Effect of Potential Waste Constituents
on the Reactivity of Hanford Ferrocyanide
Wastes: Diluent, Catalyst, and Initiator Studies

R. D. Scheele
J. W. Johnston
J. M. Tingey
L. L. Burger
R. L. Sell

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Pacific Northwest Laboratory
Richland, Washington 99352

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Summary

During the 1980s, scientists at the Hanford Site began considering disposal options for wastes in underground storage tanks. As a result of safety concerns, it was determined that special consideration should be given to ferrocyanide-bearing wastes to ensure their continued safe storage. In addition, Westinghouse Hanford Company (WHC) chartered Pacific Northwest Laboratory (PNL) to determine the conditions necessary for vigorous reactions to occur in the Hanford Site ferrocyanide wastes. As part of those studies, PNL has evaluated the effects of selected potential waste constituents to determine how they might affect the reactivity of the wastes.

Our investigations of the diluent, catalytic, or initiating effects of potential waste constituents included studies 1) to determine the effect of the oxidant-to-ferrocyanide ratio, 2) to establish the effect of sodium aluminate concentration, 3) to identify materials that could affect the explosivity of a mixture of sodium nickel ferricyanide (a potential aging product of ferrocyanide) and sodium nitrate and nitrite, 4) and to determine the effect of nickel sulfide concentration.

We also conducted a thermal sensitivity study and analyzed the results to determine the relative behaviors of sodium nickel ferrocyanide and ferricyanide. A statistical evaluation of the time-to-explosion (TTX) test results from the catalyst and initiator screening study found that the ferricyanide reacted at a faster rate than did the ferrocyanide analog. The thermal analyses indicated that the ferricyanide form is more thermally sensitive, exhibiting exothermic behavior at a lower temperature than the ferrocyanide form. The increased thermal sensitivity of the ferricyanide, which is a potential oxidation product of ferrocyanide, relative to the ferrocyanide analog, does not support the hypothesis that aging independent of the reaction pathway will necessarily reduce the reaction hazard of ferrocyanide wastes.

Based on our oxidant-to-ferrocyanide studies, we found that the range of compositions that produced explosive reactions varied depending on temperature, with the largest range at the highest temperature. At 400°C, the mixtures that were explosive ranged from a stoichiometric ratio (oxidant-to-ferrocyanide) of 0.1 to 2.5. At 320°C, the explosive compositions ranged from a stoichiometric ratio of 0.5 to 1.0; mixtures having less or more oxidant did not explode. The explosivity of a mixture significantly deficient of oxidant is somewhat surprising. Previous studies indicate that sodium nickel ferrocyanide does not explode by itself as determined by TTX tests at temperatures up to 400°C.

In our studies to determine the effect of an inert diluent, we found that added sodium aluminate delays the explosive reaction, but even at a weight ratio of 12:1 [NaAlO₂:Na₂NiFe(CN)₆], the ferrocyanide mixture continued to explode at 350°C. Increasing the mass ratio from 0:1 to 2:1 had a much greater effect than increasing the mass ratio from 2:1 to 4:1. Additional work was conducted to determine the diluent effects of other potential ferrocyanide waste constituents on the explosivity of ferrocyanide and nitrate and nitrite mixtures. Results showed that the higher heat capacity equimolar sodium nitrate and nitrite was more effective in preventing an explosion than the lower heat capacity sodium aluminate.

In the screening study to determine the effect of EDTA and the hydroxides of chromium (III), iron (III), and nickel (II) on the explosivity of a mixture of sodium nickel ferricyanide and nitrate and nitrite, at 0.03 mole/mole ferrocyanide only EDTA was observed to have a statistically significant effect and only at temperatures $> 350^{\circ}\text{C}$. An earlier test with similar mixtures containing the sodium nickel ferrocyanide form found similar results. EDTA alone at 380°C had a statistically significant effect; however, other treatments containing EDTA at 380° and 350°C also had statistically significant effects. The results of these two screening studies suggest that ferrocyanide wastes containing EDTA or, by extrapolation, organic complexants merit special concern.

The nickel sulfide study results indicated that nickel sulfide increases the reactivity of a mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite. Adding NiS at $\text{NiS}:\text{Na}_2\text{NiFe}(\text{CN})_6$ mass ratios of 0.6:1.0 and 1.0:1.0 accelerated the reaction and reduced the minimum observed explosion temperature. Adding NiS at 0.15:1 and 0.30:1 accelerated the reaction but did not reduce the minimum observed explosion temperature within the 60-min test period.

In general, these experimental studies on mixtures of sodium nickel ferrocyanides or ferricyanides and equimolar sodium nitrate and nitrite indicated that the chemical composition of the waste, the nature of the cyano species, and the nature of the other waste constituents can affect the explosivity of ferrocyanide wastes. Some materials effectively dampen the tendency to explode, while other materials accelerate and/or increase the thermal sensitivity of the mixture. None of the additives reduced the explosion temperature below 200°C . If actions were to be taken that would change the conditions of the ferrocyanide wastes, a careful evaluation including experimental studies should be performed to determine the compositional effects on the behavior of the ferrocyanide waste at the new conditions.

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1.0 Introduction

During the 1950s, the United States identified a need to produce additional nuclear defense materials. The operating contractor of the Hanford Site, which had responsibility for producing these materials, determined that there was insufficient storage capacity for the wastes that would be generated by increased production. To accommodate the need for additional radioactive waste storage capacity, the contractor used a "radiocesium scavenging" process. This process removed soluble cesium from the aqueous wastes by precipitating an insoluble mixed alkali nickel ferrocyanide, which then allowed disposal of the decontaminated aqueous wastes to a soil column. The use of this radiocesium scavenging process created tons of potentially reactive waste having a wide range of chemical compositions.

Historically, the potential reactivity of mixtures of ferrocyanides, nitrates, and nitrites was first recognized when the radiocesium scavenging process using ferrocyanide was investigated for application to radioactive wastes produced by the next generation processing technology for recovery of defense materials. Hepworth, McClanahan, and Moore (1957) discovered that cesium zinc ferrocyanide and nitrate exploded when heated. Later investigations on the reactivity of Hanford Site ferrocyanide-bearing wastes (Burger and Scheele 1991; Scheele et al. 1992a, 1992b, 1992c) found that mixtures of cesium or sodium nickel ferrocyanides and alkali nitrates and nitrites began reacting when heated above 230°C and typically exploded in small-scale (<100 mg) explosion tests when heated above 300°C.

