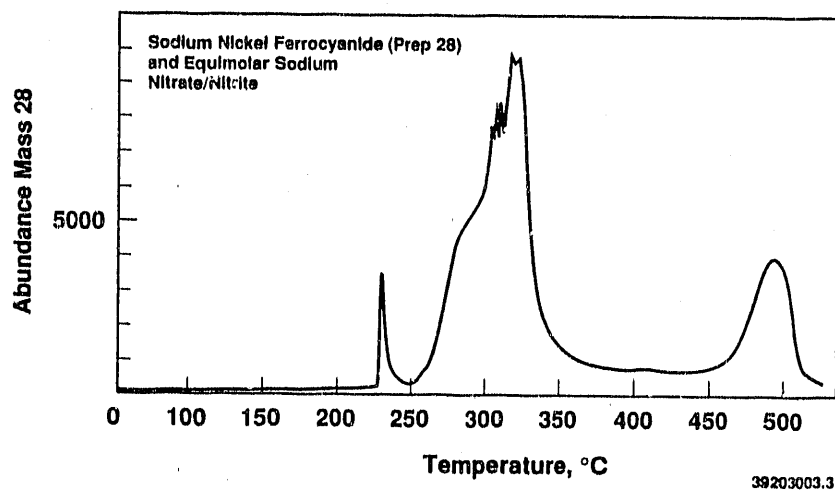FIGURE 4. N_2 and/or CO Produced from Temperature Programmed Pyrolysis of $Na_2NiFe(CN)_6$ and Equimolar Sodium Nitrate and Nitrite Mixture (Scheele et al. 1992)

because of the small sample size and the excellent thermal conductivity of the thermocouples. The thermocouples transferred heat out of the system very rapidly, thus causing overestimation of the time to reach temperature.

Because of our difficulties in measuring the actual time to temperature and explosion, we estimated the time to temperature and adjusted the TTX by different constant amounts. Even with this adjustment, the bilinear relationship between ln(TTX) and 1/T continued to exist indicating that the time lag hypothesis is not an adequate explanation for the bilinear relationship.

Not all of the plots of ln(TTX) versus 1/T produced a bilinear relationship. The exceptions to this apparent bilinear behavior are the plots of treatments E*F, E*C, E*N*C, and perhaps N*F*C. All these exceptions are for treatments having only one observation at each temperature and, therefore, less reliable response patterns over temperature than the treatments with some replication. These plots also show that the data were well behaved, with no obvious outliers.

3.2 IDENTIFICATION OF POTENTIAL CATALYST/INITIATORS

This screening study was designed so that analysis of variance (AOV) methods could be used to analyze the results. The general linear models procedure (PROC GLM in the computer-based statistical analysis package SAS) was used to estimate the means and variances and to provide significance tests and confidence limits for testing the null hypothesis that there were no significant catalytic or initiator effects.

The first AOV model investigated was the full model with the five factors: nominal temperature (TG), E, N, F, and C and the two-, three-, four-, and five-factor interactions that could be formed from them. This analysis indicated that the main effects for TG, E and F, and the two-factor interactions TG*E, E*C and F*C had a statistically significant effect on the TTX (at least at the 95% confidence level). The only higher order interaction that was statistically significant was TG*E*C.

This AOV also showed that the mean TTX at one temperature is statistically different from the mean TTX at each of the other temperatures as shown

in Figure 5. This result would be predicted assuming Arrhenius kinetic behavior with the rate constant inversely proportional to the exponential of reciprocal temperature.

Since the TG main effect accounted for 98% of the total variability in the data, and there were significant interactions involving TG, we analyzed the data using Dunnett's test (1955) to determine the effects of each of the C/Is and their combinations at each temperature. Dunnett's test is used to compare several treatments with a control, which in this case is sodium nickel ferrocyanide with equimolar sodium nitrate and nitrite. Dunnett's test maintains 95% confidence (<5% chance of judging a difference significant when it is not significant) for all comparisons made within a temperature level.

