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R. D. Scheele
J. M. Tingey
M. A. Lilga

L. L. Burger
R. T. Hallen

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Pacific Northwest Laboratory
Richland, Washington 99352

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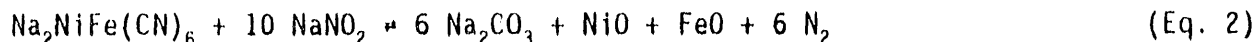
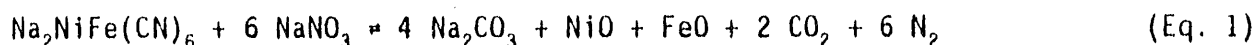
ABSTRACT

Ferrocyanide-bearing wastes were produced at the Hanford Site during the 1950s. Safe storage of these wastes has recently drawn increased attention. As a result of these concerns, the Pacific Northwest Laboratory was chartered to investigate the chemical reactivity and explosivity of the ferrocyanide-bearing wastes. We have investigated the thermal sensitivity of synthetic wastes and ferrocyanides and observed oxidation at 130°C and explosions down to 295°C. Coupled with thermodynamic calculations, these thermal studies have also shown a dependence of the reactivity on the synthetic waste composition, which is dependent on the solids settling behavior.

INTRODUCTION

During the 1950s, ferrocyanide was used to remove radiocesium from wastes resulting from the production of defense materials at the Hanford Reservation, which is located in southeast Washington state. In these cesium scavenging campaigns, soluble ferrocyanide and nickel salts were added to liquid wastes containing nitrate thus likely precipitating an alkali nickel ferrocyanide containing the radiocesium. The resulting ferrocyanide solids were allowed to settle, and the decontaminated supernate was transferred to soil.

For over 30 years, the ferrocyanide solids have been stored in the Hanford underground waste storage tanks. Concern has arisen that mixtures of ferrocyanide and nitrate, and its radiolytic decomposition product nitrite, could be intimately mixed in concentrations under conditions that could result in an uncontrollable reaction or explosion initiated by heat or a physical event (1,2). Two of the potential reactions of concern are:



As a result of this concern, chemical reactivity studies have been and are continuing to be performed at Pacific Northwest Laboratory^(a) (PNL) and Los Alamos National Laboratory (LANL) to determine the conditions under which an uncontrollable reaction between the likely ferrocyanide species and nitrate and nitrite could be initiated. At PNL, we have emphasized research of thermal initiation to determine the temperatures at which an observable reaction begins (3). LANL has investigated the sensitivity of a mixture of ferrocyanide, nitrate, and nitrite to both thermal and nonthermal initiation (4).

(a) Pacific Northwest Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

We have prepared and characterized ferrocyanide precipitates by using representative waste solutions and flowsheets. To investigate the thermal reactivity of the ferrocyanide and nitrate and nitrite mixtures, we are using differential scanning calorimetry (DSC), scanning thermogravimetry (STG), a small-scale time-to-explosion (TTX) test, and temperature programmed pyrolysis coupled with mass spectrometry (pyrolysis/MS). We are also evaluating the effects of diluents such as water and other waste constituents, both experimentally and through thermodynamic calculations.

In this paper, we will first present brief descriptions of the processes that produced the ferrocyanide wastes, describe the preparation of two synthetic In-Farm flowsheet wastes and a relatively pure sodium nickel ferrocyanide, and discuss the results of our reactivity and explosivity tests for these materials.

HANFORD PRODUCTION OF FERROCYANIDE-BEARING WASTES

There were three basic flowsheets used to scavenge radiocesium from Hanford wastes (4). The two predominant flowsheets were the U-Plant and In-Farm flowsheets, which respectively produced roughly 70% and 20% of the ferrocyanide-bearing wastes. The remaining 10% of the ferrocyanide wastes were produced by using the T-Plant Test flowsheet.

Schematics of the three basic radiocesium scavenging flowsheets are presented in Fig. 1 and implemented in the manner presented in Fig. 2. The

