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**Ferrocyanide Safety Project
Dynamic X-Ray Diffraction Studies
of Sodium Nickel Ferrocyanide Reactions
with Equimolar Nitrate/Nitrite Salts**

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Summary

Dynamic X-Ray Diffraction (DXRD) has been used to identify and quantify the solid state reactions that take place between sodium nickel ferrocyanide, $\text{Na}_2\text{NiFe}(\text{CN})_6$, and equimolar concentrations of sodium nitrate/nitrite, reactions of interest to the continued environmental safety of several large underground waste storage tanks at the Hanford site in eastern Washington. The results are supportive of previous work, which indicated that endothermic dehydration and melting of the nitrates take place before the occurrence of exothermic reactions that begin about 300°C . The DXRD results show that a major reaction set at these temperatures is the occurrence of a series reaction that produces sodium cyanate, NaCNO , as an intermediate in a mildly exothermic first step. In the presence of gaseous oxygen, NaCNO subsequently reacts exothermally and at a faster rate to form metal oxides. Measurements of the rate of this reaction are used to estimate the heat release. Comparisons of this estimated heat release rate with heat transfer rates from a hypothetical "hot spot" show that, even in a worst-case scenario, the heat transfer rates are approximately eight times higher than the rate of energy release from the exothermic reactions.

Abbreviations

DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DXRD	dynamic x-ray diffraction
EIS	Environmental Impact Statement
FTIR	Fourier transform infrared (spectroscopy)
GAO	General Accounting Office
ICP/AES	inductively coupled argon plasma atomic emission spectroscopy
IR	infrared
MS	mass spectroscopy
PNL	Pacific Northwest Laboratory
SEM	scanning electron microscopy
SST	single-shell waste storage tank at Hanford
STG	scanning thermogravimetry
TTX	time to explosion
USQ	unreviewed safety question
WHC	Westinghouse Hanford Company

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1.0 Introduction

The research performed for this project is part of an effort that started in the mid-1980s to characterize the materials stored in the single-shell waste storage tanks (SSTs) at the U.S. Department of Energy (DOE) Hanford Site. Various radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s.

During the 1950s, additional tank storage space was required to support the defense mission. Hanford Site scientists developed two procedures to obtain this additional storage volume within a short time period without constructing additional storage tanks. One procedure involved the use of evaporators to concentrate the waste by removing water. The second procedure involved developing precipitation processes for scavenging radiocesium and other soluble radionuclides from tank waste liquids. The scavenging processes used sodium and potassium ferrocyanide and nickel sulfate to precipitate radioactive cesium from solutions containing nitrates and nitrites. Radioactive strontium and cobalt were scavenged from some of the solutions using calcium or strontium nitrate and sodium sulfide respectively. After allowing the radioactive precipitates to settle, the decontaminated solutions were pumped to disposal cribs thereby providing additional tank storage volume. Later, some of the tanks were found to be leaking and pumpable liquids were removed from these tanks, leaving behind a wet solid (sludge) residue containing the ferrocyanide precipitates.⁽¹⁾ In implementing this process, approximately 140 metric tons of ferrocyanide, [calculated as $\text{Fe}(\text{CN})_6^{4-}$], was added to waste that was later routed to 24 large underground (750,000-1,000,000 gallon) single-shelled tanks (SSTs).

The explosive nature of ferrocyanides in the presence of oxidizers has been known for decades, but the conditions under which impure mixtures containing nitrates and nitrites can undergo propagating reactions have not been thoroughly studied. At the Hanford Site, 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. The investigation found that cesium zinc ferrocyanide and nitrate exploded when heated.⁽²⁾ In the laboratory mixtures of ferrocyanide and oxidizing materials, such as nitrates and nitrites, have been shown to undergo energetic reactions when heated to high temperatures (above 270°C) or exposed to an electrical spark of sufficient energy to heat the mixture. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate and nitrite, an intimate mixture of ferrocyanides and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

Efforts have been under way since the mid-1980s to evaluate the potential for ferrocyanide reactions in Hanford Site SSTs.^(3,4) The 1987 Environmental Impact Statement (EIS), *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington*,⁽⁵⁾ included an environmental impact analysis of potential explosions involving ferrocyanide-nitrate mixtures. The EIS postulated that an explosion could occur during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a short-term radiation dose of approximately 200 mrem. A General Accounting Office (GAO) study⁽⁶⁾ postulated a greater worst-case accident, with independently calculated doses of one to two orders of magnitude greater than postulated in the DOE EIS. Uncertainties regarding the safety envelope of the Hanford Site ferrocyanide waste tanks led to the declaration of the ferrocyanide unreviewed safety question (USQ) in October 1990.