Since the 1950s, the range of ferrocyanide-bearing waste compositions has developed from many factors including 1) a large amount of other solids in some of the treated wastes, 2) the coupling of other precipitation scavenging processes with the radiocesium scavenging process, 3) waste management operations at Hanford including transfer and mixing of different wastes, and 4) the high radiation field and the harsh chemical environment to which these wastes were exposed during 30 years of storage.

The radiocesium scavenging process was used to decontaminate Uranium Recovery Plant (U-Plant) waste or neutralized U-Plant waste supernates. In the basic process, equimolar amounts of soluble sodium or potassium ferrocyanide and nickel sulfate were added to alkaline wastes to precipitate an alkali nickel ferrocyanide, including the cesium form. Because of the high sodium concentration in the waste, it is believed that sodium nickel ferrocyanide was the predominant ferrocyanide precipitate.

In the cases where an aqueous waste supernate was treated solely with the radiocesium scavenging process, the resulting ferrocyanide-bearing waste should have been a mixture of relatively pure sodium nickel ferrocyanide and interstitial solution containing largely sodium nitrate and, with time, sodium nitrite from radiolysis of nitrate. Small amounts of sodium sulfate, sodium chloride, and sodium hydroxide were also present in the solution.

In the cases where the U-Plant wastes were treated, large quantities of dissolved iron precipitated when the acidic waste was neutralized with sodium hydroxide. Initially, the resulting ferrocyanide waste

was probably a mixture of sodium nickel ferrocyanide, ferro or ferric hydrous oxides, and an interstitial solution containing largely sodium nitrate with small amounts of sodium chloride, sodium phosphate, and sodium hydroxide.

Before the radiocesium scavenging process was implemented, the operating contractor often used other scavenging processes to remove radiostrontium and radiocobalt from the wastes. The coupling of these two scavenging processes added strontium or calcium phosphate or nickel sulfide to the solid ferrocyanide wastes. Sulfide has the potential to react with nitrate or nitrite.

The dynamic nature of waste management operations at the Hanford Site added to the complexity of the ferrocyanide-bearing wastes. During 30 years storage in Hanford's single-shell tanks (SSTs), some wastes were heated in-tank to evaporate excess water, other wastes were transferred to the tanks containing the ferrocyanide wastes (these wastes included concentrated and thermally hot wastes), and some of the ferrocyanide-bearing wastes were themselves moved to other tanks.

An important consequence of the 30-year storage period is the potential aging of the ferrocyanide wastes due to exposure of these wastes to high levels of radiation, possibly high pH, and oxidizing chemical environment. Radiation could cause oxidation of the iron in the ferrocyanide complex, resulting in the formation of ferricyanide, which exhibits a different reactivity or could be more thermally sensitive or possibly more susceptible to succeeding aging reactions than the parent material. The high pH could result in decomposition of the ferrocyanide into its constituents or could result in partial substitution of hydroxide for cyanide, which would be expected to react differently with nitrate or nitrite than parent ferrocyanide. Many other potential aging reactions could occur resulting in materials with unknown hazards from a reactivity standpoint.

These normal tank management activities and exposure of the ferrocyanide wastes to different storage conditions have potentially caused the addition of different materials to or altered the nature of the original ferrocyanide-bearing wastes. Additional materials include organic complexants, solvents, transition metal hydroxides, chlorides, fission product oxides or hydroxides (Klem 1988), and nitrite from nitrate radiolysis (roughly 30% to 50% of original nitrate). The organic complexants and solvents are themselves potentially susceptible to rapid oxidation by nitrates and nitrites when heated. Some may react slowly with the nitrite ion in solution at ambient temperature.

Waste constituents can affect the reactivity or hazard associated with the ferrocyanide wastes by acting as a diluent, a catalyst, or an initiator. A diluent could be excess oxidant or a nonparticipatory material, and because of its ability to absorb heat, could prevent the reaction mixture from reaching very high temperatures, thus reducing or eliminating the hazard. Halides and transition metal hydroxides from fission products or tank corrosion are known potential catalysts for some reactions (Burger and Scheele 1991; Scheele et al. 1992c; Bryan, Pederson, and Scheele 1993). A catalyst might reduce the initial reaction temperature or allow the explosive reaction to occur at a lower temperature. An initiator could react with nitrate and nitrite at a lower temperature than the ferrocyanide reaction, providing sufficient heat to cause the ferrocyanide reaction to occur. Potential initiators include reactions between reduced species, such as organics and sulfides, with the ever present nitrates and nitrites.

Because of concerns about the safety of storing ferrocyanide wastes, Westinghouse Hanford Company [WHC, the current operating contractor for the U.S. Department of Energy's (DOE) Hanford Site] chartered Pacific Northwest Laboratory (PNL)^(a) to investigate the reactivity and explosivity of these wastes. As part of these reactivity studies, PNL is investigating the effects of waste constituents that have been mixed with the precipitated ferrocyanides. This paper discusses some of our continuing studies to identify waste constituents that act as catalysts or initiators. Chapter 2 describes our experimental methods. Chapter 3 presents the results of our diluent studies, and Chapter 4 contains the results of the catalyst and initiator studies. Chapter 5 presents conclusions and recommendations.

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2.0 Experimental

We performed a variety of studies to investigate the diluent, catalyst, or initiator effects of potential Hanford Site ferrocyanide waste compositions or constituents on waste reactivity and explosivity. We performed studies to determine 1) the effect of the oxidant-to-ferrocyanide ratio, 2) the effect of sodium aluminate concentration (a low heat capacity inert diluent) on the explosivity of a mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite, 3) the effect of selected potential waste constituents on the explosivity of a mixture of sodium nickel ferricyanide (a potential ferrocyanide oxidation product) and equimolar sodium nitrate and nitrite, and 4) the effect of the nickel sulfide (a known ingredient of some Hanford Site ferrocyanide wastes) concentration on the explosivity of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite mixtures.

2.1 Materials

When possible we used commercially available reagent grade chemicals. Sodium nickel ferrocyanide, sodium nickel ferricyanide, and hydroxides of chromium (III), iron (III), and nickel (II) were prepared at PNL. The ferrocyanide and ferricyanide preparations mimicked the cesium scavenging processes.