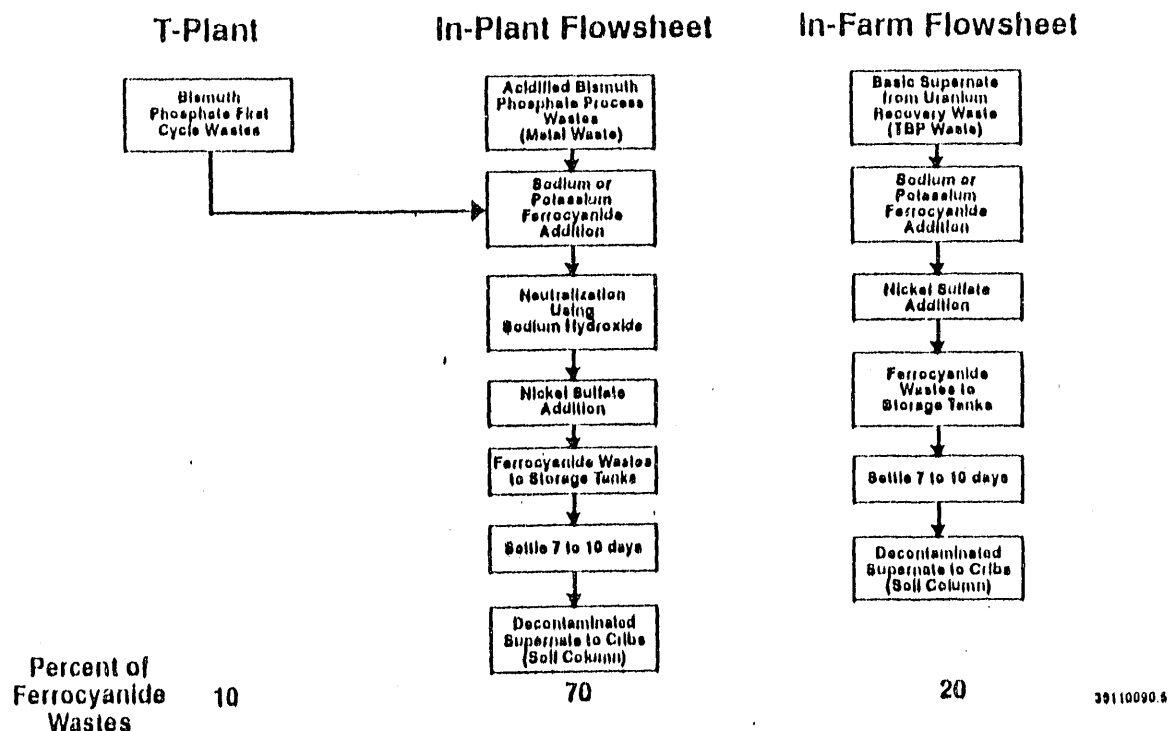
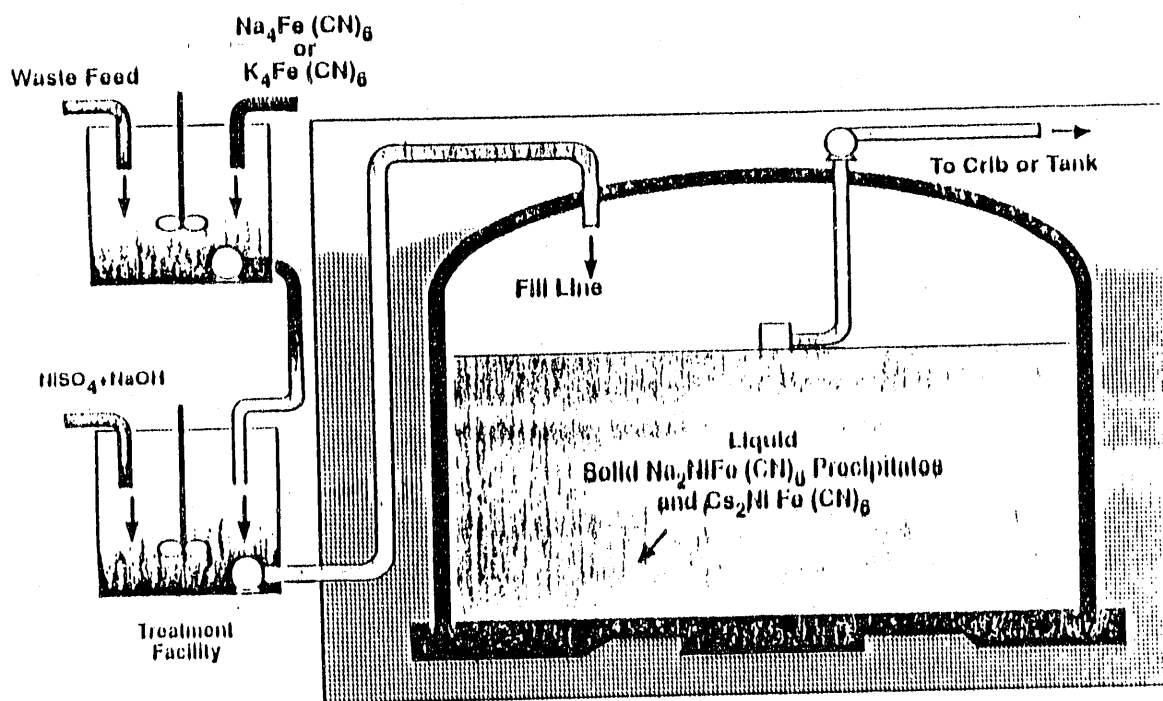


FIGURE 1. Schematic of Radiocesium Scavenging Flowsheets



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FIGURE 2. Illustration of Radiocesium Scavenging Operations

nominal ferrocyanide concentration used at Hanford was 0.005 M, but many scavenging campaigns used 0.0025 M, and a few used 0.0075 M. In addition, these processes were often coupled with other processes to ensure that other radionuclides were not released to the environment when the scavenged wastes were sent to the soil columns or cribs. The use of different concentrations of ferrocyanide and combinations of different scavenging processes on an as-needed basis produced ferrocyanide-containing wastes of variable concentrations and compositions.

In the U-Plant flowsheet, the alkaline metal waste (MW) produced from the Bismuth Phosphate Process was sluiced from the underground waste tanks, dissolved in acid, processed in U-Plant to remove uranium by solvent extraction, treated to remove radiocesium, and in some cases, to scavenge radiostrontium. As shown in Fig. 1, the treatment to remove radiocesium consisted of 1) addition of sodium or potassium ferrocyanide to the acid waste, 2) adjustment to about pH 9, 3) addition of nickel sulfate equivalent to the ferrocyanide addition, 4) transferral to a settling tank where the cesium-bearing solids were settled for 7 to 10 days, and 5) the disposal of decontaminated aqueous waste to cribs. In some cases, calcium or strontium nitrate was added to the wastes to scavenge any remaining radiostrontium. The ferrocyanide-bearing wastes were then transferred to underground storage tanks. The amount of solid waste that resulted from dissolved MW was relatively larger than the amount of ferrocyanide.

The flowsheet used for the T-Plant Test was very similar in concept to the U-Plant flowsheet. The difference being instead of scavenging acidic dissolved MW, the acidic first-decontamination-cycle waste (ICW) from the Bismuth Phosphate Process was scavenged.