Because of expected Arrhenius behavior, we used the natural logarithm of the TTX for this statistical analysis to identify which additives acted as
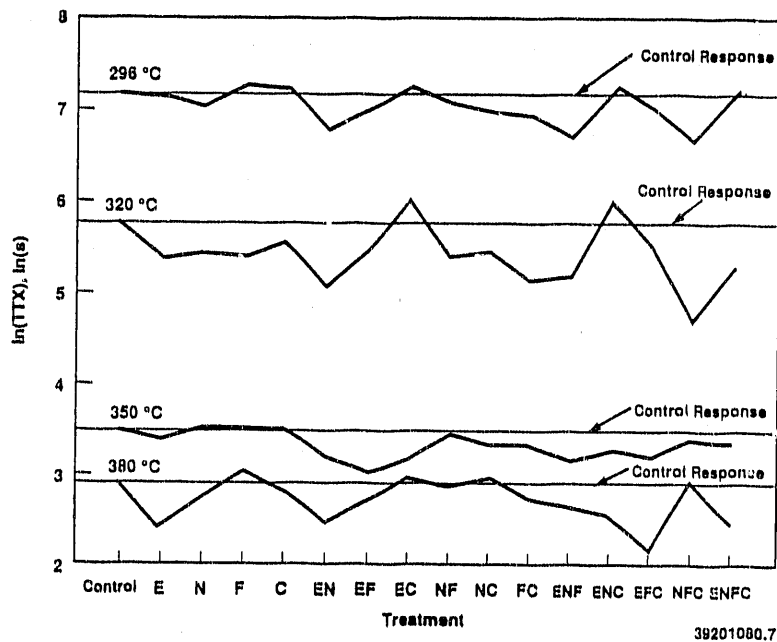
FIGURE 5. Effect of Treatments on Mean ln(TTX) at Different Temperatures [E = EDTA, N = Ni(OH)$_2$, F = Fe(OH)$_3$, C = Cr(OH)$_3$, EN = EDTA plus Ni(OH)$_2$ (as an example of treatment combinations)]

catalyst and/or initiators. The mean ln(TTX)s for each treatment and for the control at each temperature are presented in Table 2, and graphically compared in Figure 5.

To illustrate the effect of each C/I on the TTX at a particular temperature in Figure 5, we included a horizontal line marking the mean for the control in each temperature group. The mean TTXs for many of the C/I treatments

TABLE 2. Effect of Treatment on Mean ln(TTX)

Treatment	$N^{(a)}$	Mean ln(TTX), ln (s) 296°C	320°C	350°C	380°C	Overall Treatment Mean
Control	6	7.13	5.71	3.40	2.91	4.79
EDTA	3	7.11	5.33	3.33	$2.41^{(b)}$	$4.55^{(b)}$
$Ni(OH)_2$	3	7.01	5.37	3.45	2.74	4.64
$Fe(OH)_3$	3	7.25	5.34	3.41	3.03	4.76
$Cr(OH)_3$	3	7.21	5.49	3.42	2.83	4.74
E*N	1	6.75	5.02	3.14	2.48	$4.35^{(b)}$
E*F	1	7.01	5.43	$2.94^{(b)}$	2.71	4.52
E*C	1	7.23	5.97	3.09	2.94	4.81
N*F	2	7.05	5.34	3.37	2.88	4.66
N*C	2	6.96	5.42	3.28	2.97	4.66
F*C	2	6.94	5.09	3.26	2.74	$4.50^{(b)}$
E*N*F	1	6.70	5.14	3.09	2.64	$4.39^{(b)}$
E*N*C	1	7.20	5.99	3.22	2.56	4.74
E*F*C	1	7.01	5.48	3.14	$2.20^{(b)}$	4.46
N*F*C	1	6.65	4.68	3.33	2.94	$4.40^{(b)}$
E*N*F*C	2	7.14	5.27	3.31	$2.52^{(b)}$	4.56
Mean of Means	$16^{(c)}$	7.02	5.38	3.26	2.72	4.60
Weighted Mean	$33^{(d)}$	7.07	5.42	3.32	2.76	4.64
Error Std. Dev.		0.17	0.38	0.12	0.13	0.23

(a) Number of treatment replications at each temperature.
(b) Mean is significantly (one-sided 95% Confidence Level) smaller than control using Dunnett's test for significant differences from control.
(c) Number of means.
(d) Number of observations for each temperature.

are less than the control, indicating that many of the C/Is reduce the TTX relative to the control. It is valuable to note that most of those treatments exhibiting a TTX less than the control contain EDTA. However, when the statistical variation about the mean for a treatment is taken into consideration, there were few of the C/Is that had a statistically significant effect.