The scavenging of radiocesium from the aqueous Hanford Site wastes was accomplished by adding $K_4Fe(CN)_6$ (or the sodium analog) ranging from 0.0025 to 0.0075 M in the aqueous waste, adjusting the pH to about 9, and adding $NiSO_4$ at a concentration equal to the ferrocyanide. The ferrocyanide compound used for our studies was prepared in a similar manner. Sodium ferrocyanide [$(Na_4Fe(CN)_6 \cdot 10 H_2O)$] (0.17 M) was dissolved in a pH 10 aqueous solution with a high ionic strength (2 M $NaNO_3$). This solution was agitated and heated to 40°C, followed by the addition of $Ni(NO_3)_2$ solution to bring the final $[Ni^{2+}]$ to 0.14 M (equivalent to the final $[Fe(CN)_6^{4-}]$). The solution was agitated for 30 min at 40°C and allowed to settle overnight at ambient temperature. To obtain a pure sodium nickel ferrocyanide, the majority of the solids was washed 3 times with 2 volumes of deionized (DI) water; the solids were recovered after the first two washes by centrifuging at 1,100 g for 1 h and after the third wash by centrifuging at 4,200 g for 1.6 h. The high centrifugal force required to recover the solids after the final wash resulted from the tendency toward colloidal behavior of the final washed solids. The recovered solids were air dried overnight at ambient temperature, dried further at 60°C in 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 included inductively coupled argon plasma atomic emission spectroscopy (ICP/AES) to measure elemental content, ion chromatography (IC) to measure anion content, x-ray diffraction (XRD) to identify specific chemical species, total cyanide, total carbon, and scanning thermogravimetric analysis (STG). The composition of this sample as determined by these analyses was nominally $Na_2NiFe(CN)_6 \cdot 1.5 H_2O$.

Sodium nickel ferricyanide was prepared by heating 1.2 L of 6 M $NaNO_3$ and 0.038 M $Ni(NO_3)_2$, to 60°C and adding 600 mL of 0.075 M $K_3Fe(CN)_6$. This solution was mixed for a few hours and aged

without stirring at 60°C for 72 h. After the supernate was decanted, the solids were centrifuged at 1,000 g for 1 h. The recovered solids were washed 3 times. The first wash was performed with 2 volumes of DI water, followed by two washes with 3 volumes of DI water. The solids were recovered each time by centrifuging for 2 h at 1,000 g. The recovered sodium nickel ferricyanide was dried at 60°C for 16 h and ground and sieved to <200 mesh.

Three of the candidate catalysts [iron (III), nickel (II), and chromium (III) hydroxides] were prepared from 3 M solutions of $\text{Fe}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, and $\text{Cr}(\text{NO}_3)_3$. 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 was discarded. Chemical analyses of these salts indicated their nominal compositions were $\text{Cr}(\text{OH})_3 \cdot \text{H}_2\text{O}$, $\text{FeO}(\text{OH}) \cdot 2 \text{H}_2\text{O}$, and $\text{Ni}(\text{OH})_2$. Sodium ethylenediaminetetraacetate (EDTA), the fourth suspect catalyst and/or initiator (C/I), 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 ambient temperature, and the resulting solid was ground to <200 mesh. The ground solid was dried in a 60°C oven for 2 h and then stored in a desiccator. The sodium aluminate (technical grade) used for the diluent studies was ground using a mortar and pestle, sieved to <200 mesh, and dried overnight at 90°C. The sample lost 5 wt% during drying or 25% of the total water in the as-received sodium aluminate as determined by STG.

The samples used for the catalyst and initiator screening study were prepared by mixing the C/I with the oxidant. The sodium nickel ferricyanide was then mixed 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 ferricyanide as shown in equations 1 and 2. The reactions resulting in N_2 and CO_2 produce the greatest amount of energy for the ferrocyanide reaction (Burger 1993).

The composition of each of 16 different C/I test samples was selected to allow use of statistically based analytical methods to identify significant factors. The amount of each of the C/I samples was equivalent to 3 mol% of the ferricyanide. The concentration for each of the components in these samples is given in Table 1.

Table 1. Composition of Tested Samples

Treatment	Concentration, Mole Per Mole Ferricyanide						
	NaNiFe(CN) ₆	NaNO ₃	NaNO ₂	Cr ^(a)	Fe ^(a)	Ni ^(a)	EDTA ^(b)
Control	1	4.12	4.12	0	0	0	0
E ^(c)	1	4.12	4.12	0	0	0	0.033
N ^(d)	1	4.12	4.12	0	0	0.033	0
E*N ^(e)	1	4.12	4.12	0	0	0.033	0.033
F ^(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 ^(g)	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) Sodium ethylenediaminetetraacetate.

(c) E is EDTA.

(d) N is Ni(OH)₂.

(e) E*N is a treatment combination.

(f) F is Fe(OH)₃.

(g) C is Cr(OH)₃.

2.2 Test Methods

To investigate the effects of various materials on the reactivity and explosivity of ferrocyanide wastes, we used the PNL time-to-explosion (TTX) test, which is a modification of the so-called Henkin test method developed by Henkin and McGill (1952) and later employed by Caldwell et al. (1984) and Faubian (1984). We have used the PNL TTX test (Burger and Scheele 1991; Scheele et al. 1992c) to investigate the effects of selected potential C/Is on the explosivity of cesium or sodium nickel ferrocyanides. We also used differential scanning calorimetry (DSC) and STG to measure thermal sensitivities and to provide insight on the chemical mechanisms.

The PNL TTX test is particularly effective for determining the relative effects of composition on explosivity because the test is designed to measure TTX (reaction) at a particular temperature and thus embeds kinetic information within its results.

In TTX testing, a 5-mm-diameter test tube (a thin wall nuclear magnetic resonance tube) containing 60 to 100 mg of sample is placed snugly into a 2.75-cm-deep hole in an insulated, heated stainless steel right cylinder measuring 3.6 cm diameter by 4 cm tall. Cylinder temperature is monitored using a thermocouple located in an adjacent hole. The cylinder is heated using a hot plate, and the temperature is maintained as desired by a temperature controller. The time from insertion to explosion is measured and recorded along with any visual observations.