In the In-Farm flowsheet (Fig. 1) the alkaline supernate that was treated resulted from stored unscavenged neutralized waste produced in uranium recovery operations. The supernate was transferred to a mixing tank, and the pH was adjusted nominally to 9; ferrocyanide and then nickel sulfate were added. The slurry was transferred to a settling tank, and the decontaminated aqueous waste was cribbed. The ferrocyanide-bearing wastes were then transferred to an underground storage tank.

Occasionally, the ^{60}Co content of the wastes was too great and the In-Farm flowsheet was coupled with a radiocobalt scavenging flowsheet. In this case, just before scavenging the alkaline waste tank supernate for radiocesium, pH was adjusted to between 8.5 and 9.2, and sodium sulfide and nickel sulfate were added to precipitate nickel sulfide.

Scheele et al. (3) provide more detailed descriptions of the ferrocyanide scavenging processes and the history of wastes resulting from these processes.

PREPARATION OF SYNTHETIC FERROCYANIDE-BEARING WASTES

To investigate the hazards associated with storage of wastes produced by the cesium scavenging campaigns, we prepared several synthetic wastes using the Hanford cesium scavenging flowsheets and several different alkali nickel ferrocyanides from sodium nitrate based solutions. The Westinghouse Hanford Company (WHC) prepared one synthetic waste using a variation of the U-Plant flowsheet. We have previously reported some of the reactivity and explosivity results obtained at PNL for the WHC U-Plant waste and one PNL-prepared In-Farm synthetic waste (3).

The two In-Farm wastes and one sodium nickel ferrocyanide were prepared using the recipes presented in Table I; In-Farm 1 is the material that was previously discussed (3). In each case, sodium ferrocyanide and nickel(II) solutions were added to synthetic U-Plant alkaline waste after adjusting the pH to 9.5. In-Farm 1 was prepared to represent a solution having the highest concentrations of dissolved solids as described by Smith and Coppinger (5). To produce the In-Farm 1 sample, the material was gravity settled for 8 days, the supernate decanted, the settled solids air dried at room temperature, ground with a mortar and pestle, and sieved to -230 mesh.

In-Farm 2 was prepared to represent a solution having lower concentrations of dissolved salts as described by Schulz (6). We prepared three In-Farm 2 samples for testing. Sample 1 was settled by gravity for 4 days, sample 2 was centrifuged for 1 h at 2000 g (2000 g-h), and sample 3 was centrifuged between 3000 and 4200 g for the equivalent of 30 g-yr. These In-Farm 2 samples were air dried at ambient conditions for 16 h, then ground and sieved to -120 mesh. The samples for TTX testing were dried at 80°C for 1 h under a vacuum. We do not know whether centrifuging for 30 g-yr at 3000

Table I. Recipes for Preparation of Synthetic Ferrocyanide Wastes

Constituent	Concentration, M		
	In-Farm 1	In-Farm 2	Prep 28
<u>Synthetic Waste or Parent Solution Compositions</u>			
Na ₂ SO ₄	0.2	0.20	NA ^(a)
Na ₃ PO ₄	NA	0.15	NA
NaNO ₃	4.0	2.0	2.0
NaNO ₂	2.0	1.0	NA
NaCl	NA	0.01	NA
KNO ₃	NA	0.01	NA
NH ₄ NO ₃	0.05	0.02	NA
pH	9.5	9.5	9.5
<u>Precipitate Formers Added</u>			
Na ₄ Fe(CN) ₆	0.005	0.005	0.2
Ni ₂ SO ₄	0.005	0.005	NA
Ni(NO ₃) ₂	NA	NA	0.2

(a) Not added.

to 4200 g yields a synthetic waste representative of a waste that has settled for 30 yr at 1 g. We felt that the experiment would provide an estimate of the effect.

We prepared sodium nickel ferrocyanide preparation 28 (Prep 28) to use as a source for some of our investigations into the effects of other potential tank waste constituents on the reactivity or explosivity of sodium nickel ferrocyanide. The precipitate from this preparation was recovered by centrifuging. The recovered solids were washed twice with 2 volumes of deionized (DI) water followed by a final wash with dilute sodium hydroxide solution.

We attempted to separate the solids from the third DI water wash by centrifuging. However, our efforts were thwarted by the formation of a colloid, and we were forced to increase the ionic strength of the solution to recover the solids. Because a colloid tended to form on the third water wash, we have been unable to produce an alkali nickel ferrocyanide free of any associated ion.

The fact that only a limited number of water washes can be performed to remove the soluble salts indicates that complete separation of the waste ferrocyanides from the nitrate and nitrite oxidants by washing would be difficult, if not impossible. Whether two washes is sufficient to reduce the oxidant concentration and eliminate the reaction hazard has yet to be determined.

CHARACTERIZATION OF SYNTHETIC FERROCYANIDES

Two important factors affecting the reactivity hazard associated with storage or management of the ferrocyanide wastes are the chemical identity and the concentration of the reduced species. The identity of the cyanide species is important since the rate of reaction and the thermal sensitivity are or could be dependent on the cyanide species. The concentrations of the reduced species and of the oxidizing species, nitrate or nitrite, determine potential energy content and heat capacity of the system and thus determine the maximum temperature achievable by a reaction.

We prepared synthetic wastes using the Hanford flowsheets and in 1991 began investigating the effect of aging on the chemical nature of the reduced species due to radiation exposure of over 30 years and exposure to a caustic and oxidizing environment. To determine the composition or identity of these flowsheet precipitates, we employed elemental analysis using inductively coupled argon plasma atomic emission spectroscopy (ICP/AES), x-ray diffraction spectroscopy (XRD), scanning electron microscopy coupled with energy dispersive spectroscopy (SEM/EDS), scanning thermogravimetry (STG), ion chromatography (IC), carbon-hydrogen-nitrogen analysis (CHN), total organic carbon analysis (TOC), and total cyanide analysis.