Using Dunnett's test, a total of four treatments were found to cause a statistically significant difference in the TTX relative to the control at a particular temperature. At the two lower temperatures, no statistically significant difference was found. For the 350°C treatments, only the difference for the E*F interaction was significant. At 380°C, the treatments E, E*F*C, and E*N*F*C were determined to have significant catalytic or initiating effects.

Figure 6 illustrates graphically the statistical analysis of the data obtained at 380°C. Figure 6 presents a comparison of the mean ln(TTX) for the
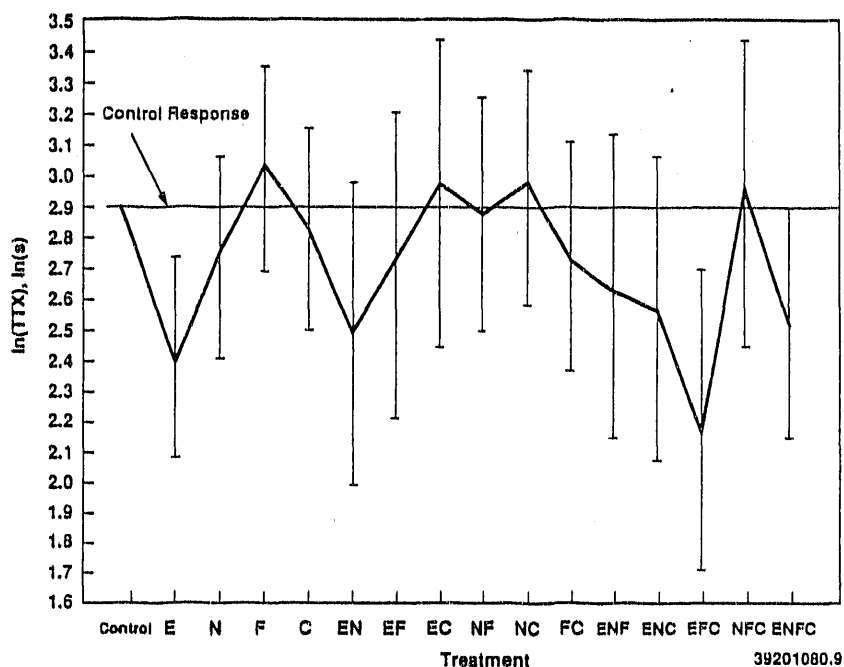
FIGURE 6. Effect of Treatments on Mean ln(TTX) at 380°C Including 95% Confidence Limits Based on Dunnett Difference from Control [E = EDTA, N = Ni(OH)$_2$, F = Fe(OH)$_3$, C = Cr(OH)$_3$, EN = EDTA plus Ni(OH)$_2$ (as an example of treatment combinations)]

control and the mean ln(TTX)s for the different treatments; included are the 95% confidence intervals for the treatments. If a treatment had a statistically significant effect, the control's mean would be outside the treatment's confidence interval. Using this criteria, Figure 6 shows that at 380°C the addition of EDTA alone, E*F*C, and E*N*F*C caused a statistically significant reduction in the TTX. Similar presentations for the other three temperatures are presented in Appendix B, and they show the same results as reported in the previous paragraph.

The error standard deviation reported in Table 2 is the statistic that estimates the experimental variability. Based on the ln(TTX) units, the standard deviation for each temperature relative to the mean for that temperature is between 2% and 7%, and when pooled over all temperatures, it is about 5%. This level of variability in the units of the statistical testing is not large for physical measurements such as the TTX.

All these analyses were conducted using the ln(TTX). In an effort to gain additional information from our data, we transformed the ln(TTX) data presented in Table 2 back into time by computing their natural antilogarithm. The results of this back transformation appear in Table 3, which presents the confidence limits and medians in seconds. Also given are the upper and lower half-widths (HW) for the 95% confidence limits in seconds. This simple transformation is called the Naive Transformation by Land (1975). The Naive Transformation provides exact confidence limits for the median, thus resulting in confidence levels for the medians at somewhat less than the 95% obtained for the natural log data. Because of the back transformation, the confidence limits in seconds are asymmetric (compare the upper and lower HW in Table 3).