For the TTX test, an explosion is defined as either a loud noise or a flash of light; often both occur. If no pronounced chemical reaction occurs within nominally 30 min, the test is stopped. The absence of an explosion does not mean an exothermic reaction did not occur. Gases that normally evolve during the testing of ferrocyanide and nitrate and/or nitrite mixtures include oxides of nitrogen (identified by the characteristic brown color of NO_2 produced either just above the reaction mixture or slightly higher after the NO reacts with air), and often the contents of the tube are splattered at lower temperatures. Although the explosion itself occurs at a temperature much greater than exists in the waste tanks, a reaction begins in the TTX test at a much lower temperature (Scheele et al. 1992b). The TTX test provides one of the best measurements of the true hazard of an oxidant-reductant mixture, because it indicates whether a reaction stops or proceeds to the explosion point. The deficiency in the TTX test is that it does not in itself predict the explosion temperature of a larger sample or of samples at different geometries. But coupled with other thermal sensitivity tests, such as DSC, the TTX test results allow preliminary predictions of the minimum temperature at which an explosion could occur. In addition, the critical temperature determined using a Henkin test can be extrapolated to larger sample sizes by using the Frank-Kamenetskii equation (Frank-Kamenetskii 1969), given the geometry, heat of reaction, activation energy, the Arrhenius equation pre-exponential, density, and thermal conductivity.

Differential scanning calorimetry and STG measure enthalpy and mass changes, respectively, as the temperature is increased at a known and constant rate. These methods can provide an observed reaction start temperature, an onset temperature, enthalpy of reaction, mass change due to a reaction, and kinetic parameters. Interpretation of the results from these two analytical techniques can be complicated by overlapping reactions. For example, if an exothermic reaction occurs simultaneously with an endothermic reaction, the magnitude of DSC response will be different than if each reaction occurred independently.

3.0 Diluent Studies

We performed two sets of studies to determine the diluent effects of different potential ferrocyanide waste constituents. The objective of the first study was to investigate the effect of the oxidant- (equimolar sodium nitrate and nitrite) to-ferrocyanide ratio. For the second study, our objective was to determine the effect of a nonparticipating material having a low heat capacity.

We hypothesized two mechanisms whereby a material could function as a diluent. The first mechanism acts to absorb the heat produced by the reaction between ferrocyanide and the nitrate and/or nitrite oxidant. The second mechanism acts by reducing the number of collisions between the two reactants. In a past report (Scheele et al. 1992b), we presented thermodynamic calculations, with respect to diluent effects, that indicated it would require about 3 g of water, or 25 g of sodium nitrate, or 60 g of sodium aluminate to prevent the reaction temperature for a near-stoichiometric mixture of 1 g of sodium nickel ferrocyanide and 1.6 g of sodium nitrate from reaching 200°C and thus thermal runaway. The differences in the amount of diluent required are the results of different heat capacities and different physical behaviors, such as boiling or melting.

3.1 Oxidant and Ferrocyanide as Diluents

The most explosive mixture of ferrocyanide and a nitrate and/or nitrite should be a stoichiometric mixture. That is, if the explosive reaction proceeds via the most energetic postulated reactions, which recent results obtained by Fauske suggest may not be the case (Jeppson and Wong 1993), the mixture would contain 6 moles of NaNO_3 or 10 moles of NaNO_2 per mole of ferrocyanide. Without any excess material to absorb the heat produced by the reaction, temperature should increase at the maximum rate possible, and the reaction will occur at the fastest rate possible. If the ratio of oxidant-to-ferrocyanide differs either direction from stoichiometry or if other diluents are present, the reaction rate should be lower.

To investigate the effect of the oxidant-to-ferrocyanide ratio, we used the TTX test, about 20 mg of sodium nickel ferrocyanide, and the requisite amount of equimolar sodium nitrate and nitrite to achieve the desired ratio. Each experiment was terminated after 30 min, which is the normal maximum time used for the Henkin test.

The results of this portion of the diluent study are shown in Figures 1 and 2. Figures 1 and 2, respectively, present the dependency of TTX and sound emitted at different temperatures on the composition of the tested mixture, respectively. The composition of the mixture is presented in terms of stoichiometry for the most energetic postulated reactions for nitrate and nitrite. That is, at a ratio of 4, there is 4 times the stoichiometric amount of oxidant present, while at a ratio of 0.5, there is half the needed oxidant for complete oxidation via the most energetic pathways.

A number of conclusions can be drawn based on the data in Figures 1 and 2. According to Figure 1, the range of compositions that produced explosive reactions varied depending on temperature, with the

Figure 1. Effect of Stoichiometric Oxidant-to-Ferrocyanide Ratio on Explosivity Within 30 Min in PNL TTX

largest range occurring at the highest temperature. At 400°C, the explosive mixtures ranged from a stoichiometric ratio of 0.1 to 2.5, and at 320°C, the explosive mixtures ranged from a stoichiometric ratio of 0.5 to 1.0. Mixtures having less or more oxidant than these did not explode. The explosivity of a mixture significantly deficient of oxidant is somewhat surprising to us. Our past PNL TTX tests indicated that sodium nickel ferrocyanide does not explode by itself at temperatures up to 400°C.

Figure 2 suggests first that, as expected, the stoichiometric mixture is the most explosive, and that the sounds from the explosions for near-stoichiometric mixtures are nearly equivalent independent of temperature. Second, the range of explosive mixtures is smaller at lower temperatures. Third, a mixture of ferrocyanide and equimolar sodium nitrate and nitrite is explosive even at a deficiency of oxidant. For example, a mixture with an oxidant-to-ferrocyanide stoichiometric ratio of 0.1 is explosive at 400°C. Fourth, since the sounds are nearly equivalent for explosions of near-stoichiometric mixtures independent of temperature, temperature may have little or no effect on the peak energy of the explosive reaction.

In drawing conclusions regarding the absolute behavior of the tested mixture, remember that the results of the Henkin test are dependent on a number of factors including geometry, confinement, and mass. The PNL TTX test as used here allows comparison of different test conditions and provides a relative measure of explosivity. It would be expected that testing at a larger scale would affect the results.

Figure 2. Effect of Oxidant-to-Ferrocyanide Ratio on Explosion Sound Level in Mixtures of $\text{Na}_2\text{NiFe}(\text{CN})_6$ and Equimolar $\text{NaNO}_3/\text{NaNO}_2$

3.2 Sodium Aluminate (Inert) as Diluent

In this second set of experiments to investigate the diluent effects of other waste constituents, we studied the effect of sodium aluminate concentration on the explosivity of a near-stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite using two experimental approaches. In the first approach, we determined the TTX at 350° and 400°C for samples containing differing amounts of sodium aluminate. In the second approach, we measured the TTX (60-min time limit) of mixtures containing 2 and 4 g of sodium aluminate per g of sodium nickel ferrocyanide as a function of temperature. For both approaches, we used the PNL TTX test and about 25 mg of sodium nickel ferrocyanide with the requisite amount of oxidant and desired amount of added sodium aluminate. The test sample was mixed by shaking before testing to ensure homogeneity.