Based principally on the ICP, total cyanide, and STG analyses, In-Farm 1 has the nominal composition $\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot 5.3 \text{ H}_2\text{O} \cdot 4 \text{ NaNO}_3 \cdot 2 \text{ NaNO}_2$ (assumes nitrate to nitrite ratio in parent solution). One would expect traces of the other soluble salts in the same proportion to the nitrate and nitrite as found in the treated solution.

Table II presents the calculated compositions and measured ferrocyanide concentration for air dried In-Farm 2 samples after they settled for 10 days

Table II. Calculated Compositions of In-Farm 2 Samples

Constituent	Concentration, wt%		
	Settled Solids	Centrifuged, 2000 g-h	Centrifuged, 30 g-yr
Na_2SO_4	8.6	5.3	4.7
Na_3PO_4	7.5	4.6	4.1
NaNO_3	52	32	28
NaNO_2	21	13	11
NaCl	0.2	0.1	0.1
KNO_3	0.3	0.2	0.2
NH_4NO_3	0.5	0.3	0.3
$\text{Na}_2\text{NiFe}(\text{CN})_6^{(a)}$	10 (11) ^(b)	45 (44) ^(b)	51 (44) ^(b)

(a) Assumed nominal nickel ferrocyanide composition.

(b) Measured by Total Cyanide Analysis.

and were centrifuged for 2000 g-h and 30 g-yr. These compositions were estimated using the solution composition and the amount of water measured for the In-Farm 2 samples. Based on this estimate, settled In-Farm 2 has the nominal composition $\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot 3 \text{H}_2\text{O} \cdot 19 \text{NaNO}_3 \cdot 9.5 \text{NaNO}_2 \cdot 1.9 \text{Na}_2\text{SO}_4 \cdot 1.4 \text{Na}_3\text{PO}_4$. These samples are currently being analyzed using the same methods enumerated above, but were yet incomplete at the time this paper was prepared.

In addition to our determinations of the compositions of the synthetic wastes, we also measured selected physical properties of some of the prepared wastes. Selected properties for In-Farm 2 are presented in Table III. This information is presented to allow calculation of tank specific properties such as the volume of ferrocyanide-bearing solids, energy density, and total energy content for the tank.

REACTIVITY AND EXPLOSIVITY STUDIES

To determine the thermal chemical reactivity and explosivity of our ferrocyanides or synthetic ferrocyanide flowsheet wastes, we used DSC, STG, TTX, pyrolysis/MS, and thermodynamic calculations. The first two methods, DSC and STG, are standard thermal analytical methods used to investigate the thermal sensitivity of chemical reactions. Pyrolysis/MS provides a complimentary method used to determine when a reaction begins and to gather information on

Table III. Selected Physical Properties of In-Farm 2 Solids

<u>Physical Property</u>	<u>Scavenged Waste Slurry</u>	<u>Settled Solids</u>	<u>Centrifuged Solids, 2000 g-h</u>	<u>Centrifuged Solids, 30 g-yr</u>
Supernate Density, g/mL	1.2	1.2	1.2	1.2
Density, g/mL	(NM) ^(a)	1.3	1.4	1.5
vol% settled solids	5.0	>100	NA	NA
vol% centrifuged solids 2000 g-h	0.7	14	100	NA
vol% centrifuged solids 30 g-yr	0.5	11	NA	100
wt% settled solids	5.4	100	NA	NA
wt% solids (air dried ambient)	2.5	46	48	54
wt% centrifuged solids 2000 g-h (wet)	0.8	16	100	NA
wt% centrifuged solids 30 g-yr (wet)	0.7	12	NA	100

(a) Not measured.

the reaction pathway. Our TTX test is a modification of the Henkin time-to-explosion test, which is a standard test used in the explosives industry (7,8,9).

Differential scanning calorimetry and STG measure enthalpy changes and mass changes, respectively, as the temperature is changed at a known and controlled rate. In our pyrolysis/MS analyses, we heated the sample at the same known and controlled rate as in the DSC and STG, and determined the molecular masses of the evolved gases. Combined, these three methods provide the following information: the temperature at which a reaction begins at an observable rate, the onset temperature, the enthalpy of a reaction, the mass changes of a reaction, and the identity of the gases evolved.