Despite the fact that the measured temperatures in these tanks continue to drop (3°C/year) and the highest temperature currently recorded is 56.7°C,⁽⁷⁾ there has been a good deal of speculation as to the possibility of "hot spots" forming in the tanks due to radiolytic heating. In order to address these concerns, a number of studies have been conducted by Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory (PNL)^(a) and others in an effort to identify the reaction(s) that occur and to quantify the magnitude of the energy released during reaction(s).^(3,4,8-12) Although these studies have yielded many insights, the specific reactions have yet to be identified and the prevailing reaction rates have yet to be quantified.

Since thermally explosive reactions only occur when exothermic reaction (heating) rates exceed the heat transfer (cooling) rates, the goal of the present study was to obtain the necessary reaction and rate data. Specifically, dynamic x-ray diffraction (DXRD),^(13,14) a technique that can follow a reaction between solids and show the appearance or disappearance of reacting crystalline species, was used to identify the reactions that occur between sodium nickel ferrocyanide and equimolar sodium nitrate and sodium nitrite mixtures. The measured rate of reaction for key reaction(s) was then compared to the rate of heat dissipation in the tank to assess the possibility of runaway reaction(s).

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

2.0 Background

Synthetic sodium nickel ferrocyanide wastes were produced by Westinghouse Hanford Company (WHC) in order to study the behavior of the ferrocyanide wastes in a nonradioactive environment. Three different ferrocyanide flowsheet simulants were produced by following the three flowsheets; U-Plant, In Farm and T Plant, used to produce the original wastes.⁽¹⁵⁾ The compositions of each of these waste types was significantly different since scavenging treatments varied according to feed-stream composition, process development and chemicals available at a particular time.

PNL has estimated the chemical formula of synthetic sodium nickel ferrocyanide to be $\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ based on elemental analysis using inductively coupled argon plasma atomic emission spectroscopy (ICP/AES), scanning thermogravimetry (STG), and total cyanide analysis.⁽¹¹⁾ To determine thermochemical reactivity of ferrocyanide-nitrate/nitrite reactions, early studies used differential scanning calorimetry (DSC),^(1,4,9,11) STG,^(9,12) differential thermal analysis (DTA),^(8,10) time to explosion (TTX),^(4,9,12) pyrolysis/mass spectroscopy (MS),^(11,12) and thermodynamics.⁽¹¹⁾ The results indicated that the reaction between sodium nickel ferrocyanide and sodium nitrate and sodium nitrite is complex and multistep. Differential scanning calorimetry, which measures enthalpy changes, detected only endothermic reactions prior to 220°C. Exothermicity began at 230°C and was followed by a rapid exothermic reaction at 300°C and ended with a final endothermic reaction at 410°C.^(1,4,9,12)

Scanning thermogravimetry, which measures weight changes during a chemical reaction, showed that weight losses accompanied the exothermic and endothermic reactions.^(9,12) Differential thermal analysis, which provides a measure of the initiation of a reaction and its onset temperatures, did corroborate the results of the DSC measurements^(4,10) and, in addition, DCS, DTA, and STG experiments all indicated that there are differences in the mechanisms for the nitrate reaction and the nitrite reaction with ferrocyanide. However, since these three methods can measure only the net reaction effects and are not capable of distinguishing among simultaneous events, they did not provide any data about the reaction sequences or products that form. Time to explosion experiments, on the other hand, measure the time in seconds until an explosion occurs (indicated by either a flash of light or loud noise). The TTX procedure employed a 50 to 100 mg sample containing 20 to 30 mg of ferrocyanide which was placed in a metal block at temperatures ranging from 280 to 400°C. The TTX results^(4,9,12) varied with the sample composition and handling procedures, but the variations did corroborate the overall complexity of the reaction. The TTX data also indicated that the reaction mechanism changes at about 350°C, although no explanation was available. A "pyroprobe" equipped with a mass spectrometer (MS) was also used to measure the mass of gaseous chemical species that are produced at different temperatures during a chemical reaction.⁽¹¹⁾ As the temperature was raised at 5°C/min, a "washed" ferrocyanide flowsheet simulant sample produced H_2O up to 250°C, N_2 and/or CO

between 200°C and 500°C, N₂O and/or CO₂ between 200°C and 500°C, NO between 150°C and 300°C, and HCN between 200°C and 250°C. Finally, thermodynamic calculations^(9,11,12) predicted that the most energetic reactions occur when the nitrogen present in the cyanide is released as N₂, as shown in Equations (1) and (2).

Wells⁽¹⁶⁾ reported on the crystal structure of complex ferrocyanides and showed that several of them were simple cubic. He also addressed the insertion of waters of hydration into the structure and reported that the water of hydration can, in some cases, displace cyanides out of the cubic lattice. The structure of sodium nickel ferrocyanide was later corroborated by Hallen⁽¹¹⁾ on the basis of x-ray pattern matching to similar ferrocyanide structures.

