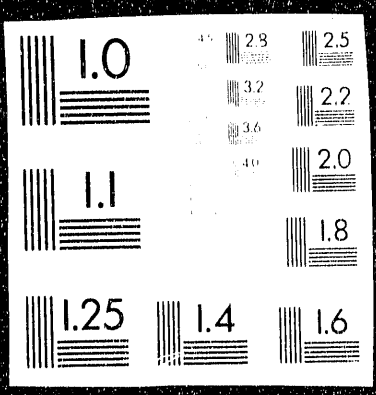


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INTERIM REPORT CYANIDE SAFETY STUDIES

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Introduction

Over the past few years several proposals have been prepared to investigate the potential hazard of ferrocyanide-nitrate reactions that may occur in some Hanford waste tanks. These were based on a survey paper submitted to Rockwell Hanford Operations in 1984, (Burger, LL 1984. Complexant Stability Investigation Task 1, Ferrocyanide Solids, PNL-5441(1)). In 1988 Westinghouse Hanford Company (WHC) decided to perform some of the suggested experimental work.

Based on the proposal submitted in July, 1988, it was agreed to do a portion of the work during FY 1988. This report summarizes the results of that work, provides a preliminary analysis of the results, and includes recommendations for further study. The work completed consists of a brief literature search, preparation and analysis of several cesium nickel ferrocyanide, $Cs_2NiFe(CN)_6$, oxidation studies using Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG), and small scale explosion tests.

Literature Search

No recent reports on ferrocyanide explosive reactions have been found. Earlier reports were reviewed and indicate that with nitrates such as $Cu(NO_3)_2$, presumably more unstable, explosive reactions occur at temperatures as low as 220°C.

Experiments described in the literature on aqueous phase oxidation of cyanides, either chemical or electrochemical, show that several metal ions are catalysts. These include Ag, Cu, Ni, and Ru.

No information was found on the effects of organic compounds.

Preparation of Materials

The cesium nickel ferrocyanide ($FeCN$) was prepared by mixing aqueous solutions of potassium ferrocyanide, cesium nitrate and nickel sulfate. Variables used included concentrations, order of mixing, pH, and temperature. A similar product, a green blue solid was obtained in each case. Analysis was performed by dissolving the solids in sulfuric acid heated to the boiling

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point followed by dilution with water for ICP analysis. An alternative was to ignite the solids at about 500°C followed by dissolution in hot HCl. All samples gave the desired 2:1:1 ratio for the metal constituents within about 15%. Precipitation from a dilute solution seemed to produce a more filterable precipitate than from concentrated ones. The method chosen to prepare most of the FeCN samples used in the experimental studies was to add the nickel last to a solution of pH about 9 and at a temperature of 60 to 80°C. The precipitate was filtered and washed with water. This method closely simulates that actually used in the tank process. The solids dried under ambient room conditions contain about 5 to 10% water. Reagent grade chemicals were used to prepare the FeCN samples and the synthetic waste mixtures described in the following.

Several mixtures of nitrates, nitrites, and inert materials characteristic of waste tanks were made. Mix #4 had inert components roughly equivalent to those in one of the tanks. Its composition was in mol ratios nitrate 9.2, nitrite 3.7, sulfate 0.7, alumina (-325 mesh) 3.1, and carbonate 1.2. Mix #2 had the composition nitrate 13.7, nitrite 3.7, sulfate 0.5, and alumina 7.0. A 50-50 mol ratio sodium nitrate-sodium nitrite mixture having a melting point of 235°C, which is very close to the eutectic was used as the "eutectic" in this work.

Thermal Analysis Studies

To determine when the reaction begins and how it proceeds, DSC and TG were used to study the oxidation of potassium ferrocyanide and a few samples of FeCN by oxygen (in air), sodium nitrate, sodium nitrite, and a synthetic waste mixture. The analyses were performed at heating rates of 10°C/min.

Differential Scanning Calorimetry Studies

We used the DSC to investigate the oxidation of potassium ferrocyanide and several FeCNs by oxygen in air, pure sodium nitrate, and sodium nitrate and nitrite in a synthetic waste mixture. The kinetic parameters for the initial stage of air oxidation of one of the FeCNs were calculated using software supplied by Perkin-Elmer. These parameters were then used to calculate the time to completion under adiabatic conditions beginning at selected temperatures.

The results of the DSC studies are presented in table 1. The temperature of the reaction is presented in table 1 in two ways. The first is the onset temperature which is defined as the temperature at which a line tangent to the steepest part of the DSC peak intersects a line tangential to the baseline. The second is the temperature range observed for the start and finish of the reaction.