Sodium aluminate was selected for study because it has a low heat capacity, it does not undergo phase transition until it reaches very high temperatures, and it should not react with either ferrocyanide, nitrate, or nitrite. Sodium aluminate is representative of those materials that will not participate in the reaction and will not slow the reaction by absorbing excessive amounts of heat.

The results of the inert, low heat capacity diluent studies are presented in Figures 3 and 4. Figure 3 presents the results of the first experimental approach and shows the dependency of the TTX on the concentration of sodium aluminate at 350° and 400°C. Figure 4, which presents the results of the second approach, compares the behavior of mixtures with weight ratios of 2:1 and 4:1 sodium aluminate-to-sodium nickel ferrocyanide to the behavior of a mixture without added aluminate.

As shown in Figure 3, a near-stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite remains explosive up to an added sodium aluminate-to-sodium nickel ferrocyanide weight ratio of 12:1 at 350° and 400°C. Figure 3 also shows that small amounts of added aluminate increase the TTX. However, above a particular level, 2 g/g at 400°C and 4 g/g at 350°C, added aluminate causes either a less significant change or no further increase in the TTX. Because we exceeded the volume capacity of our test apparatus, we were unable to determine the amount of aluminate at which explosions would not occur at these two temperatures.

As shown in Figure 4, adding 2 and 4 g sodium aluminate per g sodium nickel ferrocyanide to a near-stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite increased the TTX at different temperatures relative to the reference. For example, at 380° and 340°C, adding 2 g/g increased the TTX from 22 to 45 s, and from 45 to 125 s, respectively. Doubling the aluminate-to-ferrocyanide ratio from 2:1 to 4:1 had a less dramatic effect. At 380° and 340°C, doubling

Figure 3. Effect of Sodium Aluminate Concentration on the Explosivity of a Near-Stoichiometric Mixture of $\text{Na}_2\text{NiFe}(\text{CN})_6$ and Equimolar $\text{NaNO}_3/\text{NaNO}_2$

Figure 4. Effect of Added Sodium Aluminate on the TTX of a Mixture of $\text{Na}_2\text{NiFe}(\text{CN})_6$ and Equimolar $\text{Na}_2\text{CO}_3/\text{NaNO}_2$

the weight ratio from 2:1 to 4:1 delayed the explosion by 10 s and 50 s, respectively. Adding aluminate at the 2 and 4 g/g levels caused the minimum observed explosion temperature to increase from 290° to 340°C at a test time of 60 min; no explosion occurred at 320°C with aluminate added at these two levels.

A long incubation time, 60 min, was required for the mixture to explode at 290°C. Based on the sample size and earlier test results, we are confident that the sample reached temperature within 10 s. This long incubation time indicates that there was(were) precursor reaction(s) to the explosive reaction(s). The minimum temperature at which an explosion occurs depends on the kinetics of the rate controlling reaction. Isothermal studies at lower temperatures using both calorimetric and gravimetric methods are recommended to investigate the mechanism and to measure kinetic parameters for the precursor reaction(s).

In determining the diluent effects of other potential ferrocyanide waste constituents on the explosivity of ferrocyanide and nitrate and nitrite mixtures, these studies showed that the higher heat capacity equimolar sodium nitrate and nitrite was more effective in preventing an explosion than the lower heat capacity sodium aluminate. Note that the sodium nitrate and nitrite was liquid at the explosion temperature, whereas the sodium aluminate was solid, which may explain some of the behavior difference.

In summary, these diluent studies show that other waste constituents can effectively prevent an explosive reaction from occurring, depending on concentration. The amounts of materials found to be required to prevent explosion cannot be considered absolute because of geometry and mass dependencies of thermal explosive behavior. To determine absolute amounts and to predict the behavior of large samples:

1) measure activation energies and Arrhenius pre-exponentials for the explosive ferrocyanide and nitrate and nitrite reactions, 2) test other sample configurations, and 3) perform calculations using the Frank-Kamenetskii equation (Frank-Kamenetskii 1969). We recommend that the necessary testing and calculations be performed to predict the behavior of the expected masses and geometries of ferrocyanide wastes present in the Hanford Site waste tanks.

4.0 Catalyst and Initiator Studies

Ferrocyanide wastes may contain materials that could act as catalysts or initiators, thereby accelerating the reaction or reducing the initiation temperature of the reaction between alkali nickel ferrocyanides and nitrate and/or nitrite. To investigate the effects of selected materials on the reactivity of ferrocyanide wastes, we performed two sets of experiments. First, we studied the effects of EDTA and hydroxide precipitates of chromium (III), iron (III), and nickel (II) on the explosivity of a near-stoichiometric mixture of sodium nickel ferricyanide (a potential aging product) and equimolar sodium nitrate and nitrite. In the second study, we looked at the effect of added nickel sulfide, which would have resulted from scavenging of radiocobalt just before radiocesium scavenging, on the explosivity of a near-stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite. We also studied the thermal reactivity of sodium nickel ferrocyanide and sodium nickel ferricyanide. The results are presented in the Appendix.

4.1 Screening Study of Sodium Nickel Ferricyanide

In this section, we discuss 1) the results of our screening study to identify potential ferrocyanide waste constituents that could affect the explosivity of aged ferrocyanide wastes containing a potential preliminary oxidation product, ferricyanide, and 2) preliminary studies to measure thermal sensitivity. We investigated the effects of EDTA and the hydroxide precipitates of chromium (III), iron (III), and nickel (II) on the explosivity of a near-stoichiometric mixture of sodium nickel ferricyanide and equimolar sodium nitrate and nitrite. This study was not designed to determine the effect of these materials on the minimum explosion temperature. That objective is reserved for future studies in which the effect of the material and its concentration on the explosivity of potential ferrocyanide wastes will be investigated.

