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# The Reactivity of Cesium Nickel Ferrocyanide Towards Nitrate and Nitrite Salts

A Status Report

L. L. Burger  
R. D. Scheele

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September 1991

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## SUMMARY AND CONCLUSIONS

Beginning in late 1988, the Pacific Northwest Laboratory (PNL) began an experimental program at the request of Westinghouse Hanford Company (WHC) to investigate the effects of temperature on the oxidation reaction between synthetic nickel cesium ferrocyanide (FeCN) and nitrates and nitrites representative of materials present in some of the Hanford single-shell tanks (SSTs). After completing a preliminary series of experiments in 1988, the program was expanded to include five tasks to evaluate the effect of selected compositional and operational parameters on the reaction and explosion temperatures of FeCN and nitrate and/or nitrite mixtures.

The first, second, and fourth tasks in the expanded program were respectively to examine the effect of the melting point of the oxidant (the nitrate and/or nitrite salts), the nitrite/nitrate ratio, and selected catalysts and/or initiators on the observed reaction and explosion temperatures. The third was to examine the effect of the oxidant/ferrocyanide ratio on the explosion temperature. The fifth was to determine the effect of increasing mass and bulk on the thermal behavior of a FeCN and nitrate and nitrite mixture (large-scale test).

To investigate the first four parameters, we used the thermoanalytical techniques, differential scanning calorimetry (DSC) and scanning thermogravimetry (STG), and small-scale, time-to-explosion tests (TTX). As a prelude to the large-scale test, the Los Alamos National Laboratory (LANL) was contracted to perform a series of safe-handling experiments to determine if the large-scale test could be performed safely.

The preliminary evaluation of the data from the present work indicates that the oxidation of FeCN by nitrate and/or nitrite is a complex series reactions. DSC data for some of the tests show an enthalpy change that approaches the theoretical maximum of about 3000 kJ/mol ferrocyanide, but in general a somewhat lower value was found suggesting that the most energetic mechanism was not necessarily the only pathway followed. Because of the complex nature of the reaction, it was often difficult to assign a temperature value to the actual beginning of the observed exothermic reactions. The difficulty was

compounded by the occurrence of an endotherm (melting of the oxidant) immediately preceding the reaction. For the tests described here, the observed reaction start temperature is probably near 230°C. STG data generally confirm the DSC data, but some inconsistencies were found. Using the TTX, the minimum observed explosion temperature (critical temperature) was about 280°C.

A molten oxidant is apparently required for the reaction to begin; however, lowering the oxidant melting point below 220°C did not reduce the reaction start temperature but did reduce some of the observed explosion temperatures. To achieve the lower melting points a variety of nitrate and nitrite compounds that are not expected in the SSTs were used, i.e., lithium nitrate.

The nitrite/nitrate ratio effect in the thermal analysis experiments has not been completely analyzed, but the general trend was a lowering of the reaction temperature as the nitrite concentration increased. There were exceptions, and the data seem to suggest that either a cation effect or the presence of a small amount of water, as absorbed water or water of hydration, may be obscuring a simple interpretation. The TTX tests showed a decrease in explosion temperature and in the time to explosion as the nitrite concentration increases.

In terms of the oxidant/FeCN ratio, the maximum reactivity as defined by the explosion tests occurred at the stoichiometric ratio (for the most energetic reaction). As would be predicted by theory, higher or lower ratios gave higher critical temperatures. At a weight ratio of 5 parts oxidant to 1 part FeCN, the mixture reacted less vigorously, and at a ratio of 6 parts oxidant to 1 part FeCN did not explode; however, experimental difficulties confounded the results of this last test. The effect of diluents other than the oxidant were not evaluated.

In the catalyst and initiator tests, the explosion experiments showed that the presence of 5 mol% of hydrous ferric oxide, nickel hydroxide, or the sodium form of ethylenediaminetetraacetic acid (EDTA) significantly reduced the explosion temperature and the time to explosion; the effect increased in that order. A much smaller effect was observed with the addition of 5 mol% ammonium nitrate or sodium hydroxide to the oxidant.

In the catalyst and initiator tests, the thermal analysis data indicate that the presence of sodium hydroxide or EDTA reduces the reaction temperature. Suspected decomposition reactions of the iron and nickel hydroxides, which preceded the FeCN oxidation, complicated the interpretation of both of the DSC and STG data when either of these two materials were present.

The ferrocyanide oxidation reaction is complex. Many different reactions can be hypothesized, several of which probably are apt to depend strongly on the concentrations of reactants, the temperature, and the rate of temperature rise. Likewise, the heat of reaction also varies over wide limits depending on which products are formed.

A modest attempt was made to interpret the time-to-explosion versus temperature plots in terms of an activation energy. Because of the multiple chemical and physical factors involved in the heat transfer rate, no absolute significance could be given to the values found.

LANL's preliminary evaluation of their safe-handling tests indicated that a 1 to 1 weight ratio mixture of FeCN and 50 mol% sodium nitrate and 50 mol% sodium nitrite was insensitive to explosive initiation by impact and friction and relatively insensitive to explosive initiation by spark. Their thermal testing results qualitatively agree with our thermal testing results.

It must be emphasized that the present tests are using simulated waste constituents or mixtures to gain a preliminary understanding of the reactivity of ferrocyanides in the SSTs. These tests are intended to provide a first approximation of waste behavior, which must eventually be confirmed using synthetic wastes prepared using a recipe based on actual tank analyses and ultimately using actual ferrocyanide waste.





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## 1.0 INTRODUCTION

Sodium or potassium ferrocyanide and nickel sulfate were added in the 1950s to the bismuth phosphate wastes in the 200 East and West Areas of the Hanford Site to scavenge cesium from the supernate as a nickel cesium ferrocyanide [ $\text{NiCs}_2\text{Fe}(\text{CN})_6$ ], hereafter designated as FeCN. By removing the cesium and strontium (also scavenged separately), the concentration of long-lived radioisotopes was sufficiently reduced in the supernate so that it could be transferred to cribs, thus creating more tank space. A concern for potential hazardous reactions between the ferrocyanide precipitates and the nitrate and nitrite salts also present in the Hanford waste tanks has been expressed for many years. Burger (1984) summarized the situation and recommended experimental investigations to better understand the problem.

Very little is known about the oxidation of ferrocyanide by nitrates and/or nitrites. A large number of reactions between FeCN or other ferrocyanides or cyanides and a nitrate or nitrite can be postulated, which can result in different reaction products and consequently different heats of reaction.

In 1988 the Westinghouse Hanford Company (WHC) funded work to look at the effects of temperature on the reaction between synthetic FeCN and nitrates and/or nitrites. The brief study conducted in 1988 was summarized in an interim report (Burger and Scheele 1988).

The work scope was expanded in 1989-1990 and consisted of an energetics study task and a large-scale explosion test task. The energetics study was performed at PNL; the preliminary small-scale safety evaluation tests and the large-scale test have been or are to be performed at LANL. PNL is responsible for overall technical coordination and reporting.

The energetics study was to investigate on a screening basis the effects of the oxidant melting point, selected potential waste constituents that could act as catalysts or initiators, the nitrite/nitrate ratio, and the oxidant/ferrocyanide ratio on the reaction and explosion temperatures.

The large-scale explosion test task consisted of two subtasks. The first was a series of preliminary safe-handling tests to determine if the large-scale test could be performed safely. LANL evaluated the sensitivity of

a mixture of FeCN and nitrate and nitrite to impact, friction, spark, and thermal initiation. The second subtask was a large-scale test using kilogram quantities of the previously tested mixture.

This status report presents the results of the data analyses performed to date for the energetics study. The experimental data are incomplete and the analyses of the data are not yet complete. A brief discussion about the results of the small-scale safe-handling tests performed at LANL is also presented.