Comparison of the medians of the control and treatments at each temperature presented in Table 3 yields the same results regarding statistically significant treatments as obtained using the ln(TTX). Again, the four treatments that caused reductions in the TTX were E*F at 350°C and E, E*F*C, and E*N*F*C at 380°C.

The statistical analysis of the TTX test data indicates that only EDTA alone and the mixed treatments E*F*C and E*N*F*C at 380°C, and E*F at 350°C caused statistically significant (at the 95% confidence level) reductions in

3.9

TABLE 3. ln(TTX) Means and Dunnett-Based 95% Confidence Limits
           Transformed Back to Seconds

Temperature, °C	Treatment	N	Lower Limit, s	Median	Upper Limit, s
296	N*F*C	1	415.10	771	1432.06
296	E*N*F	1	438.25	814	1511.93
296	E*N	1	460.32	855	1588.08
296	E*F*C	1	597.01	1109	2059.85
296	E*F	1	597.61	1110	2061.73
296	E*N*C	1	724.13	1345	2498.21
296	E*C	1	741.90	1378	2559.51
296	F*C	2	646.88	1033	1649.59
296	N*C	2	660.48	1054.71	1684.24
296	N*F	2	725.22	1158.10	1849.37
296	E*N*F*C	2	786.20	1256.25	2007.35
296	N	3	735.99	1103.85	1655.59
296	E	3	814.13	1221.05	1831.37
296	C	3	902.07	1352.95	2029.19
296	F	3	941.68	1412.36	2118.30
296	Control	6	--	1254.84	--
320	N*F*C	1	27.44	108	425.10
320	E*N	1	38.36	151	594.36
320	E*N*F	1	43.45	171	673.01
320	E*F	1	58.18	229	901.37
320	E*F*C	1	60.97	240	944.67
320	E*C	1	99.34	391	1539.03
320	E*N*C	1	101.11	398	1566.58
320	F*C	2	57.37	161.63	455.37
320	E*N*F*C	2	68.71	193.56	545.27
320	N*F	2	73.99	208.45	587.21
320	N*C	2	80.14	225.78	636.09
320	E	3	84.30	206.71	506.91
320	F	3	85.39	209.40	513.49
320	N	3	87.74	215.16	527.63
320	C	3	99.02	242.82	595.46
320	Control	6	--	301.03	--

TABLE 3. (contd)

Temperature, °C	Treatment	N	Lower Limit, s	Median	Upper Limit, s
350	E*F	1	12.41	19.00	29.08
350	E*N*F	1	14.37	22.00	33.67
350	E*C	1	14.37	22.00	33.67
350	E*F*C	1	15.03	23.00	35.21
350	E*N	1	15.03	23.00	35.21
350	E*N*C	1	16.33	25.00	38.27
350	N*F*C	1	18.29	28.00	42.86
350	F*C	2	18.83	25.98	35.84
350	N*C	2	19.20	26.50	36.55
350	E*N*F*C	2	19.93	27.50	37.93
350	N*F	2	21.01	28.98	39.98
350	E	3	21.15	27.95	36.94
350	F	3	22.95	30.33	40.08
350	C	3	23.17	30.62	40.46
350	N	3	23.95	31.64	41.81
350	Control	6	--	29.94	--
380	E*F*C	1	5.46	9.00	14.84
380	E*N	1	7.28	12.00	19.79
380	E*N*C	1	7.88	13.00	21.43
380	E*N*F	1	8.49	14.00	23.08
380	E*F	1	9.10	15.00	24.73
380	N*F*C	1	11.52	19.00	31.33
380	E*C	1	11.52	19.00	31.33
380	E*N*F*C	2	8.50	12.41	18.11
380	F*C	2	10.57	15.43	22.51
380	N*F	2	12.16	17.75	25.90
380	N*C	2	13.32	19.44	28.37
380	E	3	8.06	11.19	15.52
380	N	3	11.12	15.43	21.40
380	C	3	12.24	16.98	23.56
380	F	3	14.88	20.65	28.64
380	Control	6	--	18.29	--

the TTX. However, comparing the mean effect of each treatment to the control mean indicates that many of these suspect catalysts and/or initiators and their combinations reduce the TTX.