3.0 Experimental

All measurements were made using the DXRD apparatus shown in Figure 1. Specific details of the DXRD equipment can be found elsewhere,^(13,14) but the equipment consists of a Siemens D-500 diffractometer, a position-sensitive detector, and an Anton-Parr hot stage (a schematic of the latter is shown in Figure 1).

Figure 1. Schematic of DXRD Reaction Chamber

Powder samples were placed on an Inconel[®] heating strip for both non-isothermal (2°C/min to 20°C/min) and isothermal (± 1 K) conditions. Heating strip temperatures were measured and controlled by a type S Chromel-Alumel thermocouple attached to the base of the heating strip. The entire enclosed hot stage, the "DXRD chamber,"

allows gases such as helium or compressed air to be passed through the apparatus at rates up to 250 mL/min. Attempts were also made to qualitatively monitor the gases exiting the DXRD chamber using nondispersive infrared (IR) detectors for CO and CO₂ and a chemilluminescence NO/NO_x detector. However, due to the small sample sizes (0.1 g), CO or CO₂ in the product gases were below the detection limits (200 ppm). The maximum NO concentration observed during these reactions was on the order of 50 ppm and may also include nitrous oxide as well, since the production of ozone by the detector can oxidize N₂O to NO. Nitric oxide and/or nitrous oxide production was observed for a 1:1:1 molar ratio of ferrocyanide:nitrate:nitrite between 180°C and 350°C in helium and between 180°C and 500°C in air, which indicated that differences existed between the air and helium environments. However, the gases produced in a helium environment and their corresponding temperature range did corroborate the results obtained using the MS/pyroprobe at PNL.⁽¹¹⁾

The sample of sodium nickel ferrocyanide used in this work was obtained from PNL and designated as FECN. It was necessary to remove sodium sulfate from this sample due to considerable peak overlapping and, consequently, it was ion exchanged with nitrate to replace the sulfate and had a final chemical formula Na₂NiFe(CN)₆ · 3H₂O.⁽¹¹⁾ Subsequent XRD scans of FECN confirmed the absence of sodium sulfate peaks, but also indicated that there were no excess nitrates. It is possible that these were removed during the washing of the ion-exchanged ferrocyanide.

An equimolar nitrate/nitrite mixture was produced by weighing the sodium nitrate and sodium nitrite, grinding them into a fine powder using a mortar and pestle, melting them on a hot plate to obtain uniform concentrations, and then regrinding the cooled mixture. The mean particle diameter of FECN was measured as 0.4 ± 0.05 μm using a Quantachrome Microscan Particle Size Analyzer and confirmed with scanning electron microscopy (SEM) micrographs. All the ferrocyanide and equimolar nitrate/nitrite mixtures were prepared by sample weighing and admixing, followed by grinding with a mortar and pestle.

The samples employed in this work consisted of equimolar mixtures of sodium nitrate and nitrite with FECN:NaNO₃:NaNO₂ ratios equal to 1:1:1, 1:4:4, and 1:8:8. Selected experiments with the latter were conducted since it most closely corresponds to estimates of what are the most likely current concentrations in the tanks.⁽¹⁾ The 1:4:4 mixture was studied because it is the ratio required to completely oxidize the ferrocyanide, according to Burger and Scheele,⁽⁹⁾ and is shown as Equation 3:

However, the eutectic melting of the equimolar nitrate/nitrite salts used at higher molar ratios (1:8:8) resulted in significant sample melting, which made DXRD observations somewhat difficult. Consequently, the 1:1:1 mixture was used so that the ferrocyanide XRD peaks could be easily followed along with the nitrate/nitrite peaks.

Chemical tests⁽¹⁷⁾ for the detection of ferrocyanide ions $[\text{Fe}(\text{CN})_6]^{4-}$ in the product powders were used to corroborate the XRD data. The test consisted of placing a small sample (0.05 g) of powder into a 5-mL test tube and adding distilled water. The sample was centrifuged to separate undissolved solids, and the supernatant was placed into another 5-mL test tube. A few drops of Fe^{3+} ions from a 10% ferric chloride solution were added to the supernatant to promote the formation of Prussian blue, a dark blue precipitate of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. A detection limit of 20 ppm $[\text{Fe}(\text{CN})_6]^{4-}$ has been reported by Charlot.⁽¹⁷⁾ Fourier transform infrared (FTIR) spectroscopic analyses were also selectively performed to confirm the presence or absence of ferrocyanide, sodium cyanate, nitrate, and nitrite in the reacted sample powders.

4.0 Results

Table 1 lists the XRD lines that were measured during the course of this study and are associated with the cyanide-containing species, which are not commonly found in the literature. Both the hydrated and dehydrated phases of sodium nickel ferrocyanide are included in Table 1 along with sodium ferrocyanide. The latter was found only at temperatures greater than 350°C in helium experiments using the 1:1:1 mixture or a sample of FECN in the absence of nitrates/nitrites. The line for sodium cyanate is also shown, and it was observed in all experiments containing any nitrate/nitrite at temperatures above 290°C.