## 2.0 EXPERIMENTAL

When evaluating explosives, potential explosives, propellants, and other energetic materials, various physical properties, thermodynamic properties, kinetic properties, and other special properties are often determined. Physical properties commonly measured include density, thermal conductivity, melting points, and thermal decomposition behavior. The thermodynamic data gathered include heats of formation, heats of oxidation, and heats of explosion. The kinetic information gathered includes the parameters of the Arrhenius equation, which is needed to predict the efficiency of the material as an explosive or detonator and to aid in scale-up calculations. Special tests (Dobratz and Crawford 1985) have been developed to determine the sensitivity of the material to initiation by friction or electric discharge. Other special tests include tests to measure thermal sensitivity such as gas evolution upon heating, tendency towards adiabatic thermal excursions, the time required for explosions to occur at a fixed temperature, and the actual explosive behavior of large (kilogram) samples.

This section describes the preparation of the FeCN used for these experimental studies, the experimental methods used, and the basis for selecting the parameters evaluated in the energetics study.

### 2.1 PREPARATION OF MATERIALS

The cesium scavenging flowsheet (Sloat 1954; Schmidt and Stedwell 1954) called for 1) adding  $K_4Fe(CN)_6$  (or the sodium analog) to the waste supernate, 2) adjusting the pH to about 9, and 3) adding  $NiSO_4$  at a concentration equal to the ferrocyanide. The solution was agitated for 10 min and transferred to the waste tank. The ferrocyanide solids were allowed to settle and the supernate, after being analyzed, was transferred to cribs.

Laboratory preparation of the FeCN for the present work followed the same basic procedure. However, in the laboratory preparation, an excess of cesium was used to ensure formation of  $NiCs_2Fe(CN)_6$ . The temperature was held at about 65°C. After settling, the FeCN precipitate was washed twice with water and centrifuged to separate the solids. The precipitate was nearly impossible to filter. Once dried it formed a hard mass that was pulverized with a mortar

and pestle. Chemical analysis indicated metal atom ratios within a few percent the theoretical composition. The cyanide,  $CN^-$ , analysis was more difficult and was uncertain to about  $\pm 10\%$ , but within this analytical variability indicated the theoretical composition.

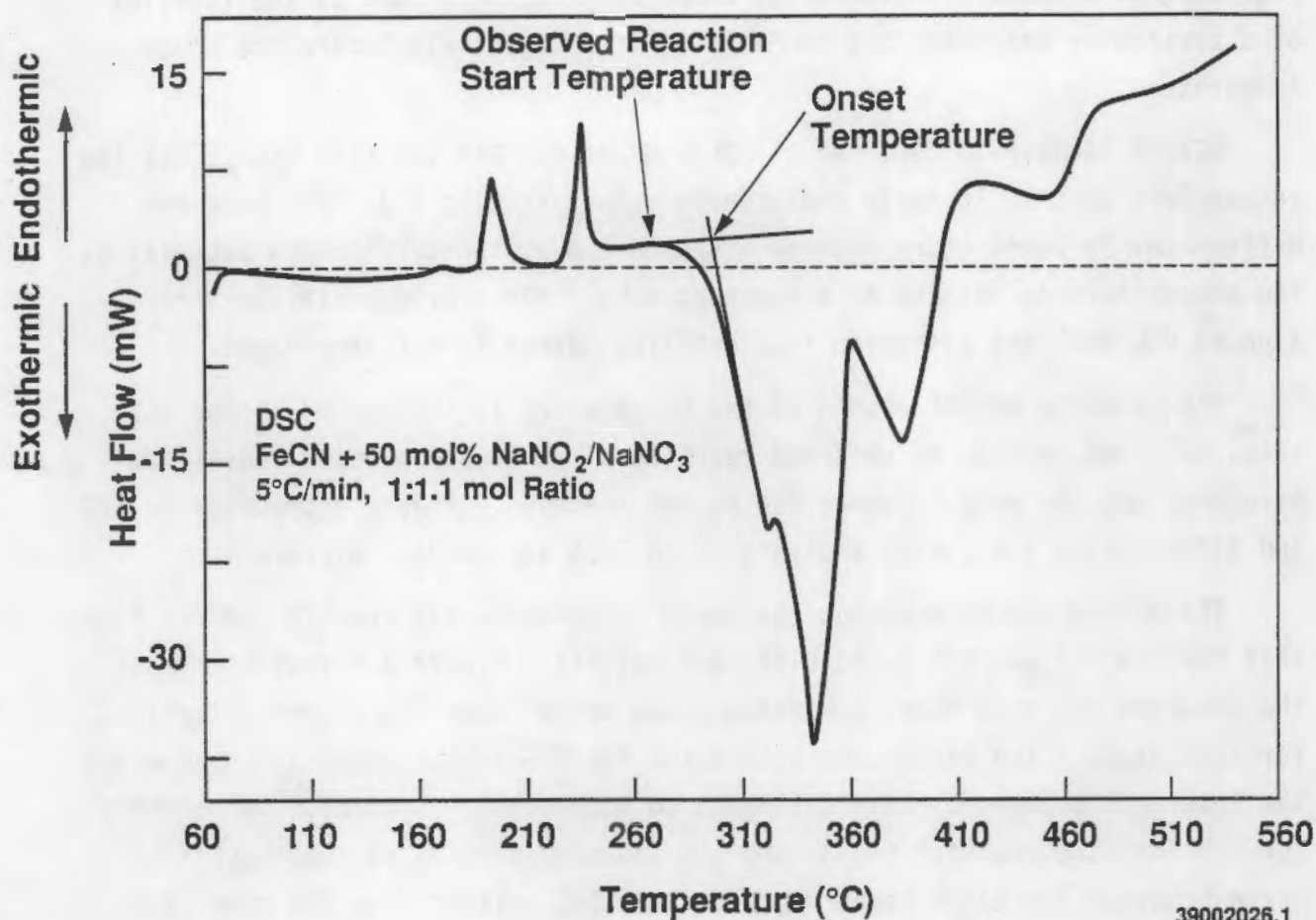
In the thermal analysis and TTX, test mixtures of FeCN and nitrates and/or nitrites were prepared by adding the FeCN powder and then the oxidant to the reaction vessel for each experiment. For the TTX, the test tube was shaken to distribute the two components. The two and three component oxidants were prepared using reagent grade chemicals and were premelted to ensure a uniform mixture and then ground using a mortar and pestle. The oxidant mixtures containing potential catalysts and/or initiators were mechanically blended before use.

It is expected that in the SSTs, the precipitate ferrocyanide will be immersed in an interstitial solution containing nitrates, nitrites, and other soluble constituents. As the wastes dry, the soluble constituents will precipitate on the surface of the ferrocyanide particles providing intimate contact.

## 2.2 THERMAL ANALYSIS TESTING

We used DSC and STG to investigate the effect of temperature and other various parameters on the reaction between FeCN and nitrates and/or nitrites. These two methods and a third thermoanalytical method, differential thermal analysis (DTA), are often used to investigate explosive reactions.

DSC measures enthalpy change as the temperature is changed at a constant rate. DSC can provide an observed reaction starting temperature, an onset temperature, and the enthalpy of a reaction. Interpretation of the resulting curve can be complicated by different reactions occurring at the same time, thus masking each other (e.g., an endotherm due to the reactants melting at the same time that a lower enthalpy exotherm or endotherm occurs). Figure 1 presents an example of a DSC analysis for a FeCN and oxidant mixture and of how the onset temperature and observed reaction start temperature were determined for this work.