The common additive to all the statistically significant and most all the near-statistically significant treatments is EDTA. We do not know enough about the reaction mechanism to explain why the ferrocyanide and nitrate and nitrite reaction is accelerated by EDTA. The important role of EDTA in these reactions may be due to its hydrocarbon fuel content. At the high temperatures used in this study, it is possible for EDTA to react exothermically with the oxidants present in the test matrix. The heat liberated from this reaction could then initiate or accelerate the reaction of the $Na_2NiFe(CN)_6$ with the oxidants. An alternative hypothesis is that the EDTA complexes with the nickel or iron in the sodium nickel ferrocyanide increasing the susceptibility of the carbon and nitrogen to oxidation by the nitrate or nitrite.

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APPENDIX A

TTX RESULTS OF FIRST C/I SCREENING STUDY

TABLE A.1. TTX Results of First Catalyst and/or Initiator (C/I) Screening
Study for Reaction Between Sodium Nickel Ferrocyanide and
Equimolar Sodium Nitrate and Nitrite

Treatment	Time-to-Explosion, s			
	296°C	320°C	350°C	380°C
Control (no C/I added)	1335	354	31	16
	1257	401	34	19
	1296	232	28	18
	1353	249	29	20
	1365	289	29	18
	972	314	29	19
E	1060	242	30	10
	1458	292	26	14
	1178	125	28	10
Ni(OH)	1200	166	24	17
	1229	219	44	12
	912	274	30	18
Fe(OH)$_3$	1370	358	30	22
	1398	249	30	20
	1471	103	31	20
Cr(OH)$_3$	1800	336	30	16
	1489	212	29	17
	924	201	33	18
E*N[a]	855	151	23	12
E*F	1110	229	19	15
E*C	1378	391	22	19
N*F	1235	275	28	21
	1086	158	30	15
N*C	927	331	26	21
	1200	154	27	18
F*C	1036	209	27	14
	1030	125	25	17
E*N*F	814	171	22	14
E*N*C	1345	398	25	13
E*F*C	1109	240	23	9
N*F*C	771	108	28	19
E*N*F*C	1436	262	28	11
	1099	143	27	14

(a) E*N = EDTA + Ni(OH)$_2$ added to control mixture
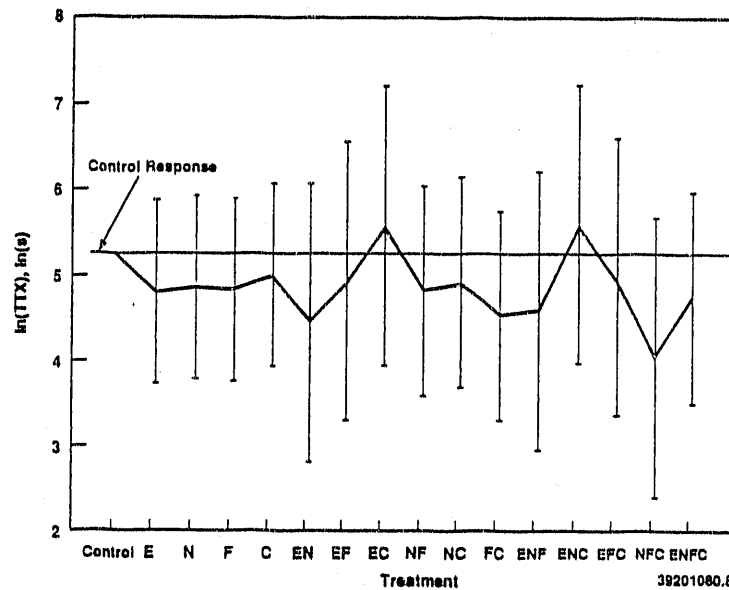[Na$_2$NiFe(CN)$_6$ + Equimolar NaNO$_3$ + NaNO$_2$].