Table 1. Observed Cyanide XRD Peaks

Major Peaks			
Species	d-spacing	$2\theta^*$	Relative Intensity
$\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$	4.8659	21.201	100.0
	3.5392	29.301	67.8
	2.5149	41.701	97.0
	2.2448	47.001	48.9
	1.7768	60.502	48.2
$\text{Na}_2\text{NiFe}(\text{CN})_6$	4.6493	22.201	100.0
	3.8909	26.601	45.3
	3.464	29.951	62.4
	2.5034	41.901	44.3
	2.3792	44.201	53.8
	2.2181	47.601	53.2
$\text{Na}_4\text{Fe}(\text{CN})_6$	5.8343	17.651	65.3
	2.7811	37.551	100.0
	1.9649	54.202	66.7
NaCNO	2.9161	35.752	100.0

*Cobalt radiation ($\lambda = 1.790$).

Figures 2 and 3 show typical DXRD non-isothermal results in helium with a 1:1:1 mixture and in air with a 1:4:4 mixture, respectively. Based on these results, the reaction sequence is hypothesized to proceed in three separate steps designated as Events A, B, and C (see Figures 2 and 3):

- A - dehydration of the ferrocyanide at $200 \pm 20^\circ\text{C}$
- B - melting of the equimolar nitrate/nitrite at $235 \pm 5^\circ\text{C}$
- C - appearance of degradation products at $300 \pm 10^\circ\text{C}$.

The first major structural change (Event A) occurs at $200 \pm 20^\circ\text{C}$ and is attributed to the dehydration of the ferrocyanide [Equation (4)]:

Since dehydration would be reversible, this result was corroborated by experiments where the synthetic FECN in helium was heated and cooled with and without the addition of water vapor and the results are shown in Figures 4 and 5. The results in Figure 4 are for an experiment where FECN was heated in dry helium from 50 to 222°C and then cooled back down to 45°C . As can be seen in Figure 4, heating FECN in dry helium results in a crystallinity change at 200°C , which remains unchanged even after cooling back to room temperature. On the other hand, when 5% steam is added to the helium gas stream after the crystallinity change at 200°C , the original XRD reflections are recovered upon cooling back to room temperature (Figure 5). Given these results, there is little doubt that the crystallinity change at 200°C is due to the dehydration of the ferrocyanide.

Although sodium nitrate melts at 308°C and sodium nitrite melts at 270°C , mixtures of nitrate and nitrite salts exhibit eutectic melting at temperatures well below the normal melting point of either salt.⁽⁴⁾ Following the dehydration of the ferrocyanide, Figures 2 and 3 show that the equimolar nitrate/nitrite melts at $235 \pm 5^\circ\text{C}$ (Event B), as evidenced by the disappearance of the combined $\text{NaNO}_3/\text{NaNO}_2$ peaks at this temperature ("2" in Figures 2 and 3). Since the melt is noncrystalline, the nitrate/nitrite peaks are not detected in the scans above 240°C .

At about 300°C , the ferrocyanide reacts to form sodium cyanate (NaCNO), which is the primary degradation product associated with Event C. While the sodium cyanate persists throughout the experiments in a helium environment and is clearly evident in Figure 2, it reacts in the presence of oxygen at about 320°C to form Na_2CO_3 , N_2O , and CO_2 , and thus is difficult to see in Figure 3. As the temperature is further increased, the degradation products are more numerous, and these are listed in Table 2 as a function of reactant ratios and gas environment. It is readily apparent in Table 2 that reduced species such as Ni and NiN_3 are only produced in helium and then only at low concentrations of nitrate/nitrite. Although Table 2 shows iron oxide, nickel oxide, and sodium

Figure 2. Sample 1:1:1 ($\text{FeCN}:\text{NaNO}_3:\text{NaNO}_2$), $2^\circ\text{C}/\text{min.}$, in Helium

Figure 3. Sample 1:4:4 ($\text{FECN}:\text{NaNO}_3:\text{NaNO}_2$), $2^\circ\text{C}/\text{min.}$, in Air

Figure 4. Sample FECN, 2°C/min., in Helium

Figure 5. Sample FECN, Cooling @ 2°C/min., 5% Steam in Helium

Table 2. Products from Reactions Above 350°C

Species Observed	FECN:NO ₃ :NO ₂ -->					
	Helium			Air		
	1:0:0	1:1:1	1:4:4	1:0:0	1:1:1	1:4:4
Fe ₂ O ₃ ^{(a)(b)}		X	X	X	X	X
Ni	X	X				
Ni ₃ N	X	X				
NiO ^b		X	X	X	X	X
Na ₂ CO ₃ ^b		X	X	X	X	X
NaCNO	X	X	X			
Na ₄ Fe(CN) ₆	X	X				
Na ₂ O ₂		X	X			