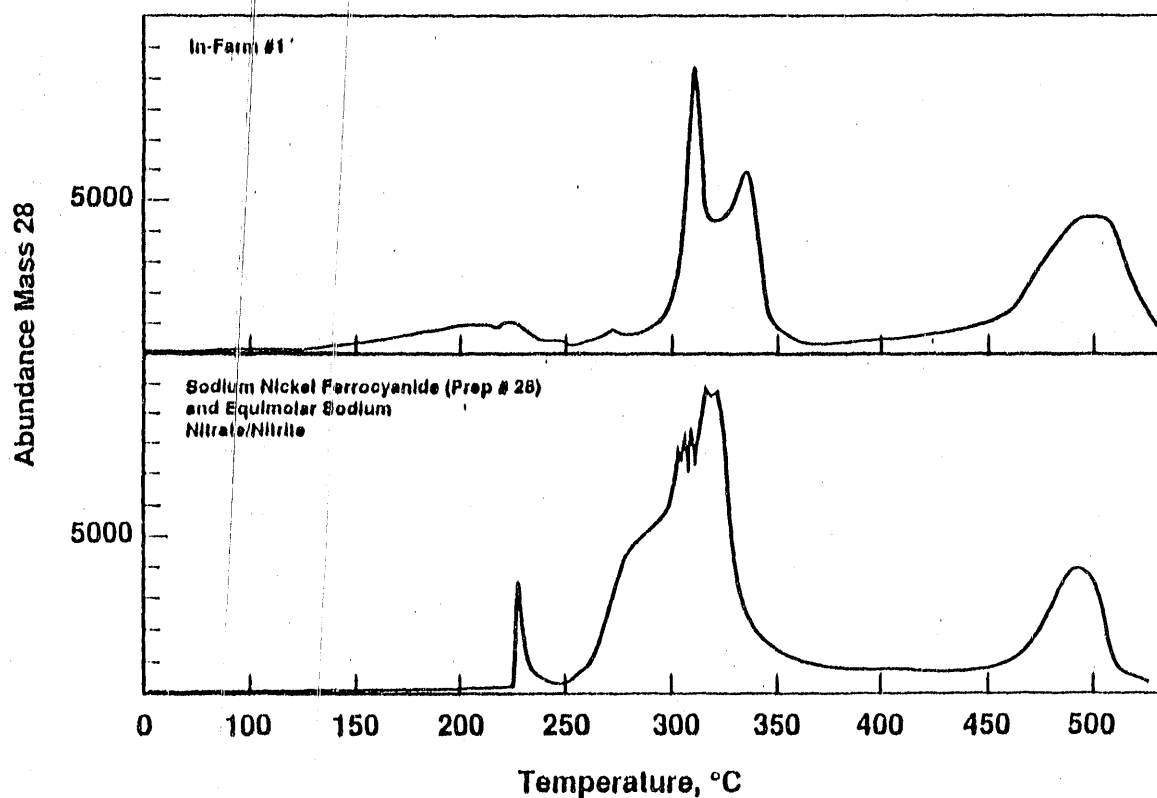
In our TTX test, a 20 to 50 mg sample is placed in a thin walled 5-mm diameter test tube, which is inserted into a temperature controlled stainless steel cylinder. The time to explosion or other event is then measured for a known temperature. Depending on the sample, the event can be accompanied by a loud retort, a quick release of gas, a flash of light, or by products spewing out of the test tube.

Thermal Reactivity Studies

Our DSC, STG, and pyrolysis/MS analyses of the synthetic ferrocyanide flowsheet wastes show that the oxidation of ferrocyanide by nitrate and/or nitrite is a complex, multistep reaction. Fig. 3 presents the pyrolysis/MS analyses for mass 28 gases (N_2 and/or CO) of In-Farm 1 and Prep 28 mixed with a near-stoichiometric (about 4.4 mole of $NaNO_3$ and 4.4 mole of $NaNO_2$ per mole of ferrocyanide) amount of equimolar sodium nitrate and nitrite. Fig. 4 presents the DSC and STG analyses of In-Farm 2, which was centrifuged for 30 g-yr respectively.

Until we added pyrolysis/MS to our suite of analyses, the endothermic behavior and the corresponding mass losses observed in the DSC and STG analyses below 200°C were attributed to water loss and the melting of the salts. However, inspection of Fig. 3 shows that either N_2 or CO is being released from In-Farm 1 beginning at about 130°C. Since both of these gases are potential products of the oxidation reaction between ferrocyanide and nitrate and/or nitrite and no other source of these gases exists, this indicates that the oxidation reaction of concern begins near 130°C. Note that we have observed NO production during TTX testing in the early stages of the reaction. We observed a colorless gas immediately above the sample and above the characteristic brown NO_2 produced by NO reaction with air.

The pyrolysis/MS mass 28 analyses for Prep 28 mixed with sodium nitrate and nitrite, which is also shown in Fig. 3, indicate that the oxidation of ferrocyanide in this mixture does not begin until about 220°C, which is near the melting temperature of equimolar sodium nitrate/nitrite. This is in contrast to In-Farm 1, which begins to react at 130°C.



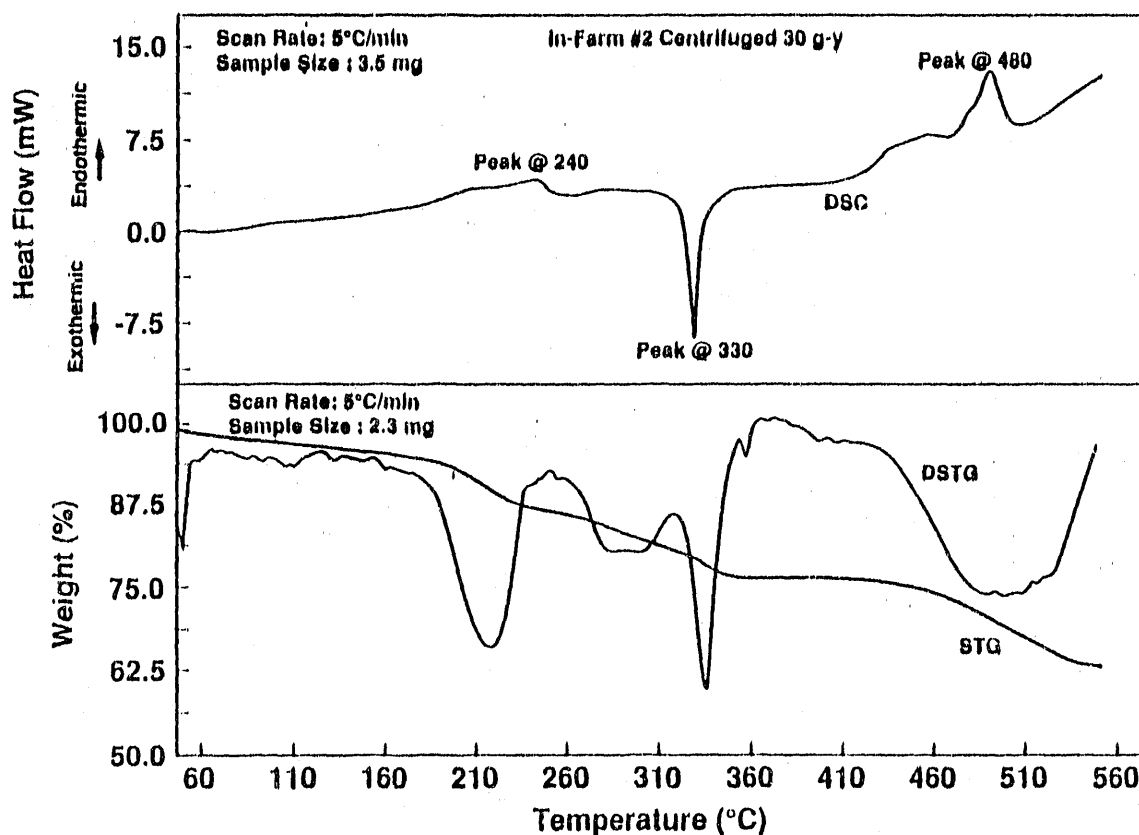
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FIGURE 3. N_2 and/or CO Releasing During Temperature Programmed Pyrolysis/MS Analysis of a) In-Farm 1, and b) Mixture of Prep 28 and Equimolar Sodium Nitrate and Nitrite