Table 1. Results of DSC Analysis

<u>Sample</u>	<u>Oxidant</u>	<u>Onset, °C</u>	<u>Start/Finish- °C</u>	<u>-ΔH, cal/g</u>
K ₄ Fe(CN) ₆ *3H ₂ O	Air	350		NM
K ₄ Fe(CN) ₆ *3H ₂ O	NaNO ₃	390	320/>500	>230
K ₄ Fe(CN) ₆ *3H ₂ O	Mix #2	400	340/410	>190
FeCN #3	Air	320	360/410	370
		405	270/360	60
FeCN #3	NaNO ₃	340	390/470	200
FeCN #6	Air	310	310/380	500
		400	260/380	400
FeCN #7	Air	300	360/500	25
		340	280/315	25
		450	330/390	425
FeCN #11	Air	315	390/500	380
		360	290/350	60
FeCN #11	NaNO ₃	340	350/400	75
FeCN #11	Mix#2	350	310/370	210
FeCN #11	Eutectic	295	315/370	980
			285/432	

The results of the DSC studies of the air oxidation of potassium ferrocyanide indicate that the reaction is complex. The onset temperature for the potassium ferrocyanide oxidation by air was 350°C. The peak was very noisy and non-reproducible suggesting possible diffusion blockage during the reaction(s). The enthalpy of the reaction was indeterminate because the oxidation was incomplete by the time the runs were stopped and due to the variability of the results. Additional software would be required to perform the calculation.

The reactions between the nickel ferrocyanides and air varied between materials. The oxidation appears to proceed in several stages. For #3 and #6 the onset temperatures for the two observed stages of oxidation were roughly 310 and 340°C. The onset temperatures for the three stages observed for #7 were 300, 340, and 450°C. The magnitude of the enthalpy changes for these different stages varied between materials. For #3 and #6 the largest and most rapid reaction was the first stage of oxidation. For #7 the last reaction released the most energy and was the most rapid. This indicates that the method of formation of the FeCN affects the susceptibility of the material to oxidation by air. The TG studies indicate that the air oxidation is not complete by 500°C and the enthalpies reported represent a fraction of the total energy which would be released for full oxidation.

The ΔH for the air oxidation of the nickel ferrocyanides up to 500°C was about 38 kcal/mole CN^- which is less than the predicted 95 kcal/mole CN^- . Air oxidation, as discussed later in the TG results, is not complete by 500°C so this enthalpy change represents a fraction of the total expected change.

As a point of interest, we used Perkin-Elmer supplied software to calculate the kinetic parameters for the first and largest peak observed for the air oxidation of the FeCN #3. The calculated kinetic rate parameters to define the rate constant k for this first stage of the air oxidation reaction where $k = k_0 \ln(E_A/RT)$ are $\ln(k_0) = 46.62/\text{sec}$ and $E_A = 250 \text{ kJ/mole}$. The order of the reaction was calculated to be 0.72. Using these parameters, assuming adiabatic conditions, and a heat capacity of 2 J/g-°C, we used the Perkin-Elmer software to predict the time to completion beginning at a specified temperature. At a starting temperature of 150°C it would take 8250 d to complete the reaction. At the starting temperatures of 200, 250, 300, and 350°C, the respective predicted times to completion are 4.77 d, 16.9 min, 0.12 min, and 0.00 min. This illustrates that the reaction can occur rapidly even at a temperature of 250°C. Additional work should be done to determine the kinetic parameters of the nitrate oxidation, and reactions involving other oxidants present in the tanks.

Only a few DSC experiments have been completed using nitrates and nitrites as oxidants. The reaction between sodium nitrate and potassium ferrocyanide appears to occur more rapidly than air oxidation, see table 1,

though at a higher onset temperature of 395°C. The enthalpy of the reaction is at least -200 cal/g of potassium ferrocyanide or -15 kcal/mole CN⁻. This -15 kcal/mole CN⁻ compares to the expected ΔH of -95 kcal/mole CN⁻. Additional software is required to obtain a better measure of the enthalpy change.

Two experiments involving sodium nitrate and FeCN samples #3 and #11 showed a reaction that began shortly after the sodium nitrate melted at about 305°C and gave an onset temperature of 340°C. The observed enthalpy changes of -200 cal/g of #3 and -74 cal/g of #11 is surprising. An experiment using sample #11 with the eutectic gave an onset temperature of 295°C and an enthalpy of reaction of -981 cal/gram. This is close to the theoretical value for complete oxidation and formation of N₂. It appears that we did not always measure all of the energy released during the oxidation. Some changes in experimental procedure are needed to investigate these reactions further. This work also shows that the reaction between nickel ferrocyanide and sodium nitrate occurs within 10°C of air oxidation. The low onset temperature with the eutectic mixture suggests that formation of a liquid phase may be a definitive factor.