- (a) In helium, the iron oxide may be Fe₃O₄. A clear distinction was not possible.
(b) Only observed as minor phases in helium.

carbonate forming in a 1:1:1 mixture in helium, these products formed in low quantities and the resulting low XRD peak heights are not obvious in Figure 2. Because different products did form using the different reactant ratios, complete degradation of the ferrocyanide is dependent on the total quantity of equimolar nitrate/nitrite present in the mixture. The formation of oxide products such as nickel or iron oxide was far more substantial in an air environment than in the helium atmosphere. This is probably due to additional reactions with oxygen in the air rather than with the oxygen formed during some of the degradation reactions (see below). Finally, when the sodium nickel ferrocyanide was exposed to high temperatures in helium in the absence of nitrate/nitrite, Na₄Fe(CN)₆ was formed along with Ni and NiN₃. There were a number of unidentified XRD peaks that appeared during these experiments, and it is likely that these are other ferrocyanide species.

Based on the DXRD observations and the wet chemistry analyses, Equations (5) through (11) are the reactions hypothesized to occur in both helium and air immediately following the eutectic melting. However, we should be careful to point out that the reaction network here is probably quite complex. These reactions are hypothesized solely on the basis of the DXRD measurements and supported by limited wet chemistry analyses. The NO given off in reaction (8) between 270 and 320°C is consistent with previous pyroprobe measurements,⁽¹¹⁾ and too small for accurate integration,

Hypothesized Reaction Sequence

270-320°C

290-310°C

300-350°C

but detectable traces of Na_2O were observed by DXRD at these temperatures. In all experiments with nitrates/nitrites, the sodium nickel ferrocyanide reacted to form NaCNO , as shown in reaction (7), which is then further oxidized via reaction (8). The major difference in the two gaseous environments is that, in helium, oxygen reactant is supplied autogenously. Thus reactions (8), (9), and (11) occur very slowly since the generated oxygen can easily escape from the thin samples employed in the experiments. In air, on the other hand, oxygen is readily supplied from the surrounding gas and species such as Ni and Fe_3O_4 are rapidly oxidized so that they are undetected by DXRD. Finally, it should be noted that reaction (8) proceeds very slowly in helium, fueled only by the liberation of O_2 from reactions (5) through (7). It should also be noted that previous observations⁽¹⁸⁾ indicate that this reaction is accelerated in the presence of small quantities of iron and nickel oxide. In discussing these reactions, it must be emphasized that several of these reaction steps could be bypassed if heating rates were excessive. No attempts were made in this study to identify alternative reaction pathways at high heating rates since temperature changes in ferrocyanide-containing wastes would not be expected to be rapid, even in the presence of a hot spot.

Safety issues relative to the explosiveness of exothermic reactions are a consequence of the comparative rates of chemical reaction and heat transfer (cooling). Consequently, once the various reaction events had been identified, attempts were made to quantitatively model the pertinent reaction rates. With respect to the dehydration of FECN in air, Figure 6 shows the results of an attempt to model the dehydration as a first-order reaction. Only the low conversion data were able to be used for this fit as a consequence of the overlapping of the hydrated and dehydrated XRD peaks at higher conversions. In addition to the first order fit to the low conversion data, Figure 6 also lists the rate constants between 443K and 473K. A subsequent Arrhenius analysis of the rate constants resulted in an activation energy of 8.8 ± 2.3 kcal/mole.

The key reactions in this system correspond to Event C. From the behavior observed in the DXRD experiments, it was apparent that reactions (7) and (8) occur by way of a series reaction system. It is theoretically possible to model these two reactions in an air environment (where the oxygen pressure is known and constant), and to then determine the reaction rate constants by fitting the data to the model results. However, there was only a very narrow temperature range where both the $\text{Na}_2\text{NiFe}(\text{CN})_6$ and the NaCNO x-ray peaks can be detected. That is, at temperatures above 300°C , reaction (7) was essentially complete by the time isothermal conditions were achieved. Consequently, the approach taken was to first verify that the reactions were indeed in series and to then concentrate on the reaction rates of reaction (8).

Figure 6. Dehydration Rate Constants, First-Order Fit, Sample 1:4:4(FECN:NaNO₃:NaNO₂), in Air

In order to achieve the first objective, it was assumed that reaction (7) was first order with respect to both nitrate and ferrocyanide and that reaction (8) was first order with respect to sodium cyanate. The differential equations describing these two reactions are then

$$\frac{dC_{CN}}{dt} = -k_1 C_{CN} C_{NO_3} \quad (12)$$

$$\frac{dC_{CNO}}{dt} = k_1 C_{CN} C_{NO_3} - k_2 C_{CNO} P_{O_2} \quad (13)$$

or, since P_{O_2} is constant,

$$\frac{dC_{CNO}}{dt} = k_1 C_{CN} C_{NO_3} - k'_2 C_{CNO} \quad (14)$$

where $k'_2 = k_2 P_{O_2}$

Using the stoichiometry of reactions (7) and (8) for the 1:1:1 mixture, these equations were then solved using Simusolv,⁽¹⁹⁾ a software program capable of solving sets of differential equations by a variety of methods.