Our approach for this study was the same used for work conducted by Scheele et al. (1992c). The earlier work identified potential ferrocyanide waste constituents or combinations of potential waste constituents that could act as catalysts or, by reactions of their own with the ever present nitrate and nitrite, could initiate the explosive ferrocyanide and nitrate/nitrite reaction(s). Both studies used a partial replication of a 2-level full factorial experiment in a randomized experimental block design. This design allowed us to use the Dunnett test (Dunnett 1955) to identify, at the 95% confidence level, whether an additive or treatment affected the TTX relative to the reference mixture or the control mixture. We conducted 4 sets of 33 tests; i.e., 1 set per day for 4 days, 132 tests in all. The TTX was measured at four different temperatures: 285°, 320°, 350°, and 380°C with a time limitation of 20 min per test. The 285°C level was based on experiments conducted to determine the minimum temperature. The four temperatures were randomly assigned to the individual experimental apparatus. Each catalyst/initiator (C/I) was added at the rate of 0 or 0.03 mole/mole ferricyanide, and the same order of C/I addition was maintained in all 4 test sets.

Screening Study Results

The objective of this screening study was to identify materials or types of materials that could affect the TTX of a mixture of the potential ferrocyanide aging product sodium nickel ferricyanide and equimolar sodium nitrate and nitrite. The experimental results of the testing are presented in Table 2 and Figure 5. Figure 5 presents the natural log of time versus each treatment. To allow easy comparison of the treatment results to the reference or control mixture of sodium nickel ferricyanide and equimolar sodium nitrate and nitrite, we included a line across the graph at the TTX measured for the control. Figure 5 presents the mean results as the natural log of time because if the rate-determining step(s) for the explosive reaction follows Arrhenius kinetic behavior, the log of the rate constant will be proportional to reciprocal temperature in K with the slope equal to the activation energy E_a .

In general, Figure 5 shows that very few of the treatments affected the TTX at all temperatures. A few of the treatments, predominately those with EDTA, appeared to reduce the TTX, though not by much. Figure 5 also shows that temperature affects the TTX of the sodium nickel ferricyanide and sodium nitrate and nitrite mixture.

Using the data in Table 2, we conducted a statistical analysis to identify those materials that reduced the TTX. We used the natural logarithm of time based on the assumption that the explosive reaction follows Arrhenius kinetic behavior. To identify the active materials, analysis of variance (AOV) methodology was used. We first investigated the full model including the four additives and temperatures. This first AOV indicated that temperature accounted for over 90% of the total variability. Thus, we performed a four-factor analysis at each temperature to investigate the effects of each C/I.

Using separate AOVs for each of the four temperatures, the effects of each treatment were tested for statistical significance by comparing the mean for each of the 15 additive combinations with the mean of the control tests. This comparison was made using Dunnett's (1955) test. Dunnett's test maintains a 95% confidence level (less than a 5% chance of judging a difference significant when it is not significant) for all comparisons made at a particular temperature. The results of this analysis are presented in Table 3 and in Figure 5.

As indicated in Table 3 and in Figure 5, only one treatment had a statistically significant effect on the TTX at the 95% confidence level, and that effect occurred only at the highest temperature. The addition of EDTA reduced the TTX of the ferricyanide, nitrate, and nitrite mixture at 380°C. As we found in our screening studies to identify active potential ferrocyanide waste constituents for wastes containing sodium nickel ferrocyanide, only those treatments including EDTA significantly reduced the TTX at the 95% confidence level and then only at temperatures $\geq 350^\circ\text{C}$.

The lack of a statistically significant effect for all but the EDTA treatment may result from the large confidence intervals around the treatment means. The width of the confidence interval is dependent on experimental variability, the number of replicate tests used to estimate the variability, the number of observations used to estimate the treatment means, and the confidence level desired.

Table 2. Results from Catalyst and Initiator Screening Study of NaNiFe(CN)_6 and $\text{NaNO}_3/\text{NaNO}_2$ Mixtures

Treatment ^(a)	Time-to-Explosion, s			
	287°C	320°C	350°C	380°C
Control	715	55	21	9
		48	19	11
		36	20	11
		45	12	11
		42	19	11
		73	13	10
E ^(b)	741	44	16	9
		80	11	7
		50	12	8
N ^(c)	775	33	18	11
		39	19	10
		36	15	9
F ^(d)	767	40	17	13
		56	18	10
		36	17	10
C ^(e)	586	42	17	9
	720	34	18	12
		36	19	12
E*N ^(f)	602	45	11	8
E*F	-- ^(g)	50	12	9
E*C	--	53	16	10
N*F	--	52	17	11
	--	45	19	10
N*C	582	35	17	11
		27	17	10

Table 2. (contd)

Treatment ^(a)	Time-to-Explosion, s			
	287°C	320°C	350°C	380°C
F*C	--	34	17	10
	--	34	18	12
E*N*F	--	34	14	10
E*N*C	--	47	18	10
E*F*C	--	74	17	11
N*F*C	582	32	16	12
E*N*F*C	613	42	17	11
		64	16	10

(a) Additive at 0.033 mole/mole ferricyanide

(b) E is EDTA.

(c) N is Ni(OH)₂.

(d) F is Fe(OH)₃.

(e) C is Cr(OH)₃.

(f) E*N is a treatment combination.

(g) No explosion occurred.

We cannot yet explain the effects of added EDTA on the explosivity of mixtures of sodium nickel ferricyanide or sodium nickel ferrocyanide and nitrate and nitrite. One possible explanation is the destabilization of the iron-cyano complex, which increases the susceptibility of the cyanide to attack by the oxidizing species. Alternatively, the EDTA could react with the oxidizer and provide sufficient heat to increase the reaction rate of the iron-cyano complex with the oxidizing species.

Both our screening studies indicated that ferrocyanide wastes containing EDTA, or possibly other organic complexants or organics, will be more reactive than those without. Thus, these wastes deserve special attention, especially if conditions approach those in which ferrocyanide wastes can react vigorously. To determine if EDTA is unique among the complexants or organics added to the Hanford Site wastes, additional studies are needed to determine the effect of the chemical nature and concentration on both explosivity, as measured by TTX, and thermal sensitivity as measured by a reduction in the minimum observed explosion temperature.

Figure 5. Effect of EDTA (E), $\text{Cr}(\text{OH})_3$ (C), $\text{Fe}(\text{OH})_3$ (F), and $\text{Ni}(\text{OH})_2$ (N) on the Explosivity of a Near-Stoichiometric Mixture of $\text{NaNiFe}(\text{CN})_6$ and Equimolar $\text{NaNO}_3/\text{NaNO}_2$

4.2 Effect of Nickel Sulfide

Before scavenging wastes for radiocesium, radiocobalt was in some cases scavenged by coprecipitating it with NiS. The molar amount of precipitated NiS was normally equivalent to the amount of alkali nickel ferrocyanide used to scavenge the waste for radiocesium, or about 0.3 g NiS/g $\text{Na}_2\text{NiFe}(\text{CN})_6$. Our DSC and STG analyses have shown that NiS is also susceptible to oxidation by nitrate and/or nitrite. Thus, NiS could act as an initiator for the explosive ferrocyanide reaction with nitrate or nitrite.