The answer to the difference in behavior may lie in the open cage-like structure of the sodium nickel ferrocyanide, similar to zeolites, and differences in the intimacy of cyanide and the oxidant due to the difference in preparation methods.

Prep 28 was washed to remove the soluble salts, including sodium nitrate, while In-Farm 1 was unwashed. Since In-Farm 1 was not washed, the soluble salts likely remained within the cage-like structure of the ferrocyanide thus providing an intimate contact between the cyanide and oxidant. The equimolar nitrate/nitrite added to Prep 28 for the experiment was crystalline and did not become mobile or free to attack the cyanide until it had melted.

With respect to the tanks, the pyrolysis/MS analyses presented here indicate that if the solids are dry and if heat is supplied, (e.g., from radiolytic decay), the oxidation reaction begins at temperatures as low as 130°C . Whether this results in the formation of a necessary intermediate for the rapid exothermic reaction is unknown and requires further study. In terms of managing the tanks, these results suggest a maximum temperature limit $<130^\circ\text{C}$.



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FIGURE 4. DSC, STG, and DSTG Analyses of In-Farm 2 Centrifuged 30 g-yr

The STG, the differential STG (DSTG), and the DSC analyses for In-Farm 2 centrifuged for 30 g-yr (Fig. 4) show a gradual endothermic mass loss until about 140°C, which could be due to the loss of free water. At 170°C, a greater endothermic mass loss occurs that could be due to loss of waters of hydration or, based on the results of the pyrolysis/MS results for In-Farm 1, N₂ or CO from reaction of nitrate or nitrite with ferrocyanide. Another reaction, which appears to be endothermic (the level of reactivity makes it difficult to determine DSC baseline) begins at 250°C and is followed by a very rapid exothermic reaction beginning at 300°C. There is a final endothermic reaction beginning at 410°C.

This last endothermic mass loss is not always observed or is recognizable by DSC or STG, even in seemingly duplicate analyses. In our Environmental Restoration paper (3) this is illustrated by comparing Fig. 2 with Fig. 4, and Fig. 3 with Fig. 5. We do not have an explanation for the appearance or nonappearance of this event in our analyses.

In-Farm 1 and In-Farm 2 exhibited different thermal behaviors based on our DSC, STG, and DSTG analyses [see our earlier paper for the In-Farm 1 analyses (3)]. In particular, the number of steps for the rapid exothermic