To show that reactions (7) and (8) were in series, the values of k_1 and k'_2 were manipulated until the simulation matched the time at which the sodium cyanate concentration reached a maximum. An initial estimate of the rate constant, k_1 , was obtained from the initial slope ($t \sim 0$) of the decrease in the ferrocyanide disappearance; i.e., at a time where the rate of reaction (8) would be much slower than that of reaction (7). Similarly, an initial estimate of k'_2 was taken from the latter stages of the disappearance of NaCNO, and then the values of k_1 and k'_2 were adjusted in the Simusolv program until a good match in time was obtained. As Figures 7 and 8 show, an excellent match in time is obtained for both the disappearance of the sodium nickel ferrocyanide and the intermediate species, sodium cyanate, verifying the series nature of these reactions. It should be kept in mind, however, that the experimental data shown in these figures are not absolute in nature and thus no particular significance can be given to the ability of the model to match XRD intensity data. Because of these limitations, it was not possible to obtain quantification of the two rate constants from the match of the Simusolv model. However, by concentrating on the latter stages of NaCNO disappearance (where reaction (7) was complete) it was possible to obtain estimates of k_2 for a number of temperatures, and these are listed in Table 3.

Figure 7. Comparison of a First-Order Model and the Absolute Intensity of Sodium Nickel Ferrocyanide, 1:1:1 Mixture (FECN:NaNO₃:NaNO₂) at 300°C

Figure 8. Comparison of a First-Order Model and the Absolute Intensity of Sodium Cyanate, 1:1:1 Mixture (FECN:NaNO₃:NaNO₂) at 300°C

Table 3. Rate Constants for Reaction (8)

T (K)	k_2 (KPa-min) ⁻¹ x 10 ⁴
573	2.9
583	3.6
593	10.5
613	13.3

While there were relatively few unobscured data points at each temperature (resulting from XRD peak overlapping), an Arrhenius analysis of these rate constants yielded an activation energy of 134 ± 8 KJ/mole, consistent with the high temperature sensitivity usually associated with fast oxidation reactions.

5.0 Discussion

The results of this DXRD study of the reaction between sodium nickel ferrocyanide and equimolar nitrate/nitrite salts compare well with DSC, STG, and MS results^(11,12) from previous work. Observed endothermic reactions that occur up to 250°C correspond well to dehydration of ferrocyanide and the melting of nitrate/nitrite, which are both observed with DXRD. Gas analyses of separate experiments using FTIR spectroscopy^(a) determined that water vapor was released up to 220°C; this finding corresponded to the temperature determined by DXRD as the point of crystal structure changes from the loss of water of hydration.

Observed exothermic reactions, which occur at temperatures greater than 300°C, correspond to the oxidation of sodium cyanate to sodium carbonate and the formation of iron and nickel oxide, which are also observed with DXRD. A temperature of 300°C was determined as the initiation of the exothermic part of the reaction sequence in reactions (8) through (11), and is consistent with DXRD data that show product formation beginning at 300°C. Again, separate FTIR traces also detected carbon dioxide and nitrous oxide released over this same temperature range, and this is consistent with the decomposition of sodium cyanate observed in the DXRD results.

The results obtained for the 1:1:1 and 1:4:4 sample mixtures were very similar, differing only in the fact that the 1:4:4 mixture produced larger quantities of the same oxidized products; namely, sodium carbonate, iron oxide (Fe_2O_3), and nickel oxide. That is, the results from both the 1:1:1 and 1:4:4 sample mixtures showed dehydration of ferrocyanide between 180°C and 220°C and had very similar dehydration rate constants and activation energies, and both formed nickel oxide, iron oxide, and sodium cyanate in both helium and air. Complete oxidation of the cyanide ions did occur in the 1:4:4 mixture, but not in the 1:1:1 mixture in helium, which formed partial oxidation products such as sodium cyanate, unreacted products such as sodium ferrocyanide, and reduced products such as elemental nickel. Because of the great excess of equimolar nitrate/nitrite in the 1:8:8 mixture, the ferrocyanide peaks were almost undetectable and resulted in no useful DXRD data concerning the dehydration rate. The effect of the nitrate/nitrite melting was enhanced to the point of yielding a liquid solution on the DXRD hot stage (Figure 1). In this case, typical oxidation products did form but were produced as a result of solidifying out of the liquid nitrate/nitrite solution.