**FIGURE 1.** DSC Analysis of Oxidation of FeCN by 50 mol% NaNO<sub>3</sub>/NaNO<sub>2</sub>

Of the various parameters that can be determined using DSC, onset temperature requires special definition since it may or may not have a relationship with the start of a reaction. Onset temperature is an empirical determination that is used by practitioners of DSC and OTA because it typically provides reproducible data for "nice" or well-behaved reactions. The onset temperature is defined as the intercept between two lines drawn tangential to the baseline and the reaction peak's steepest slope.

As an example of the use of onset temperature and its reproducibility, the DSC is temperature calibrated by adjusting the instrument so that the melting point of two standards and their onset temperatures are the same. However, even in this case the onset temperature does not represent the



beginning of a reaction. The onset temperature is dependent on the kinetics of a particular reaction, and the reaction can begin well before the onset temperature.

DTA is similar to DSC. We at PNL did not use DTA for this study, but the researchers at LANL in their preliminary safety testing did. DTA measures differences in temperature between a sample and an inert reference material as the temperature is changed at a constant rate. DTA provides similar information to DSC with the exception that enthalpy change is not determined.

STG measures weight change as the temperature is changed at a constant rate. STG can provide an observed reaction start temperature, an onset temperature, and the weight change due to the reaction. Figure 2 presents an STG and differential STG (DSTG) analysis of an FeCN and oxidant mixture.

The method for determining the onset temperature for the STG differs from that for the DSC and can yield different results. Figure 2 illustrates how the observed reaction start temperature and onset temperature were determined for this study. The onset temperature for the STG is the temperature at which the intercept between the lines tangent to the weight loss versus temperature curve before the reaction begins and the steepest portion of the reaction curve occurs. The onset temperature for the STG suffers from the same pitfalls mentioned earlier for the DSC and DTA. It is common practice to differentiate the weight loss versus temperature curve (DSTG) to make it easier to interpret the analytical results.

DSC and STG are often complimentary analytical methods and together can facilitate an understanding of the reaction of interest. Enthalpy changes detected using DSC can occur without a corresponding weight change; however, it is highly unlikely that a weight change observed by STG will occur without a corresponding enthalpy change.

### 2.3 EXPLOSIVE TESTING

The approach chosen to investigate the explosivity of mixtures of FeCN and nitrate and/or nitrites was to examine the temperature effect on the explosive behavior of small quantities, 25- to 100-mg, of various mixtures.



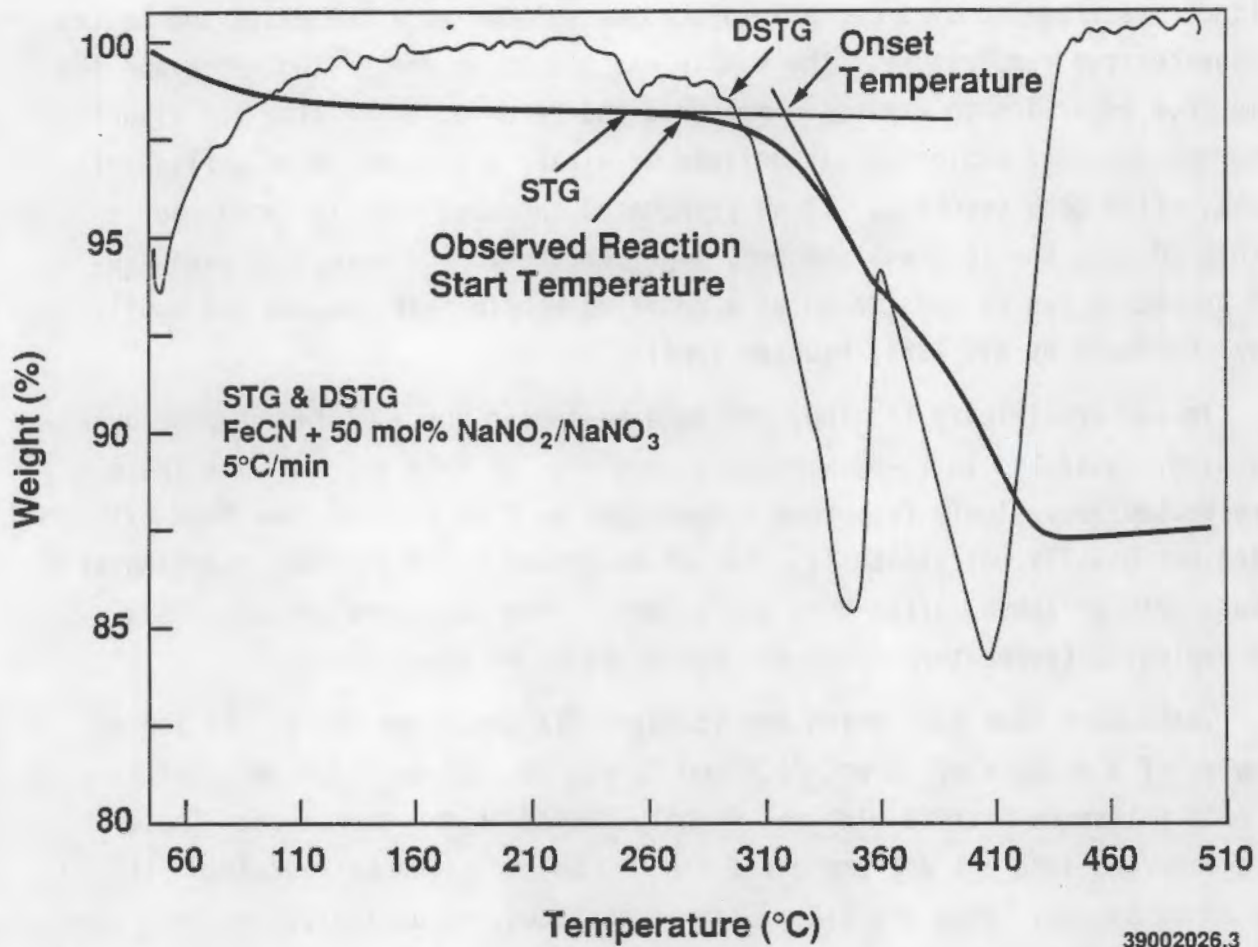


FIGURE 2. STG and DSTG Analysis of Oxidation of FeCN by 50 mol% NaNO<sub>3</sub>/NaNO<sub>2</sub>

By measuring the time required for an explosion to occur at several temperatures (TTX), it is possible to extrapolate the plot of time versus temperature to the minimum explosion temperature or critical temperature,  $T_c$ , for that particular configuration and size. Although the program scope did not include kinetic studies, it is possible to obtain some qualitative rate comparisons from this type of test.

For the standard TTX, a small diameter test tube (a thin wall NMR tube) was placed into a fitted 1.7-cm-deep hole in a stainless steel right cylinder 3.6 cm in diameter by 4.0 cm tall. A second hole was provided for a thermocouple. An exception occurred when a 2.5-cm-deep hole was used to accommodate

the increased amount of sample used in the high oxidant/FeCN ratio tests. The cylinder, surrounded by a magnesia block, was placed on a hot plate and heated to the desired temperature. The sample was placed in the heated block and the time from insertion to explosion measured and recorded along with any visual observations. An explosion was defined as either a loud noise or a flash of light; often both occurred. If no pronounced chemical reaction occurred within 20 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 our preliminary testing, the same equipment but a different procedure was used. When 25- to 75-mg samples of mixtures of FeCN and sodium nitrate were heated very slowly from room temperature at 2 to 3°C/min, the FeCN oxidized but usually not violently. Faster or slower heating rates, starting at about 300°C or above, often gave explosions. From these preliminary tests, the explosive temperature range was estimated to be above 340°C.