A.1

APPENDIX B

PLOT OF 95% CONFIDENCE LIMITS BASED ON DUNNETT DIFFERENCE FROM CONTROL
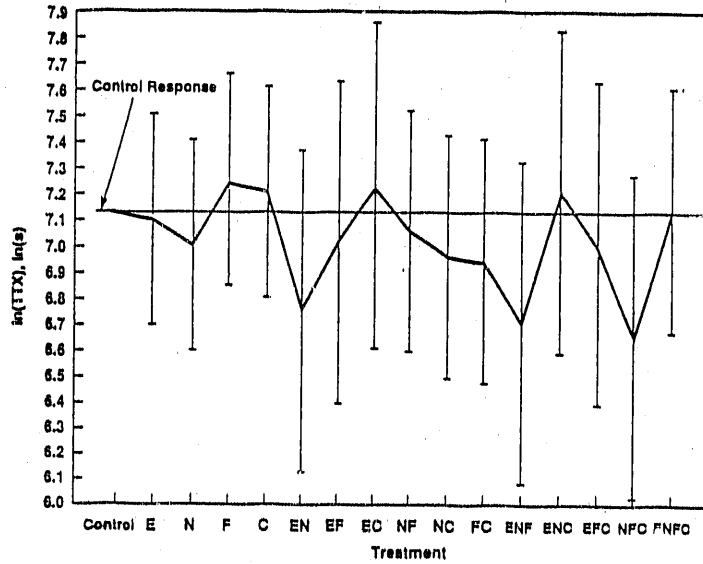
FIGURE B.1. Effect of Treatments on Mean ln(TTX) at 296°C Including 95% Confidence Limits Based on Dunnett Difference from Control [E = EDTA, N = Ni(OH)$_2$, F = Fe(OH)$_3$, C = Cr(OH)$_3$, EN = EDTA plus Ni(OH)$_2$ (as an example of treatment combinations)]

FIGURE B.2. Effect of Treatments on Mean ln(TTX) at 320°C Including 95% Confidence Limits Based on Dunnett Difference from Control [E = EDTA, N = Ni(OH)$_2$, F = Fe(OH)$_3$, C = Cr(OH)$_3$, EN = EDTA plus Ni(OH)$_2$ (as an example of treatment combinations)]
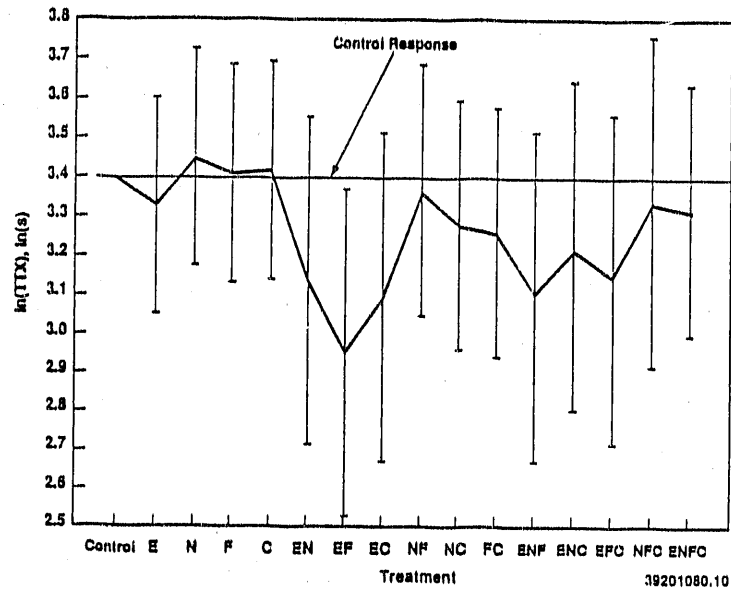
B.1

FIGURE B.3. Effect of Treatments on Mean ln(TTX) at 350°C Including 95% Confidence Limits Based on Dunnett Difference from Control [E = EDTA, N = Ni(OH)$_2$, F = Fe(OH)$_3$, C = Cr(OH)$_3$, EN = EDTA plus Ni(OH)$_2$ (as an example of treatment combinations)]

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