The primary difference between experiments conducted in helium and in air was that the helium experiments showed incomplete oxidation of the ferrocyanide when using a less than stoichiometric quantity of equimolar nitrate/nitrite (i.e., less than 4).

(a) R. Romine, Sept. 1992, Personal Communication, Pacific Northwest Laboratory, Richland, Washington.

Although oxygen is released by reactions (5) and (6) in both helium and air, the oxygen produced in the helium environment would tend to rapidly diffuse out of the sample because of the small sample sizes employed. As a result, the incomplete oxidation of the ferrocyanide in helium formed sodium ferrocyanide $[\text{Na}_4\text{Fe}(\text{CN})_6]$, sodium cyanate, nickel, and nickel nitride with small amounts of nickel and iron oxide, whereas the products from an air environment were predominantly nickel oxide, iron oxide, and sodium carbonate. It should be emphasized that the sodium cyanate forms during reactions in both helium and air but the lack of O_2 in the helium atmosphere would result in very little additional reaction [reaction (8)] of the sodium cyanate.

In order to address the question of continued safety regarding the storage of ferrocyanides and nitrates/nitrites in Hanford Site tanks, the rate of heat transfer inside the tanks should be compared to the rate of heat generated from the exothermic reactions. First, the standard heat of reaction for the first step in the series reaction sequence, reaction (7), is mildly exothermic and liberates 93.6 kJ/mole of NaCNO formed. The second step, reaction (8), liberates 267.2 kJ/mole NaCNO reacting; almost three times the heat liberated by reaction (7). While these two reactions occur at roughly the same time, reaction (7) occurs more slowly at the initiation temperature of about 280°C. While reaction (8) is three times as energetic, it requires oxygen as a reactant. If oxygen is supplied externally from contact with air, then this reaction is quite fast. However, if the surrounding environment is anoxic, then it can only proceed as fast as reaction (7), since that would be its source of oxygen. Of course, this assumes that these two are the only reactions taking place.

Strictly speaking, the most thorough rate analysis would result from a model wherein the rates of both heat transfer and chemical reactions are accounted for in a simultaneous fashion. However, the reaction complexities are such that the rates of all of the coexistent reactions are not available. Nevertheless, in a worst-case scenario, we can concentrate solely on reaction (8), assume that a hot spot does exist and has reached a temperature of 300°C (i.e., at a temperature where reaction (8) begins to take place), and that there is an externally supplied oxygen source that is not rate limiting. From the kinetic analysis of reaction (8), a reaction rate for the disappearance of sodium cyanate under isothermal conditions would be given by

$$r = k_2' C_{\text{CNO}} \quad (15)$$

Recent core samples of Tank 241-C-112⁽²⁰⁾ indicate that the "packing density" of the dry salt cake would be about 0.77 g/mL. Using this value together with the NaCNO concentration at its maximum value (scaled to the tank stoichiometry of 1:8:8), Equation (15) and the heat of reaction for reaction (8) yields an estimated heat release of 0.1 KJ/s. If we now assume that a reasonably sized hot spot is at 300°C, and is on the order of 1 ft³ (0.028m³) and model it as a cylinder (1.3 ft high and 1.0 ft in diameter),

the rate of heat generation within the volume can be compared to the rate of heat transfer from the cylinder. Assuming further that the temperature at a point 5 radii is at the currently detected temperature (57°C),⁽⁷⁾ and that the thermal conductivity of the wet salt cake is $0.87 \text{ J/ms}^{-1}\text{K}^{-1}$,⁽²¹⁾ then the heat transfer rate from the cylinder is calculated to be 0.8 KJ/s , or a factor of *eight* higher than the heat generation rate. Thus, even in the unlikely event of a hot spot suddenly existing at 300°C , the heat transfer rates are still more than sufficient to remove the generated heat.

6.0 Conclusions

The results showed that a reaction between sodium nickel ferrocyanide and equimolar nitrate/nitrite begins by dehydration of the ferrocyanide at 180°C, followed by melting of the nitrate/nitrite at 230°C, and finally resulting in an exothermic reaction at 300°C. Since the temperatures in the tanks are well below the temperatures required for the exothermic reaction to occur, the danger of an explosive reaction occurring is very low. The results here have shown that a major factor in the reactions at 300°C is the occurrence of a series reaction that produces NaCNO as an intermediate in a first step, which is mildly exothermic. In an anoxic environment, the NaCNO is relatively inactive, but in the presence of gaseous oxygen, it further reacts, rapidly and exothermally, to form metal oxides.

Furthermore, it has been shown that the rate of heat release from the oxidation of the NaCNO, even in the presence of excess oxygen, is still a factor of eight lower than the estimated heat transfer rate from a localized hot spot. This means that excessive heat will not build up in the tank causing the reaction to become uncontrollable. Given the fact that the Hanford Site waste tanks, which are thought to contain ferrocyanides, have been thermally stable for almost 20 years, the occurrence of a hot spot would be slow in developing. The reaction rates measured in this study show that a relatively slow intermediate reaction, which is mildly exothermic, precedes the high-energy exothermic reactions. This data leads to the conclusion that the danger of explosion from ferrocyanide wastes containing nitrates/nitrites in the Hanford Site tanks is very low.