The results of our study to investigate the effect of NiS on the explosive reaction between sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite are presented in Figure 6. Figure 6 shows the dependency of the TTX on temperature at different amounts of added NiS; the expected NiS level at the time the wastes were created relative to the ferrocyanide is the 0.3 g/g addition.

As shown in Figure 6, the addition of NiS reduced the minimum observed explosion temperature. The minimum observed explosion temperature was reduced from 290°C to 280°C by the addition of 1 g of NiS/g $\text{Na}_2\text{NiFe}(\text{CN})_6$.

Figure 6 also shows that increasing the amount of NiS added to the mixture of ferrocyanide and equimolar sodium nitrate and nitrite reduced the TTX at a given temperature. For example, adding 1 mg of NiS/mg of the ferrocyanide at 340°C reduced the TTX from 40 to 22 s. Similar reductions were observed at other temperatures.

Table 3. Effect of Treatment on the TTX of a Near-Stoichiometric Mixture of NaNiFe(CN)_6 and Equimolar $\text{NaNO}_3/\text{NaNO}_2$

Treatment	N ^(a)	Mean TTX, ln(s)			
		286°C	320°C	350°C	380°C
Control	6	6.57	3.88	2.83	2.35
E ^(b)	3	6.61	4.03	2.55	2.07 ^(c)
N ^(d)	3	6.65	3.58	2.85	2.30
F ^(e)	3	6.64	3.77	2.85	2.39
C ^(f)	3	6.48	3.62	2.89	2.39
E*N ^(g)	1	6.40	3.81	2.40	2.08
E*F	1	--	3.91	2.48	2.20
E*C	1	--	3.97	2.77	2.30
N*F	2	--	3.88	2.89	2.35
N*C	2	6.37	3.43	2.83	2.35
F*C	2	--	3.53	2.86	2.39
E*N*F	1	--	3.53	2.64	2.30
E*N*C	1	--	3.85	2.89	2.30
E*F*C	1	--	4.30	2.83	2.40
N*F*C	1	6.37	3.47	2.77	2.48
E*N*F*C	2	6.42	3.95	2.80	2.35
Mean of Means		6.5	3.78	2.76	2.31
Weighted Mean		6.5	3.78	2.79	2.32
Error sd		0.1456	0.2133	0.1562	0.1132
Relative sd%		2.24	5.65	5.60	4.88

(a) Number of treatment replications for the three higher nominal temperatures. For 286°C, 23 of the 33 tests did not explode after 20 min at temperature, so that 8 treatments had only 1 test and 1 treatment, C, had two tests that exploded.

(b) E is EDTA.

(c) Mean is significantly (one-sided 95% confidence level) smaller than control using Dunnett's test for significant differences from control.

(d) N is Ni(OH)_2 .

(e) F is Fe(OH)_3 .

(f) C is Cr(OH)_3 .

(g) E*N is a treatment combination.

These experiments with NiS show that wastes containing NiS, sodium nickel ferrocyanide, sodium nitrate, and sodium nitrite are more reactive than those wastes without NiS. Remember that these tests were performed with a dry, near-stoichiometric mixture of ferrocyanide and nitrate/nitrite.

Figure 6. Effect of Added NiS on the Explosivity of a Near-Stoichiometric Mixture of $\text{Na}_2\text{NiFe}(\text{CN})_6$ and Equimolar $\text{NaNO}_3/\text{NaNO}_2$

5.0 Conclusions and Recommendations

5.1 Conclusions

Based on the study results presented in this paper, several factors have been observed to affect the reactivity of simulated waste mixtures containing sodium nickel ferrocyanide or ferricyanide and nitrate and nitrite. The ratio of oxidant-to-ferrocyanide that can produce an explosive reaction increases as a function of temperature. Ratios less than the stoichiometric ratio, for the most energetic postulated reactions, can produce explosions, but the most explosive mixture is the mixture that contains the stoichiometric mass ratio of oxidant-to-ferrocyanide. No explosion is observed for sodium nickel ferrocyanide (without oxidant). Inert diluents do increase the TTX, but up to a diluent-to-ferrocyanide mass ratio of 12:1, the explosive reaction is still observed at temperatures $\geq 350^{\circ}\text{C}$. Certain materials can act as catalysts or initiators and accelerate the explosive reaction or reduce the minimum observed explosion temperature.

Of the catalysts and initiators tested, only EDTA and NiS caused a reduction in the TTX for the tested mixtures of sodium nickel ferricyanide or ferrocyanide with sodium nitrate and nitrite, respectively. Addition of EDTA to the ferricyanide-containing mixture causes a statistically significant effect only at the highest temperature tested (380°C). Addition of NiS at twice the expected average amount to a ferrocyanide-containing mixture can reduce the minimum explosion temperature from 290° to 280°C . As the NiS concentration is increased, the TTX decreases. It was also observed that sodium nickel ferricyanide was more thermally sensitive than the ferrocyanide; therefore, mixtures containing sodium nickel ferricyanide will be more reactive than those containing ferrocyanide.

5.2 Recommendations

Based on the study results described in this and earlier reports, we recommend the following:

1. Conduct a quantitative investigation to determine concentration effects of those materials that were identified as having a catalytic or initiating effect in the screening study discussed in this report. In this investigation explosion temperature and thermal behavior should be tested as a function of additive concentration. Methods applicable to this study include DSC, STG, STG coupled with mass spectroscopic analysis of evolved gases, and adiabatic reaction calorimetry (ARC). The latter would be particularly useful to determine more accurate temperature and energy data.
2. Conduct tests to determine the effects of other potential catalysts, including manganese and chloride ion, and to determine the additional effects of excess sodium hydroxide.
3. Although the TTX test provides excellent comparisons between the explosivities of small sample-size mixtures, it does not predict explosion temperatures of larger quantities. Therefore, conduct either larger-scale tests or tests to determine activation energies and the Arrhenius pre-exponential, and tests with carefully defined geometries that could be used with the Frank-Kamenetskii equation to predict critical explosion temperatures.