The addition of alumina and other inert waste constituents (Mix #2) caused about a 10°C increase in the onset temperature for the oxidation of the ferrocyanides relative to nitrate.

Thermogravimetry Studies

The TG studies were not as extensive as the DSC studies but were quite informative. The reactions studied and the conditions used are listed in Table 2.

When potassium ferrocyanide was oxidized by air, it initially gained weight. This is not yet explained; only a small increase should result from oxidation to the ferricyanide. The weight gain begins about 330°C and ends at about 510°C. At 510°C the potassium ferrocyanide began to lose weight until the TG run was stopped at 800°C.

When potassium ferrocyanide was oxidized by sodium nitrate, the reaction onset temperature was 365°C. The sodium nitrate completely oxidized the ferrocyanide to the metal oxides by 440°C at a heating rate of 10°C/min. The

theoretical weight loss for the $K_4Fe(CN)_6 \cdot 3H_2O$ /sodium nitrate mixture was 18.9 wt% compared to the measured loss of 18.95 wt%.

The air oxidation of the FeCNs #3, #7, and #11 proceeded in multiple stages and differed from that observed for potassium ferrocyanide. For #3 and #11, the reaction proceeded in three stages all with an associated weight loss. The first began at 310°C, the second began at about 400°C, and the third and last began at 540°C. For #7, the oxidation proceeded in three stages also, with the first stage beginning at 310°C with a weight loss. The second stage began at 480°C and had a weight gain. The oxidation ended with a weight loss beginning at 540°C. We have not yet developed a reaction mechanism to account for the observed changes.

Table 2. Results of Thermogravimetric Analyses

<u>Sample</u>	<u>Oxidant</u>	<u>Onset, °C</u>	<u>Start/Finish- °C</u>	<u>Δwt%</u>
$K_4Fe(CN)_6 \cdot 3H_2O$	Air	370		10.12
		640	330/510	-14.7
$K_4Fe(CN)_6 \cdot 3H_2O$	$NaNO_3$	365	510/>800	-18.95
FeCN #3	Air	310	270/460	-2.2
		400	310/380	-3.9
		710	380/500	>-17.8
FeCN #3	$NaNO_2$	290	540/>800	(-74)
FeCN #7	Air	410	288/296	-5.2
		510	285/475	2.6
		710	475/530	>-18.9
FeCN #11	Air	310	530/>800	-1.1
		410	300/400	-2.5
		700	400/540	-33.0
FeCN #11	$NaNO_3$	325	540/>900	-6.9
		395	240/370	-6.9
FeCN #11	Eutectic	310	370/460	-5.0
		365	205/355 355/440	-6.6

The oxidation of the FeCN #11 by sodium nitrate began at 310°C, shortly after the sodium nitrate melted, and was complete by 450°C. The reaction

proceeded in two stages with the second beginning at 370°C. Based on a composition of FeCN, the weight loss for the analyzed reaction mixture should have been 18.8 wt% compared to the observed loss of 13.71 wt%. The chemical composition of nickel ferrocyanide #11 has not been determined, a difference in composition from theoretical may partially explain the difference. The oxidation with sodium nitrite was instantaneous and at a lower temperature, about 290°C. The weight loss listed in the table, 74%, is not meaningful since the TG balance was upset by the violent reaction.

The DSC and TG studies have shown that rapid oxidation of ferrocyanides occur at an onset temperature of 310°C in air, 340°C with sodium nitrate, and at 290°C with sodium nitrite. No DSC runs have been made with nitrite alone as the oxidant. These preliminary results indicate that nitrate or nitrite completely oxidize the ferrocyanides to metal oxides and gases. Accurate measurement of the enthalpy of these reactions has not been made.

Explosion Experiments

These experiments were carried out to determine the actual ignition temperature for mixtures of oxidants and cyanides. A stainless steel right cylinder 4 cm in diameter and 3.6 cm high had a 1.3 cm deep hole drilled in the center to accommodate an NMR tube (a thin walled glass tube about 5 mm in diameter). This served as a reaction vessel. A thermocouple was inserted into an adjacent hole. The cylinder was surrounded by a magnesia block and the assembly placed on a variable temperature hotplate. Mixtures of FeCN (or other cyanide) and nitrates, nitrites, or other oxidant mixtures were placed in a tube and heated. Quantities up to about 150 mg total were used in the tests.