Tests were then made using the standard TTX procedure and 20- to 140-mg samples of a mixture of 30 wt% FeCN and 70 wt% of a 65 mol% sodium nitrite-35 mol% potassium nitrite mixture, lightly tamped in the test tube. These were inserted into a 370°C preheated block. No explosion was obtained with the 20-mg sample. When the 140-mg sample exploded, it destroyed the test tube and was deemed too violent for routine studies. Subsequent tests used 50 to 100 mg samples or about 20 to 60 mg of FeCN. A few tests were performed with a 4-mm metal plug resting on the sample to provide some confinement. The results seemed less reproducible when the plug was used, so an open tube was used for the remaining studies.

In the TTX, an explosion normally occurred in a few seconds, but occasionally occurred after several minutes. The absence of an explosion does not mean that an exothermic reaction did not occur. Gases were normally evolved including oxides of nitrogen (identified by the characteristic brown color of  $\text{NO}_2$ ) and often the contents of the tube were splattered at lower temperatures.



## 2.4 DISCUSSION OF PARAMETERS

The 1988 preliminary tests (Burger and Scheele 1988) indicated that melting of the nitrate and/or nitrite salt preceded the fast exothermic reaction. To determine the importance of the oxidant melting point and to provide a base oxidant for the other studies, we selected several eutectic compositions to lower the melting point well below 300°C, which is near the melting point for the nitrates and nitrites used in the 1988 studies. This required mixing different nitrates and nitrites, which complicates the analysis of the results because different cations are introduced and nitrites are generally kinetically more reactive than nitrates.

Because of the rate at which nitrites react with FeCN (Burger and Scheele 1988), the nitrite/nitrate ratio in the oxidant was chosen as a second parameter. Three different ratios of nitrite/nitrate were chosen, corresponding to 20, 60, and 100 mol% nitrite.

The ratio of the oxidant to the ferrocyanide is theoretically important because the maximum efficiency of the reaction should occur at the stoichiometric ratio for the reactants, which is 1 nitrate or 5/3 nitrite per  $\text{CN}^-$ . Smaller amounts of oxidant would result in incomplete reaction, while larger amounts would both slow the reaction rate and absorb the energy produced. Three different ratios were tested because of the variations in the wastes present in the SSTs. The ratio of oxidant to ferrocyanide could affect the explosivity of the mixture; however, it may not affect the initial reaction temperature assuming the same mechanism occurs at all reactant concentrations. Because of this, only the TTX were performed and not the thermal analysis tests.

The fourth parameter studied was the addition of catalysts or initiators. No basis existed for predicting catalytic effects on the oxidation of FeCN by nitrates and/or nitrites. No studies of the reaction have been reported in the literature, nor is anything known about the mechanism. A catalyst works by reducing the activation energy of a reaction, in the present case perhaps for a particular step in the complex reaction sequence. For an explosive reaction this can be especially important since this results in accelerating the early stages, thus determining the temperature at which the explosion begins.

Several heavy metals are catalysts for conventional explosives (Bowden and Yoffe 1958). We studied several compounds, conceivably present in the wastes, that could possibly attack the ferrocyanide complex or raise the temperature through a separate reaction, for example, with the nitrate salt. Although not acting as true catalysts, the net result could be the same.

The presence of an inert diluent was included as a tentative final parameter for the test plan. This parameter was to be studied providing it could be completed within the schedule and funding available. Preliminary work (Burger and Scheele 1988) indicated that alumina, sodium sulfate, or sodium carbonate raised  $T_c$  about 30 to 40°C but did not prevent the explosion. Quantitative effects were not determined in the 1988 studies, and the further work could not be accomplished in the present studies within the existing budget and schedule.



### 3.0 RESULTS AND DISCUSSION

This section presents the results of the energetics studies performed at PNL. The results from the small-scale explosion tests are presented first, followed by the results from the thermal analysis tests. Preliminary results from LANL's preliminary small-scale safety evaluation tests are discussed briefly in another section.

#### 3.1 EXPLOSION TESTS

Examples of temperature versus time-to-explosion plots resulting from the TTX are shown in Figures 3 and 4. Figures 3 and 4 also include plots of  $\ln$  time ( $t$ ) versus  $1/\text{Temperature}$  ( $T$ ). Attempts to fit the temperature versus time TTX curves by exponential and hyperbolic functions in order to extrapolate to longer times and estimate  $T_c$  were not successful. The plots of  $\ln t$  versus  $1/T$  suggest that the reaction is complex and that the mechanism of the reaction changes at a point somewhere above  $300^\circ\text{C}$ .

It is tempting to assign an activation energy to the slope of the high-temperature line since this region represents a rapid liquid phase reaction. It is mathematically valid to do so if the assumption is made that the reaction is the same in each case and reaches a fixed degree of completion in the measured time.

However, such a treatment is complicated by many factors, some of which are chemical and some of which are purely physical such as the rate of heat transfer to the reactants and the apparent need for a molten oxidant. It was found that the time required for partial melting of the oxidant occurred in 5 to 8 s, depending on the temperature used in these studies. These measurements were done using miniature thermocouples inserted in the test tubes and by visual observation. It can be argued that a time correction for thermal lag, e.g., for the time required for the material to reach the melting temperature, should be made, but this is also a function of temperature.

With one system, explosions were seen in as little as 5 s. Thus it would seem unreasonable to subtract more than a few seconds from the observed

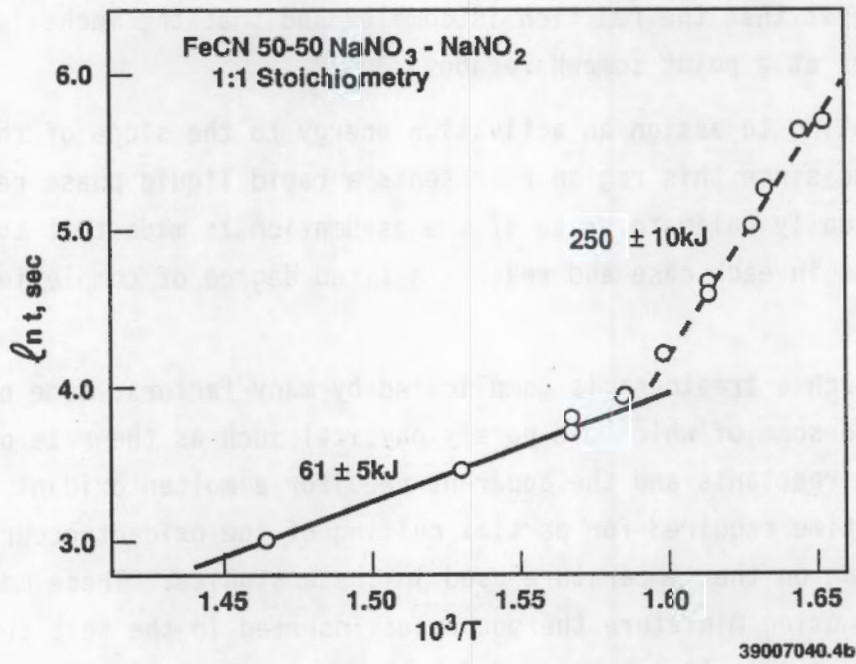
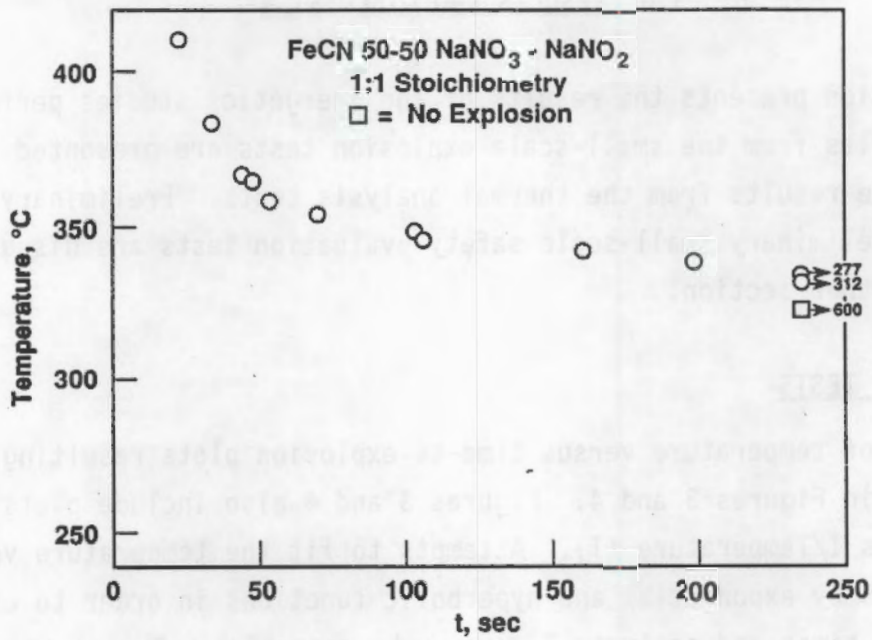