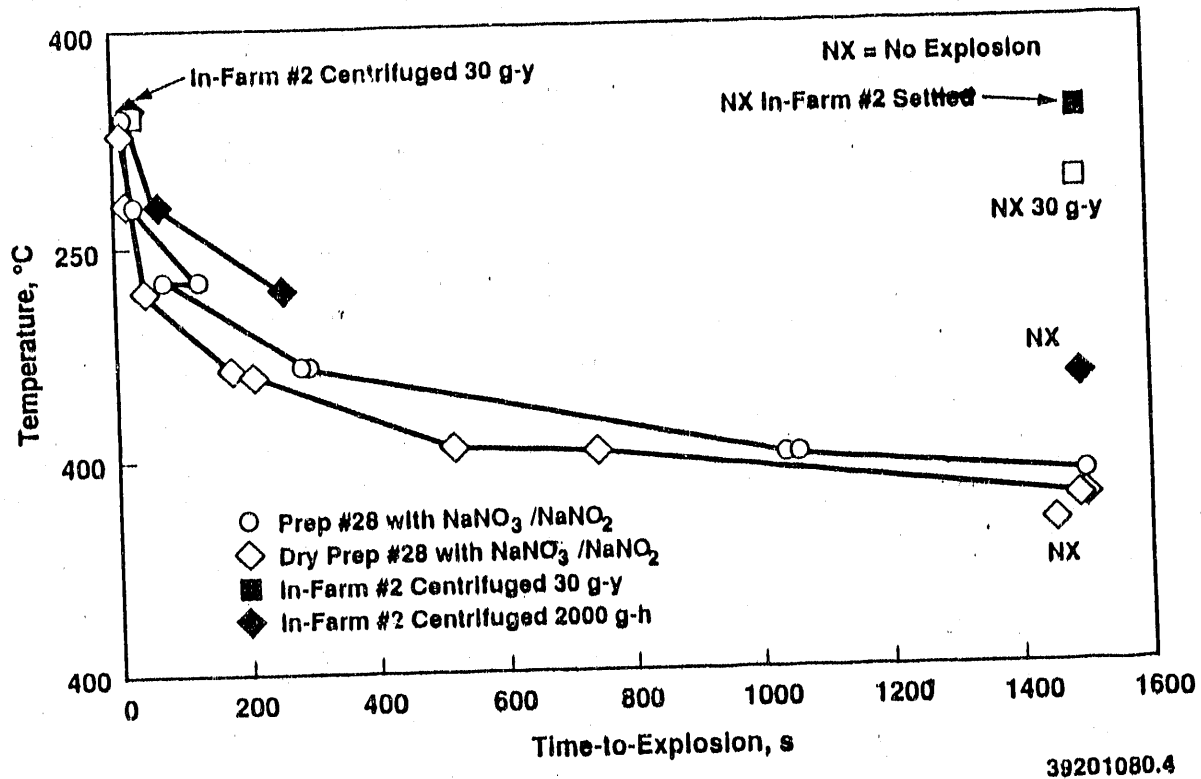


FIGURE 5. TTX Test Results for In Farm 2 Solids and Prep 28 Mixture

reactions differ. The reaction for In-Farm 1 proceeds in two distinct and overlapping steps while the exothermic behavior for In-Farm 2 proceeds in a single step.

We do not yet have sufficient information to explain the behavior difference between these two In-Farm flowsheet synthetic wastes. The difference is not due to the ratio of nitrate and nitrite since the ratios should be the same for both materials based on the makeup of the parent solution (Table II). The difference is not due to the ratio of oxidant to ferrocyanide since the samples of In-Farm 2 have oxidant ratios ranging from 4 to 0.4 of stoichiometry and the DSC analyses show only a single exothermic peak not two peaks for these three samples, assuming stoichiometry of reactions (1) and (2). Differences between In-Farm 1 and 2 include the presence of sodium phosphate, sodium chloride, and potassium nitrate in In-Farm 2.

In addition to the thermal sensitivities of ferrocyanide wastes, the energy released by reactions of nitrate and nitrite with ferrocyanide is important in the evaluation of the hazard. The final temperature of a reaction mixture is dependent on the enthalpy released, which in turn affects the kinetics of the reaction, which in turn determines whether an explosion occurs.

The enthalpy releases measured by DSC for In-Farm 1 and the three In-Farm 2 samples, presented in Table IV, are much less than predicted. The maximum measured exothermic enthalpy change was -1100 kJ/mole ferrocyanide or

roughly an energy yield of 30% of the nominal predicted maximum of -3200 kJ/mole ferrocyanide for a 2:1 nitrate to nitrite mole ratio mixture. Expected energy yields for explosive reactions from good explosives are usually about 80%.

Though all the enthalpy changes in Table IV are reported in terms of kJ/mole of ferrocyanide, indicating a dependency of enthalpy change on ferrocyanide content, the enthalpy change for the 170° to 270°C range is likely due to a number of different reactions including melting of the salt mixture and oxidation of ferrocyanide. Fig. 3 shows that ferrocyanide oxidation occurs in this region; note the similarity in this temperature region of the CO and/or N₂ evolution curve's shape to the shape of the DSC curve presented in Fig. 4. DSC analysis of a mixture of 70 mol% sodium nitrate and 30 mol% sodium nitrite shows endothermic behavior between 220° and 270°C.

The contribution of the oxidant to the endothermic behavior observed between 170° and 270°C, is illustrated by the DSC analysis of settled In-Farm 2. The DSC analysis of settled In-Farm 2, when compared to Fig. 4, shows an additional sharp third endothermic peak with a maximum at 220°C. This peak arises from the relatively large amount of dried salts from the scavenged solution associated with the precipitated ferrocyanide, see Table II. The DSC analysis of the dried solids arising from drying the scavenged supernate shows this same peak.

Table IV. Measured Enthalpy Changes for In-Farm 1 and In-Farm 2 Samples

Sample	Mole Ratio of NO ₃ + NO ₂ to Ferrocyanide	Reaction Range, °C	Peak Minimum or Maximum, °C	Enthalpy Change, kJ/mol Na ₂ NiFe(CN) ₆
In-Farm #1	6(4 + 2)	180 - 250	220	+90
		275 - 360	310, 340	-1060
		460 - 540	509	+790
In-Farm #2, settled	30(20 + 10)	170 - 270	210, 220, 260	+645
		300 - 400	360	-1150
		400 - 480	445	+815
In-Farm #2, 2000 g-h	4(3 + 1)	170 - 270	210, 240	+258
		280 - 405	335	-851
		460 - 510	490	+405
In-Farm #2, 30 g-yr	3(2 + 1)	170 - 270	210, 245	+360
		300 - 360	330	-560
		470 - 510	490	+330

Because this peak, observed for the settled In-Farm 2 sample at 220°C, is sharp and occurs at a temperature slightly less (10°C) than the melting point of equimolar sodium nitrate and nitrite, it is likely due to the melting of the mixed nitrate, nitrite, phosphate, sulfate, and chloride salt. There is, however, a corresponding mass loss observed in the STG analysis of this dried salt which confounds this hypothesis. The STG analysis suggests that waters of hydration are released simultaneously with the melt. To verify this hypothesis, pyrolysis/MS analyses or some other method for gas analysis are planned.