7.0 References

1. L. L. Burger, D. A. Reynolds, W. W. Schulz, and D. M. Strachan. 1991. *A Summary of Available Information on Ferrocyanide Tank Wastes*. PNL-7822, Pacific Northwest Laboratory, Richland, Washington.
2. J. L. Hepworth, E. D. McClanahan, and R. L. Moore. 1957. *Cesium Packaging Studies - Conversion of Zinc Ferrocyanide to a Cesium Chloride Product*. HW-48832, Hanford Atomic Products Operation, Richland, Washington.
3. L. L. Burger. 1984. *Complexant Stability Investigations. Task 1. Ferrocyanide Solids*. PNL-5441, Pacific Northwest Laboratory, Richland, Washington.
4. L. L. Burger and R. D. Scheele. 1988. *Interim Report on Cyanide Safety Studies*. PNL-7175, Pacific Northwest Laboratory, Richland, Washington.
5. U.S. Department of Energy (DOE). 1987. *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level, Transuranic, and Tank Wastes*. DOE-EIS-0113, U.S. Department of Energy, Washington, D.C.
6. J. D. Peach. October 1990. Letter B-241479 to M. Synar, "Consequences of Explosion of Hanford's Single-Shell Tanks are Understated," GAO/RCED-91-34, General Accounting Office, Washington, D.C.
7. B. M. Hanlon. April 1991. *Tank Farm Surveillance and Waste Status Report for December 1990*. WHC-EP-0182-33, Westinghouse Hanford Company, Richland, Washington.
8. R. D. Scheele, L. L. Burger, J. M. Tingey, S. A. Bryan, G. L. Borsheim, B. C. Simpson, R. J. Cash; and H. H. Cady. 1991. "Ferrocyanide Containing Waste Tanks: Ferrocyanide Chemistry and Reactivity." In the *Proceedings of Environmental Restoration '91*, University of Arizona, Tucson, Arizona.
9. L. L. Burger and R. D. Scheele. 1990. *The Reactivity of Cesium Nickel Ferrocyanide Towards Nitrate and Nitrite Salts*. PNL-7550, Pacific Northwest Laboratory, Richland, Washington.
10. R. D. Scheele and H. H. Cady. 1989. *Preliminary Safe-Handling Experiments on a Mixture of Cesium Nickel Ferrocyanide and Equimolar Sodium Nitrate/Nitrite*. PNL-7928, Pacific Northwest Laboratory, Richland, Washington.

11. R. T. Hallen, L. L. Burger, R. L. Hockey, M. A. Lilga, R. D. Scheele, and J. M. Tingey. 1991. *Ferrocyanide Safety Project FY 1991 Annual Report*. PNL-8165, Pacific Northwest Laboratory, Richland, Washington.
12. R. D. Scheele, L. L. Burger, J. M. Tingey, R. T. Hallen, and M. A. Lilga. 1992. "Chemical Reactivity of Potential Ferrocyanide Precipitates in Hanford Tanks with Nitrates and Nitrites." In the *Proceedings of Waste Management '92*, Tucson, Arizona.
13. W. J. Thomson. 1989. "Dynamic X-ray Diffraction: A Technique for Following Solid-State Reactions." *Ceramic Transactions*, 5:131-140. Advanced Characterization Techniques for Ceramics. Edited by W. S. Young, G. L. McVay, and G. E. Pike. American Ceramic Society, Westerville, Ohio.
14. D. E. Anderson and W. J. Thomson. 1987. *Ind. Eng. Chem. Res.*, 26:1628.
15. D. W. Jeppson and J. J. Wong. 1993. *Ferrocyanide Waste Simulant Characterization*. WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.
16. A. F. Wells. 1984. *Structural Inorganic Chemistry*, 5th Ed., Clarendon Press, Oxford.
17. G. Charlot. 1954. *Qualitative Inorganic Analysis*. John Wiley and Sons, New York.
18. R. E. Kirk and D. F. Othmer, Ed. 1949. *Encyclopedia of Chemical Technology*, Vol. 4, Interscience Publishers, Inc., New York.
19. *Simusolv, A New Method for Numerical Parameter Estimation*. 1986. Dow Chemical Company, Midland, Michigan.
20. B. C. Simpson, G. L. Borsheim, and L. Jensen. 1993. *Tank Characterization Data Report: Tank 241-C-112*. WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.
21. J. M. McLaren. April 1991. *Single-Shell Tank 104-BY Thermal-Hydraulic Analysis*. WHC-SD-WM-ER-083, Westinghouse Hanford Company, Richland, Washington.

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