FIGURE 3. Time-to-Explosion Test Results for FeCN and 50 mol% NaNO<sub>3</sub>/NaNO<sub>2</sub> Mixture

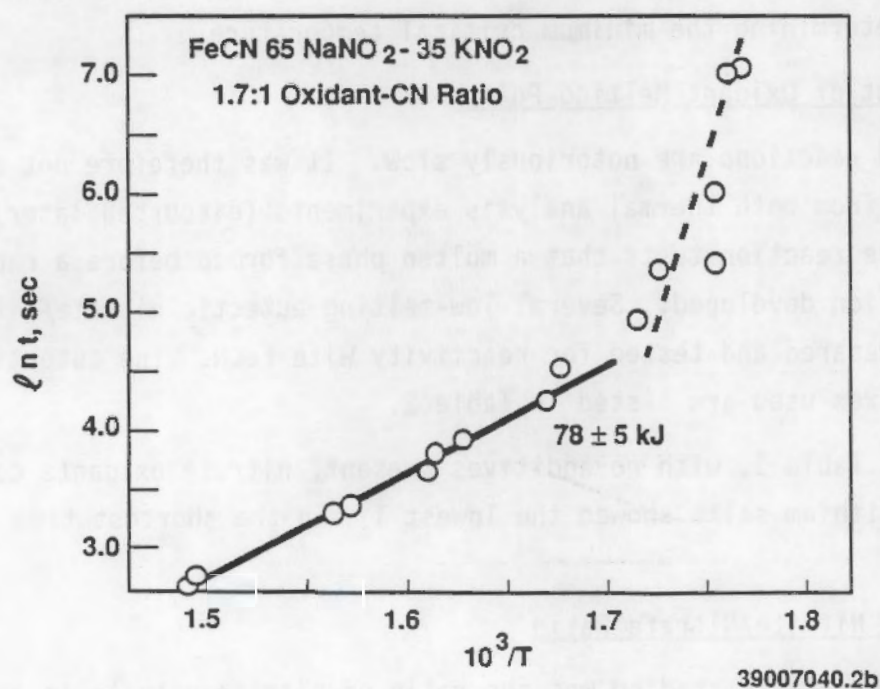
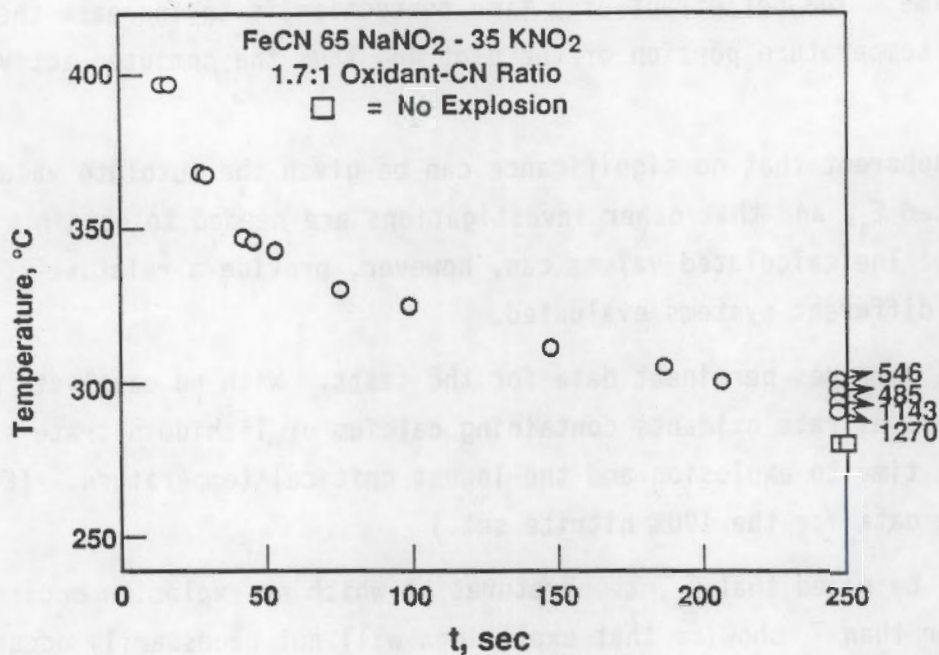


FIGURE 4. Time-to-Explosion Test Results for FeCN and 65 mol% NaNO<sub>2</sub>/KNO<sub>2</sub> Mixture



explosion time. The net effect of a time correction is to increase the slope of the high-temperature portion of the plot and thus the computed activation energy.

It is apparent that no significance can be given the absolute values of the calculated  $E_a$ , and that other investigations are needed to obtain kinetic information. The calculated values can, however, provide a relative comparison for the different systems evaluated.

Table 1 compares pertinent data for the tests. With no catalysts or initiators added, nitrate oxidants containing calcium or lithium nitrate showed the shortest time to explosion and the lowest critical temperature. (Equally low were the data for the 100% nitrite set.)

It will be noted that  $T_x$ , temperatures at which no explosion occurred, is often greater than  $T_c$  showing that explosions will not necessarily occur at  $T > T_c$ . This reflects the unpredictable nature of explosive reactions and the difficulty of determining the minimum critical temperature.

### 3.1.1 The Effect of Oxidant Melting Point

Solid-solid reactions are notoriously slow. It was therefore not surprising to note from both thermal analysis experiments (discussed later) and initial explosive reaction tests that a molten phase formed before a rapid exothermic reaction developed. Several low-melting eutectic nitrate/nitrite mixtures were prepared and tested for reactivity with FeCN. The eutectic or near-eutectic mixes used are listed in Table 2.

As shown in Table 1, with no additives present, nitrate oxidants containing calcium or lithium salts showed the lowest  $T_c$  and the shortest time to explosion.