4. The reaction mechanism remains a question. The oxidation of ferrocyanides or ferricyanides is complex, and the steps occur over a considerable temperature range. It is not known how diluents, catalysts, or initiators affect these steps. EDTA showed an effect at low temperatures, but the details of the reaction were obscured by the oxidant melting endotherm. Therefore, conduct additional DSC and STG experiments combined with mass spectrometry and infrared analysis of reaction products; also consider using ARC.

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Appendix

Preliminary Comparison of the Thermal Reactivity of Sodium Nickel Ferrocyanide and Ferricyanide

Appendix

Preliminary Comparison of the Thermal Reactivity of Sodium Nickel Ferrocyanide and Ferricyanide

The question has arisen about the effect of aging on the reactivity of Hanford Site ferrocyanide wastes. To at least partially address this question, we compared the results from our DSC and STG analyses, and the screening studies for mixtures of sodium nickel ferricyanides and ferrocyanides. To compare the results of the two screening studies, we used Student's t-test (Meyer 1975) to determine if the sodium nickel ferricyanide, a potential aging product of sodium nickel ferrocyanide, demonstrated a higher level of explosivity than its parent, as measured by TTX. As part of our studies to determine the thermal sensitivities of ferrocyanide wastes, we used DSC and STG to determine the thermal sensitivity of a near-stoichiometric mixture of sodium nickel ferricyanide and equimolar sodium nitrate and nitrite. Figure A.1 presents the DSC analysis of the ferricyanide mixture and for comparison, Figure A.2 presents the DSC analysis for a near-stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite. Figure A.3 presents the STG analysis of the ferricyanide mixture.

Comparison of Figures A.1 and A.2 shows somewhat similar behavior for ferricyanide and ferrocyanide, with the major exotherm for both mixtures having a peak minimum near 300°C. The ferricyanide peak minimum occurs at about 290°C compared to 305°C for the ferrocyanide. There are, however, significant differences in the thermal sensitivities of the two mixtures. For the ferrocyanide mixture, an endothermic reaction occurs at about 225°C, which we attribute to the melting of the nitrate and nitrite salt mixture. However, for the ferricyanide mixture, this endotherm is absent. Instead, an exotherm is observed, having sufficient energy to prevent observation of the melting endotherm. The presence of the exotherm indicates that a significant exothermic reaction begins as soon as the oxidant begins to melt.

There are also significant differences in the nature of the oxidation after the melting of the nitrate and nitrite mixture. The ferrocyanide reaction is characterized by at least two major rapid exothermic reactions having peak minimums at 305° and 335°C, while the DSC thermogram for the ferricyanide reaction is characterized by a single rapid exotherm having a peak minimum at 290°C. In both cases, there appears to be a slower reaction occurring simultaneously with the rapid reactions. The heat released between 240° and 370°C for the ferricyanide mixture was nominally 4,000 J/g $\text{NaNiFe(CN)}_6 \cdot X \text{H}_2\text{O}$ compared to 4,800 J/g $\text{Na}_2\text{NiFe(CN)}_6 \cdot X \text{H}_2\text{O}$ between 250° and 350°C.

Figure A.1. Differential Scanning Calorimetric Analysis of a Mixture of NaNiFe(CN)_6 and Equimolar $\text{NaNO}_3/\text{NaNO}_2$ in a Nitrogen Atmosphere

The lower temperature observed for the major rapid exotherm in the ferricyanide mixture and the exotherm observed at 230°C suggest that the ferricyanide mixture should show greater temperature sensitivity and, thus, a lower minimum observed explosion temperature in a small-scale explosion test. Within a 20-min time limit, the minimum observed explosion temperature for the ferrocyanide mixture was 295°C (Hallen et al. 1992) compared to the 285°C observed for the ferricyanide mixture.

The STG analysis of the ferricyanide mixture is consistent with the DSC results. The differential of the STG curve (DSTG) shows rapid mass losses occurring at 240° and 310°C, with slower reactions having peaks at 350° and 370°C. The STG analysis indicates that a rapid reaction begins at about 230°C.

Table A.1 shows the behavior differences by comparing the results of the two C/I screening studies. Table A.1 presents the mean TTXs for the two control mixtures containing either the ferrocyanide or ferricyanide alone and the average of the natural log of the TTX for the 33 tests of both ferrocyanide and ferricyanide at each temperature (see Table 3 and Scheele et al. 1992c).

We used Student's t-test (Meyer 1975) to test the hypothesis that the two cyano mixtures have the same explosive behavior at 380°C and found that the two mixtures behave differently at a confidence greater than the 99.9% level. Since the behaviors of the two mixtures were most similar at 380°C, it follows that at the lower temperatures where greater differences exist, mixtures of equimolar sodium nitrate and nitrite and sodium nickel ferrocyanide or ferricyanide exhibit different explosivities. In general, the ferricyanide was more thermally sensitive. This conclusion is consistent with the results of the DSC analyses.

Figure A.2. Differential Scanning Calorimetry Analysis of Reaction Between $\text{Na}_2\text{NiFe}(\text{CN})_6$ and Equimolar $\text{NaNO}_3/\text{NaNO}_2$ in a Nitrogen Atmosphere

Figure A.3. Scanning Thermogravimetric Analysis and Differential STG of a Mixture of $\text{NaNiFe}(\text{CN})_6$ and Equimolar $\text{NaNO}_3/\text{NaNO}_2$

Table A.1. Comparison of Explosive Behavior of Mixtures of NaNiFe(CN)_6 or $\text{Na}_2\text{NiFe(CN)}_6$ and Equimolar NaNO_3 and NaNO_2

Temperature, °C	Mean TTX, ln(s)			
	Control Mixture ^(a)		All Treatments	
	$\text{Na}_2\text{NiFe(CN)}_6$	NaNiFe(CN)_6	$\text{Na}_2\text{NiFe(CN)}_6$	NaNiFe(CN)_6
296 (287) ^(b)	7.13	6.57	7.02	6.50
320	5.71	3.88	5.38	3.78
350	3.40	2.83	3.26	2.76
380	2.91	2.35	2.72	2.31

(a) Control mixture contains sodium nickel ferrocyanide or ferricyanide alone and equimolar sodium nitrate and nitrite, i.e., no treatments.

(b) The minimum temperatures used were 296° and 287°C for the ferrocyanide and ferricyanide mixtures, respectively.

The result of this comparison of explosivities of the two iron-cyano complexes indicates that though the original ferrocyanide may have aged or oxidized, it is not necessarily less reactive—rather, it could be potentially more reactive. This result highlights the importance of understanding the aging reactions that are likely in Hanford ferrocyanide wastes.

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