Table IV also shows that as the ratio of oxidant to ferrocyanide decreases below stoichiometric, the energy yield per ferrocyanide decreases. Thus, if the wastes are deficient in oxidant, the likelihood of thermal runaway decreases.

Thermal Explosivity Studies

We also investigated the explosivity of these synthetic ferrocyanide wastes and a mixture of Prep 28 and equimolar sodium nitrate and nitrite using the PNL TTX test. The results of the TTX test for the three In-Farm 2 solids and the Prep 28 mixture tested are presented in Fig. 5. The TTX test results for In-Farm 1 were reported our earlier paper (4).

The three samples of In-Farm 2 were relatively nonreactive. Noise was seldom associated with an event. The 30 g-yr sample did not explode below 380°C, and the settled sample did not explode when heated to 380°C. The 2000 g-h sample had a time-to-explosion behavior similar to that observed for In-Farm 1. This latter In-Farm 2 sample had little brisance associated with an event in contrast to the In-Farm 1 sample.

These results were somewhat surprising to us, since as we prepared In-Farm 2 for analysis, a 0.2 g sample of the settled material exploded in a 200° to 250°C oven. The sample was dried at 150°C in a vacuum oven before being heated to the temperature at which it exploded. Subsequent preparation of this material for analysis used a slower heating rate for the second heating step. This difference in behavior from the TTX test may be due to a larger sample size (200 versus 50 mg), or it could be due to either a longer incubation time in the sample preparation for analysis with the necessary formation of a less stable intermediate, or to the more rigorous drying at a higher temperature.

The results of the thermal analyses indicate that a variety of behaviors can be expected from the wastes present in Hanford ferrocyanide tanks. These behaviors are dependent on the composition of the original aqueous phase and on the settling behavior of the wastes. Our results also indicate that the conversion efficiency for the reaction is significantly lower than maximum predicted. The pyrolysis/MS, DSC, and STG show that ferrocyanides in synthetic wastes are susceptible to reaction with nitrate or nitrite at temperatures as low as 130°C.

Thermodynamic Evaluation of Hazard

The hazard associated with energetic reactions is a combination of energy release, rate of reaction, heat capacity of the system, and thermal conductivity out of the system. If the temperature can be prevented from rising to very high levels, then the reaction will be of limited hazard. Thus, the thermodynamics of the system are important.

As we reported earlier (3), based on thermodynamic calculations the hazard associated with ferrocyanide and nitrate and nitrite wastes can be mitigated by the presence of other waste constituents. The required amounts of these constituents are 3 g H₂O, or 24 g NaNO₃, or 61 g of NaAlO₂ per g of Na₂NiFe(CN)₆ mixed with a stoichiometric amount of sodium nitrate (1.6 g) to prevent the temperature of the system starting at 60°C to exceed 200°C. This corresponds to 54 wt% water in the mix.

Table V presents the excess enthalpy that would be released from the various In-Farm 2 mixtures if they were to react at a particular temperature assuming that the reaction between sodium nitrate and sodium nickel ferrocyanide was 80% efficient. Some heat would be released from the settled and 2000 g-h materials, but there is insufficient oxidant in the 30 g-yr material to heat the samples above 200°C. Using the calculated enthalpy changes, one can calculate the amount of a particular diluent such as water needed to prevent any further temperature increase. The maximum temperatures that would be predicted for dry settled and 2000 g-h centrifuged In-Farm 2 are 525° and 300°C, respectively.

Our thermodynamic calculations show that some compositions of waste have sufficient energy to cause the tank waste to reach excessive temperatures and some do not. These calculations also show that settling behavior plays a major role in the hazard associated with ferrocyanide waste storage since the 30 g-yr sample has insufficient oxidant to react with the ferrocyanide, which precludes thermal runaway.

Table V. Estimated ΔH Released from In-Farm 2 Samples

Sample	$-\Delta H$ at 200°C,	$-\Delta H$ at 250°C,	$-\Delta H$ at 307°C,
	kJ/mole $\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$	kJ/mole $\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$	kJ/mole $\text{Na}_2\text{NiFe}(\text{CN})_6 \cdot 4\text{H}_2\text{O}$
$\text{Na}_2\text{NiFe}(\text{CN})_6 + \text{NaNO}_3$ ^(a)	1890	1850	1800
In-Farm #2, settled	872	665	291
In-Farm #2, 2000 g-h	314	308	301
In-Farm #2, 30 g-y	Insufficient ^(b)	Insufficient ^(b)	Insufficient ^(b)

(a) Assumes 80% energy efficiency for stoichiometric mixture.

(b) Insufficient oxidant to heat waste components.

CONCLUSIONS

The results of our chemical characterizations and evaluations on the chemical reactivity and explosivity of synthetic ferrocyanide flowsheet wastes and alkali nickel ferrocyanide preparations show that the likely ferrocyanide resulting from the In-Farm flowsheet was sodium nickel ferrocyanide, and that the reaction between the ferrocyanide and nitrate and/or nitrite begins at about 130°C, though the reaction below 230°C appears to be endothermic. The synthetic wastes also appear to begin reacting at a lower temperature than a washed sodium nickel ferrocyanide mixed with equimolar sodium nitrate and nitrite. We speculate that this difference in behavior may be due to the intimacy of the mixing of the oxidant with the ferrocyanide, but could be explained by minor components in the mix. The lowest explosion temperature measured in our explosivity testing was 295°C for a nearly pure sample of sodium nickel ferrocyanide and a near-stoichiometric amount of equimolar sodium nitrate and nitrite. The lowest explosion or event temperature observed for synthetic wastes is 340°C, though using an order of magnitude more material and drying at 150°C in a vacuum oven resulted in an explosion between 200° and 250°C.

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