### 3.1.2 Effect of Nitrite/Nitrate Ratio

The second parameter studied was the ratio of nitrite/nitrate in the oxidizing salt. It had been observed that sodium nitrite oxidant gave a faster reaction and a greater brisance than the nitrate. Nitrite ion can be expected in the tanks in concentrations from perhaps 50 to 80% of the nitrate ion. For the laboratory tests, the mixtures ranged from 20 to 100% nitrite. The higher



**TABLE 1. Time-to-Explosion Data for Tested Mixes**

Sample Number	Oxidant Mix, mol%	M.P. °C	Sample wt, mg Total	Ox/CN Stoich. Ratio	T <sub>x</sub> , max °C	t, 360°C sec	T <sub>c</sub> , est °C
1	40 LiNO <sub>3</sub> 60 KNO <sub>2</sub>	110	84	2.0	308	22	300±5
2	29.5 Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 70.5 KNO <sub>3</sub>	154	100	1.5	310	15	310±10
3	23.6 Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 56.4 KNO <sub>3</sub> 20.0 KNO <sub>2</sub>	163	100	2.0	308	17	315±10
4	65 NaNO <sub>2</sub> 35 KNO <sub>2</sub>	223	100	1.7	301	33	300±5
5	40 NaNO <sub>3</sub> 60 NaNO <sub>2</sub>		100	2.1	335	43	345±10
6	50 NaNO <sub>3</sub> 50 NaNO <sub>2</sub>	227	100	2.1	360	50	350±10
7	80 NaNO <sub>3</sub> 20 NaNO <sub>2</sub>		100	2.3	365	60 est	360±10
8	50 NaNO <sub>3</sub> 50 NaNO <sub>2</sub>	227	50	1.0	325	50	330±5
9	95 Sample No. 8 5 NH <sub>4</sub> NO <sub>3</sub>	227	100	2.1	344	45	345±5
10	99 Sample No. 8 1 wt% TBP-NPH	227	100	2.1	354	65	350±5
11	95 Sample No. 8 5 FeO(OH)	227	100	2.1	335	27	335±10
12	95 Sample No. 8 5 Ni(OH) <sub>2</sub>	227	100	2.1	293	18	300±5
13	95 Sample No. 8 5 NaOH	227	100	2.1	357	50	355±10
14	95 Sample NO. 8 5 EDTA(Na)	227	100	2.1	281	8	280±5
15	KCN 65 NaNO <sub>2</sub> 35 KNO <sub>2</sub>	223	100	1.2	354	~240	350±20
16	K <sub>2</sub> Fe(CN) <sub>6</sub> ·3H <sub>2</sub> O 65 NaNO <sub>2</sub> 35 KNO <sub>2</sub>	223	100	1.3	377	--	370±20
17	KCNO 65 NaNO <sub>2</sub> 35 KNO <sub>2</sub>	223	100	2.6	387	--	--

Notes: FeCN is the cyanide form except as noted in the oxidant mix column.

FeCN = Cs<sub>2</sub>NiFe(CN)<sub>6</sub>.

Melting points are estimated from the DSC plots or from phase diagram data.

Ox/CN is the ratio of oxidant to CN based on stoichiometry to produce CO<sub>2</sub> and H<sub>2</sub>, i.e., 1.0 nitrate or 5/3 nitrite per CN = 1.0.

T<sub>x</sub>, max is the maximum "no go" temperature observed, highest temperature at which no explosion occurred.

t, 360 is the time to explosion, temp, at 360°C.

T<sub>c</sub>, est is the extrapolated critical, or minimum explosion temperature for 50-100 mg of FeCN-oxidant mixture in an open cylinder geometry.

TABLE 2. Properties of Nitrate-Nitrite Melts

<u>Composition, mol%</u>	<u>Melting Point, °C</u>	<u>Nitrite/Nitrate Mole Ratio</u>
65 NaNO <sub>2</sub> , 35 KNO <sub>2</sub>	223	Not Applicable
50 NaNO <sub>3</sub> , 50 NaNO <sub>2</sub>	227	1.0
60 LiNO <sub>3</sub> , 40 KNO <sub>2</sub>	110	0.67
23.6 Ca(NO <sub>3</sub> ) <sub>2</sub> , 56.4 KNO <sub>3</sub> , 20 KNO <sub>2</sub>	163	0.25
29.5 CaNO <sub>3</sub> , 70.5KNO <sub>3</sub>	154	0.0

the nitrite/nitrate ratio, the lower the T<sub>c</sub>, as shown in Table 1. No marked difference is seen for the time to explosion.

### 3.1.3 Effect of Oxidant/Ferrocyanide Ratio

A third parameter is the ratio of oxidant to FeCN, which is expected to vary over a wide range in the 22 waste tanks containing ferrocyanide. Complete experiments to determine T<sub>c</sub> were not always carried out for this parameter. Rather, temperatures at which the mixture was known to be explosive were used and the time to explosion and nature of the reaction were used to determine the relative effect of this third parameter.

It was difficult to make comparative runs because widely differing amounts of total mass were required. The temperature versus time-to-explosion data for the 2.1/1.0 stoichiometric ratio and the 1/1 stoichiometric ratio tests showed that a stoichiometric mix is more reactive as indicated by the data in Table 1. The TTX at 400 to 410°C showed a decrease in reaction violence as the ratio was increased from unity. At a 5/1 weight ratio (4.7 stoichiometric ratio as defined in Table 1), a rapid exothermic reaction still occurred but was without the accompanying flame observed at ratios of 4.5/1 and less. At a 6/1 weight (5.7/1 stoichiometric) ratio, the mixture reacted but no sound was emitted up to 135 s; unfortunately, some of the mix rose above the uniform heating area. To determine whether a 6/1 ratio does explode, another apparatus with an increased hole depth would have to be used.

#### 3.1.4 Catalysts/Initiators

Potential "catalytic" effects could result from the presence of other metals, by initiation of other oxidation reactions or by decomposition of the FeCN or nitrate and/or nitrite by other reagents. For this screening study, six additives were studied in these scoping studies as shown in Table 1 (samples numbers 9 to 14).

The mixture of tri-butyl phosphate/normal paraffin hydrocarbon (TBP/NPH) added at the 1 wt% level had no effect. This result was not surprising in view of the relative inertness of this mixture and the low concentration.

Some of the other materials, added at the 5 mol% level, had significant effects; others had minimal effects. Sodium hydroxide might be expected to hasten the decomposition of the ferrocyanide, but little effect was noted. Ammonium nitrate produced a minimal lowering of the reaction time, but in general had little effect. The nickel and iron hydroxides and the sodium salt of EDTA lowered explosion times and the  $T_c$ . EDTA had the greatest effect of reducing the measured explosion temperature from 350 to 280°C.

The mechanism by which EDTA increases the explosivity of the FeCN and nitrate and nitrite mixture is unknown. EDTA is one of the few reagents that will dissolve FeCN (with difficulty) in aqueous solution, and it may influence the reaction by complexing the iron of the ferrocyanide complex, thus releasing the cyanide ion. Alternatively the EDTA may react itself with the oxidant creating a more reactive oxidant as suggested by DSC and STG analyses which show EDTA reacting with the oxidant in the absence of FeCN.

#### 3.2 THERMAL ANALYSIS TESTS

The following presents a brief analysis of the results from the thermal analysis testing. Because the reactions between FeCN and nitrates and/or nitrites are so complex, as shown in Figures 1 and 2, often proceeding in many steps, this report will present the minimum observed start and onset reaction temperatures for the FeCN reaction as determined by DSC and STG. A more thorough presentation will be made in a later report. As mentioned earlier, only the effects of oxidant melting point, the nitrite/nitrate ratio, and catalysts were studied using DSC and STG.

### 3.2.1 Effect of Oxidant Melting Point

In the preliminary testing performed in 1988, Burger and Scheele (1988) found that the reaction between FeCN and nitrate and/or nitrite occurred after the oxidant melted. To allow determination of the effects of other parameters, the effect of a low melting point oxidant was studied.

Table 3 presents the minimum observed FeCN reaction and onset temperatures obtained using STG and DSC. Replicate experiments were often performed and are reported in the table. Several experiments were performed using nitrogen instead of air as the atmosphere in the thermal analysis units. By using nitrogen, all oxidants except nitrate and/or nitrite are removed.