The maximum heating rate with the assembly used here was about 8°C/min (close to the 10°C per min of the DSC runs). At this heating rate FeCN and nitrate or nitrite salts start to react vigorously at about 325°C, slightly above the melting point of the salts, producing a brownish black solid. If the eutectic mixture is used the reaction starts at a much lower temperature; visible changes are apparent at about 240°C. In one experiment heating of the FeCN-eutectic nitrate at about 8°C/min caused a reaction to start at 240 to 260°C. When the temperature reached 348°C an explosion resulted. In

another a sample was heated at about 3°C/min starting at 338°C. When the temperature reached 342°C it also exploded.

In general, when mixtures of cyanides and nitrates or nitrates were heated rapidly, by inserting the tube into the block preheated to 350 to 400°C, a sharp explosion or a flash of flame was produced. If the mixture which was previously reacted at the lower heating rate was again placed in the preheated block after adding more nitrate it also exploded indicating that the low temperature reaction was not complete. About 35 tests were run and the results can be summarized as follows:

For FeCN mixed with sodium nitrate the ignition temperature, the temperature at which an explosion occurs, is about 360°C.

Substitution of nitrite for nitrate lowers the ignition temperature about 10 degrees and produces a sharper explosion.

If the mixtures of FeCN and nitrate are heated slowly a vigorous reaction begins at about 325°C but with the milligram quantities used the reaction never reached the explosive stage and often was not complete.

Addition of more oxidant to the partially reacted mixtures at temperatures above 360°C often caused explosions.

The eutectic nitrate mix reacts with FeCN starting at a much lower temperature and has a lower ignition temperature, about 340°C.

The nitrite/FeCN mix at 350°C is shock sensitive.

Addition of inert material such as sodium sulfate, alumina, or sodium carbonate raises the ignition temperature. With quantities added to simulate a tank composition the ignition temperature was about 400°C.

With the simulated mix as oxidant there may be a minimum, yet undetermined, FeCN to oxidant ratio below which an explosion does not occur. Without the inert material present the ratio is not critical.

As used here the term explosion includes reactions fast enough to produce either a loud noise or a sudden flash of light. As might be expected there was a wide range in the brisance observed. Although no explosions have yet been observed below about 340°C, nor have they with very low cyanide to oxidant ratios, the fact that an exothermic reaction still occurs starting at about 325°C with nitrates and at 260°C or lower with nitrites suggests that an explosive reaction is still possible. The minimum temperature at which

the exothermic reaction begins and the effect of other conditions on its rate of development and enthalpy have not been determined.

Conclusions and Recommendations

The thermal analysis studies show that the oxidation reaction(s) between FeCN and nitrate begin near 310°C or shortly after the melting point of sodium nitrate. Preliminary analysis of the TG results indicates that the ferrocyanide is completely oxidized leaving only the metal oxides. The reaction of the ferrocyanide with twice as much by weight synthetic waste, increased the starting temperature of the reaction by about 10°C. Substitution of nitrite for nitrate lowers the reaction temperature and increases the rate of reaction. These studies also show that the oxidation reactions are complex, often proceeding in two or more steps. The enthalpy changes observed in some of the DSC experiments were lower than predicted by theory or by comparison to the air oxidation reaction. This suggests that further investigation of the reaction requires some modifications in experimental procedure.

Milligram level explosion tests confirm the thermal analysis results with respect to initiation temperatures and produce striking evidence that the reaction between nitrate-nitrate containing solids and ferrocyanides can be violent. Neither the exact boundary conditions for explosive reaction nor the quantitative effects of such reactions can be stated at this time. It is clear that temperature and dilution with inert material are key factors. The possibility of significant exothermic reactions in some of the waste tanks is not ruled out by these preliminary experiments.

Recommended follow up work includes the following items:

1. Quantitative reaction enthalpy data as a function of mixture composition, including both the inerts and the nitrite-nitrate ratio. These data can be obtained by refined thermal analysis measurements.
2. The effect of water and organic compounds.
3. Gas analysis from different steps in the oxidation process. Gas collection and analysis using Gas Chromatography (GC), Infrared Spectroscopy (IR), and Mass Spectroscopy (MS) analysis would be easy.
4. More precise data on the effects of heating rate are needed.

5. The phenomenon of shock sensitivity needs to be examined. Does it exist only for nitrite mixtures or for nitrates also and what are the temperature limitations.

6. It may be desirable to carry out larger scale explosion tests to determine if the exothermic reactions observed for the mixtures containing inerts can lead to runaway thermal reactions.

It is anticipated that continued DSC and TG work can provide much of the needed information. Some consideration should be given to instrumenting the small scale explosion tests such that the observations could be quantified.

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