Inspection of the STG and DSC results presented in Table 3 indicates that there is little correlation between the melting point and the reaction temperatures. In fact, the lowest observed reaction start temperature occurred with the highest melting point oxidant. Interpretation of these results is confounded by changes in cations and the nitrite/nitrate ratios.

**TABLE 3.** Effect of Oxidant Melting Point on the Observed FeCN Reaction Temperature

Oxidant	Melting Point, °C	Minimum FeCN Reaction <sup>(a)</sup> Temperature Observed by STG		Minimum FeCN Reaction <sup>(a)</sup> Temperature Observed by DSC	
		Start, °C	Onset, °C	Start, °C	Onset, °C
60% KNO <sub>2</sub> /40% LiNO <sub>3</sub> in N <sub>2</sub>	110	260	292	265	281
			255	272	
		245±5	279±5	255	274
in Air		240±5	289±5	255	279
29% Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O/ 71% KNO <sub>3</sub> in N <sub>2</sub>	154	260	302	247	282
				264	290
		260±5	302±5	253	297
in Air		260±5	302±5	260	296
				260	295
				260	297
			260	299	
35 mol% KNO <sub>2</sub> / 65 mol% NaNO <sub>2</sub> in N <sub>2</sub>	223	240±5	296±5	281	285
				281	302
		230±5	304±5	281	302
in Air		230±5	299±5	281	285

(a) 5°C/min heating rate.

**TABLE 4.** Effect of Nitrite/Nitrate Ratio on the Observed FeCN Reaction Temperature

Oxidant	% NO <sub>2</sub> <sup>-</sup>	Minimum FeCN Reaction <sup>(a)</sup> Temperature Observed by STG		Minimum FeCN Reaction <sup>(a)</sup> Temperature Observed by DSC	
		Start, °C	Onset, °C	Start, °C	Onset, °C
23.6 mol% Ca(NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O 56.4 mol% KNO <sub>3</sub> / 20 mol% KNO <sub>2</sub>	80	246	312	260	278
40 mol% NaNO <sub>3</sub> / 60 mol% NaNO <sub>2</sub>	40	235	305	238	289
		240	295	236	283
35 mol% KNO <sub>3</sub> / 65 mol% NaNO <sub>2</sub>	0	230	304	281	302
		230	299	281	285

(a) 5°C/min heating

These results suggest that there are multiple factors affecting the observed start and onset temperatures presented here. For example, when calcium is in the oxidant, the STG and DSC curves are simple and have only one transition for the FeCN reaction with nitrate. In this case, it is not known whether the calcium or the presence of water, via water of hydration, were affecting the reactions. Additional experimental replication, particularly for the 100% nitrite oxidant, or another analytical method sensitive to the chemical reaction products would be required for clarification.

The results of this portion of the study show that for a pure nitrate and/or nitrite oxidant, the minimum observed reaction temperature is 230°C.

### 3.2.3 Effect of Potential Catalysts/Initiators

The results of the studies on selected catalysts and/or initiators are presented in Table 5. Replicate results are presented for information. The equimolar mixture of sodium nitrate and sodium nitrite salt was selected as the reference oxidant and base material. This mixture was selected 1) because of its relatively low melting point, 227°C, 2) because sodium is the predominant cation in the SST wastes, and 3) based on other information from available tank waste analyses.

The potential catalysts and initiators were added to the oxidant at the 5 mol% level except for 30% TBP/NPH, which was added at 1 wt%. The lower TBP/NPH concentration was used because higher levels did not mix well with the oxidant and pooled in the bottom of the container. The selected additive

Air does not appear to impact the behavior of the mixture within experimental variation based on comparison with the nitrogen results; thus, the nitrogen results provide additional replication.

Based on these results, any oxidant having a melting point less than 240°C would be a satisfactory medium for investigating the other parameters.

In addition to the melting point results, Table 3 shows some differences between the observed reaction start temperatures determined by the STG and the DSC. In the case of the 65 mol% NaNO<sub>2</sub>/35 mol% KNO<sub>2</sub>, which has a melting point of 223°C, the STG and DSC give the observed reaction start temperatures of 230°C and 280°C, respectively. We do not know why there is a difference in these results unless the melting point peak observed in the DSC masks the observed start of the reaction or the slight change from baseline observed by the STG is less than detectable by the DSC. The rate of weight loss is small until near the onset temperature, and the onset temperatures observed by the two methods are similar.

This latter difference suggests that a different method should be used to detect the start of the reaction. An alternative that could also provide some mechanistic information would be to use a mass spectrometer to determine when a change occurs in the exit gas composition from the STG and the DSC.

### 3.2.2 Effect of Nitrite/Nitrate Ratio

Because the 1988 preliminary results showed that nitrite reacted much more rapidly with FeCN than did nitrate (Burger and Scheele 1988) and that the nitrite/nitrate ratios observed in SSTs varied, the effect of the nitrite/nitrate ratio was evaluated. The start and onset temperatures obtained from duplicate DSC and STG analyses are presented in Table 4. Only three oxidants selected for this particular study are presented and discussed at this time. Additional data will be evaluated and reported in another report.

The results indicate conflicting trends. The STG shows that as the nitrate concentration decreases in the oxidant, the start and onset temperatures decrease slightly. The DSC results show that as the nitrate decreases from 80 to 40 to 0%, the start temperature decreases from 260 to 237°C, and then increases to 281°C. The DSC onset temperatures gradually increase nominally from 280 to 295°C. No explanation is currently available.

**TABLE 5. Effect of Catalysts/Initiators on the Observed FeCN Reaction Temperature**

Oxidant	Additive	Minimum Reaction <sup>(a)</sup> Temperature Observed by STG		Minimum Reaction <sup>(a)</sup> Temperature Observed by DSC	
		Start, °C	Onset, °C	Start, °C	Onset, °C
50 mol% NaNO <sub>3</sub> / 50 mol% NaNO <sub>2</sub>	None	241	241	265	280
		240	244	258	281
				258	288
				260	284
				270	291
50 mol% NaNO <sub>3</sub> / 50 mol% NaNO <sub>2</sub>	5 mol% NaOH	231	233	240	260
		228	237	247	260
50 mol% NaNO <sub>3</sub> / 50 mol% NaNO <sub>2</sub>	5 mol% NH <sub>4</sub> NO <sub>3</sub>	245	253	258	276
		246	258	261	274
50 mol% NaNO <sub>3</sub> / 50 mol% NaNO <sub>2</sub>	5 mol% FeOOH <sup>(b)</sup>	(c)	(c)	275	285
		(c)	(c)	275	285
50 mol% NaNO <sub>3</sub> / 50 mol% NaNO <sub>2</sub>	5 mol% Ni(OH) <sub>2</sub> <sup>(d)</sup>	(e)	(e)	267	284
		(e)	(e)	278	287
50 mol% NaNO <sub>3</sub> / 50 mol% NaNO <sub>2</sub>	5 mol% EDTA	226	232	219	220
		224	231	223	226
50 mol% NaNO <sub>3</sub> / 50 mol% NaNO <sub>2</sub>	1 wt% TBP/NPH	229	240	265	299
		239	243	260	301

- (a) 5°C/min heating rate.  
 (b) Iron (III) precipitated from caustic solution.  
 (c) Suspected decomposition of FeOOH masks FeCN reaction start.  
 (d) Nickel precipitated from caustic solution.  
 (e) Suspected decomposition of Ni(OH)<sub>2</sub> masks FeCN reaction start.

level of 5 mol% was higher than would be expected in the tank waste, but high enough that an effect should be detected if present.

The results show that the presence of NaOH and EDTA reduces the start and onset temperatures for the oxidant 50 mol% NaNO<sub>3</sub>/50 mol% NaNO<sub>2</sub>. The DSC results indicate that adding FeOOH and Ni(OH)<sub>2</sub> increases the start and onset temperatures. Based on the results from the STG and DSTGs of these catalyst/oxidant mixtures sans FeCN, both of these hydroxides are likely decomposing at the temperature at which the oxidation of FeCN begins, which unfortunately complicates the analysis of the STG curves. The DSC curves are again complicated by the endothermic melting peak for the oxidant, which may hide the small reaction that is observed by the STG for this oxidant; this could explain the difference in the observed start and onset temperatures between the STG and DSC analyses.

The initial reaction observed by the STG is small and is followed at higher temperatures by a much larger reaction. The more extensive data analysis using all of the multiple transitions detected using STG, DSTG, and DSC (to be reported later) should provide a better understanding of what effect each of these materials have on the oxidation.

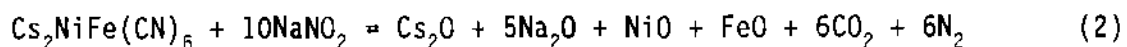
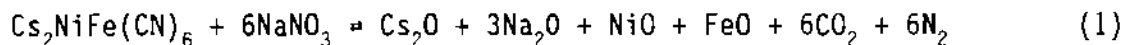
### 3.3 NATURE OF THE FERROCYANIDE OXIDATION REACTION

Very little is known about the oxidation of ferrocyanide by nitrates or nitrites. This section briefly reviews the possible chemical reactions and the associated thermodynamics.

#### 3.3.1 Thermodynamics

A large number of reactions between FeCN or other cyanides and a nitrate or nitrite can be postulated, which can result in different reaction products. The enthalpy of the reaction is determined by these reaction products. The maximum energy evolution occurs when the carbon goes to CO<sub>2</sub> and the nitrogen goes to N<sub>2</sub>. One would expect, based on thermodynamics, that sodium would form carbonate below 1800°C, cesium would form the carbonate below about 800°C and the oxide at higher temperatures, and the heavy metals would form oxides; if water is present, sodium and cesium will form hydroxides above 1400 and 700°C, respectively. Production of CO and oxides of nitrogen lower the heat of reaction by large amounts. If an explosive reaction occurs, the temperature should be high enough to form the alkali oxides or hydroxides instead of the carbonates. In reality, a mixture of reaction products form, including the gaseous products CO, N<sub>2</sub>, NO, and NO<sub>2</sub>.

Simple reactions with nitrate and nitrite salts are illustrated by Reactions (1) and (2).



The calculated enthalpies of reaction are -1655 and -1705 kJ, respectively. An uncertainty of ±300 kJ is assumed based on the estimated heat of



formation of FeCN of  $0 \pm 300$  kJ/mol. The latter value is estimated from National Bureau of Standards (NBS) (Wagman et al. 1972) data for about a dozen metal ferrocyanides that have heats of formation ranging from about -99 kJ/mol  $\text{CN}^-$  to +115 kJ/mol  $\text{CN}^-$ , and these and others having free energies of formation from -2 to +10 kJ/mol  $\text{CN}^-$ . Using this value for  $\Delta H_f$  for FeCN, the heats of reactions for several reactions are given in Table 6.

### 3.3.2 Reaction Mechanisms

The scope of this study did not permit an investigation of the reaction mechanisms for the ferrocyanide oxidation by nitrates and/or nitrites. It is apparent from both the time-to-explosion plots and the thermal analysis data that the reactions are complex. Based on visual observation, the lower temperature reactions appear to produce more oxides of nitrogen than does the very rapid higher temperature reaction(s). It is reasonable to believe that this low-level degradation could reduce the explosive potential. For example, production of the alkali metal hydroxides in reaction (1) instead of the oxides increases the heat of reaction slightly, but if, for example, 2/3 of the nitrogen appears as NO, then the heat of reaction is reduced by a factor of 5 or 6. Some potential reactions are actually endothermic. Table 6 contains an example of an endothermic oxidation of FeCN.

Many heating tests, using the TTX procedure, showed the complexity of the oxidation. Even after a slow degradation at a low temperature, the mixture exploded when heated to 360 to 400°C. Thermal tests involving the analysis of

TABLE 6. Heats of Reaction for Different Oxidation Reactions

<u>Reactants</u>	<u>Products</u>	<u>Enthalpy, kJ/mol</u>
$\text{NaNO}_3, \text{FeCN}$	$\text{FeO}, \text{NiO}, \text{CO}_2, \text{N}_2, \text{Na,Cs hydroxides}$	-2490
" "	" " " " Na,Cs carbonates	-3025
" "	" " " " Na,Cs oxides	-1566
$\text{NaNO}_2, \text{FeCN}$	$\text{FeO}, \text{NiO}, \text{CO}_2, \text{N}_2, \text{Na,Cs hydroxides}$	-2925
" "	" " " " Na,Cs carbonates	-3720
" "	" " " " Na,Cs oxides	-1705
$\text{NaNO}_3, \text{FeCN}$	" " $\text{CO}, \text{N}_2, \text{Na,Cs hydroxides}$	-1180
" "	" " " $\text{NO}$ " " "	+620

reaction products, i.e., examination of the reaction mechanism, would be required to obtain firm answers to the energetics question.

DSC and STG data also show that there is a difference in the mechanisms with nitrite as compared to nitrate. At this time we can only speculate on the true reactions.

#### 4.0 TESTING AT LANL

A 25-g sample of a mixture of 50/50 mol ratio sodium nitrate/sodium nitrite and FeCN having an oxidant-to-FeCN weight ratio of 1:1 was sent to LANL for their preliminary safe-handling tests. A battery of physical and thermal tests were run to evaluate the safety of performing a large-scale test. LANL's results have not yet been analyzed fully, but on a preliminary basis qualitatively agree with those obtained at PNL.

The mixture, based on their preliminary data analysis, has been found by LANL to be insensitive to explosive initiation by impact, friction, and static discharge from humans, and thus safe to handle in the planned large-scale explosion test. Negotiations between LANL and PNL on the large-scale test definition have begun.



## 5.0 RECOMMENDATIONS

Planned follow-on work includes the large-scale thermal test and two screening studies, similar to the energetics study discussed in this report, to determine the effect of radiation, and to determine how cesium nickel ferrocyanide behaves compared to FeCN. We recommend that this work be done, but it should also be supplemented by other studies.

The results presented in this report indicate that there is a need to understand the mechanism and kinetics of the ferrocyanide reactions before the data obtained to date can be interpreted or predictive models can be developed.

We recommend that in addition to the planned empirical studies, mechanistic and kinetic studies of the ferrocyanide oxidation reactions be performed including the following:

- Determine reaction products of the various steps in the reactions.
- Determine the enthalpy of these steps.
- Determine kinetic parameters for selected steps that appear to be significant.
- Determine the effect of inert materials (diluent) on these reactions.
- Continue the study of catalytic effects.
- Examine other cyanide complexes of metals that may be present in the ferrocyanide-containing waste tanks.
- Perform further large-scale explosive testing, for example with diluents added.
- Perform testing using actual ferrocyanide-containing wastes to determine reactivity and reaction products formed on heating.

Consideration of the thermodynamics of the possible reactions between ferrocyanides and nitrates or nitrites indicates that ferrocyanides can be decomposed in ways that are not very exothermic and hence, with adequate dilution, should not lead to explosions. However, without knowledge of the chemistry, one cannot say which of the many reactions are occurring nor how to control the reaction path taken.

This recommended work can be carried out with essentially the same techniques used to date with the addition of chemical analysis to determine products of the reactions. If successful, the study will provide key information on how to ensure safe storage and eventual safe disposal of the ferrocyanide-containing wastes.

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