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FERROCYANIDE SAFETY PROGRAM FINAL REPORT OF
ADIABATIC CALORIMETRY & TUBE PROPAGATION TESTS
WITH SYNTHETIC FERROCYANIDE MATERIALS

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7. Abstract

Based on Fauske and Associates, Inc. Reactive System Screening Tool tests, the onset or initiation temperature for a ferrocyanide-nitrate propagating reaction is about 250 °C. This is at about 200 °C higher than current waste temperatures in the highest temperature ferrocyanide tanks. Furthermore, for current ambient waste temperatures, the tube propagation tests show that a ferrocyanide concentration of 15.5 wt% or more is required to sustain a propagating reaction in the complete absence of free water. Ignoring the presence of free water, this finding rules out propagating reactions for all the Hanford flowsheet materials with the exception of the ferrocyanide waste produced by the original In Farm flowsheet.

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Ferrocyanide Safety Program: Final Report of Adiabatic Calorimetry and Tube Propagation Tests With Synthetic Ferrocyanide Materials

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Date Published
September 1995

Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

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Hanford Company**

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SUMMARY

Based on Fauske and Associates, Inc. Reactive System Screening Tool tests, the onset or initiation temperature for a ferrocyanide-nitrate propagating reaction is about 250 °C. This is at about 200 °C higher than current waste temperatures in the highest temperature ferrocyanide tanks. Furthermore, for current ambient waste temperatures, the tube propagation tests show that a ferrocyanide concentration of 15.5 wt% or more is required to sustain a propagating reaction in the complete absence of free water. Ignoring the presence of free water, this finding rules out propagating reactions for all the Hanford flowsheet materials with the exception of the ferrocyanide waste produced by the original In Farm flowsheet.

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CONTENTS

1.0 INTRODUCTION	1
2.0 CHEMICAL REACTIONS AND THEORETICAL REQUIREMENTS	3
2.1 Thermal Runaway	3
2.2 Propagating Reactions	4
3.0 RSST PROPAGATION TESTS WITH IN FARM AND U PLANT SIMULANTS	8
3.1 Comparison Between In Farm and U Plant Simulants	8
3.2 Diluted In Farm Tests	8
4.0 TUBE PROPAGATION TESTS WITH IN FARM SIMULANT	15
5.0 TUBE PROPAGATION TESTS WITHOUT DILUENTS	17
6.0 REFERENCES	19
APPENDIX	
COMPOSITION OF SODIUM NICKEL FERROCYANIDE TEST MATERIAL	A-1

LIST OF FIGURES

2-1	Illustration of Transition to a Propagating Reaction	5
3-1	Self-heat Rate as a Function of Time for U Plant Simulant	9
3-2	Temperature as a Function of Time for U Plant Simulant	10
3-3	Pressure as a Function of Time for U Plant Simulant	11
3-4	Self-heat Rate as a Function of Time for In Farm Simulant	12
3-5	Temperature as a Function of Time for In Farm Simulant	13
3-6	Pressure as a Function of Time for In Farm Simulant	14

LIST OF TABLES

2-1	Comparison of Tube Propagation Test Results with Inequalities	6
4-1	Summary of Tube Propagation Tests With In Farm Flowsheet Simulant	16
5-1	Summary of Tube Propagation Tests With Stoichiometric Fuel-Oxidizer	17

LIST OF TERMS

cm	Centimeter
CTI	Contact Temperature Ignition
FAI	Fauske and Associates, Inc.
g	Gram
min	Minute
RSST	Reactive System Screening Tool
VSP	Vent Sizing Package

1.0 INTRODUCTION

As part of the effort to assess the requirements for propagating reactions and to assure that propagating reactions do not occur in waste tanks known to contain ferrocyanide materials (DOE 1994), adiabatic calorimetry and tube propagation tests have been performed in the laboratories of Fauske & Associates, Inc (FAI).

The FAI assessment included the use of both the Reactive System Screening Tool (RSST) (Creed and Fauske 1990) and the Vent Sizing Package (VSP) (Fauske and Leung 1985). Both are widely-used industrial tools implementing the American Institute of Chemical Engineers Design Institute for Emergency Relief System methods to quantify runaway reactions to support safe design and operation in the commercial chemical industry. In these tests sizeable samples (10 g and 70 g) are slowly heated (~ 1 °C/min) under essentially zero heat loss condition, providing measurements of the adiabatic temperature rise and the onset temperature for a propagating reaction. Because of the adiabaticity of these calorimeters, the observations can be directly extrapolated to larger mass sizes.

Dedicated tube propagation tests were also conducted to verify the fuel concentration necessary to sustain a propagating reaction as well as to determine the moisture content that will inhibit such a reaction at ambient waste temperatures. In these tests, a confined cylinder of simulated waste (50 - 70 g) is ignited at the open upper end and the rate of propagation (if any) is measured by noting the time when the reaction front passes imbedded thermocouples (Epstein et al. 1994a).

Based on the RSST tests, the onset or initiation temperature for a propagating reaction is determined to be about 250 °C, i.e., approximately 200 °C higher than current waste temperatures. Furthermore, for current ambient waste temperatures, the tube propagation tests show that a $\text{Na}_2\text{NiFe}(\text{CN})_6$ concentration of 15.5 wt% or more is required to sustain a propagating reaction in the complete absence of free water. Ignoring the presence of free water, this finding rules out propagating reactions for all Hanford flowsheet materials with the exception of the waste produced by the original In Farm flowsheet.

The strong influence of water is also clearly illustrated and the data show that about 12 wt% moisture is enough to inhibit propagation with the In Farm flowsheet material while only 20 wt% will prevent propagation of a stoichiometric fuel-oxidizer mixture. The latter moisture level is about a factor of two below the moisture retention characteristics of typical ferrocyanide sludge (Epstein et al. 1994b).

The suggested lower bound theoretical fuel concentration value (x_r) for $\text{Na}_2\text{NiFe}(\text{CN})_6$ based on satisfying the Contact Temperature Ignition (CTI) condition (Fauske et al. 1995) is given by

$$x_f > 0.10 + 0.47x_w ; \quad x_w \leq 0.2 \quad (1-1)$$

where x_w is the free moisture weight fraction.

It should be noted that application of inequality (1-1), even ignoring the presence of moisture altogether, would leave all ferrocyanide tanks of concern in the *safe* category (Postma et al. 1994).

A discussion of reaction types and theoretical minimum requirements for uncontrollable reactions are provided in Section 2.0. Data obtained to date in addition to those reported in Fauske (1992), Fauske (1993), and Epstein et al. (1994a) are summarized in the remaining sections. Specific RSST propagation tests with In Farm and U Plant simulants are summarized in Section 3.0. Tube propagation tests with In Farm simulant are discussed in Section 4.0, and tests with standard ferrocyanide material (stoichiometric fuel-oxidizer mixture) are summarized in Section 5.0.

2.0 CHEMICAL REACTIONS AND THEORETICAL REQUIREMENTS

To complete the hazard assessment, it is essential to differentiate between homogeneous thermal runaway reactions and propagating reactions. These are discussed below including specific minimum requirements for such reactions. The important role of moisture in preventing uncontrollable reactions is also discussed.

2.1 Thermal Runaway

Thermal runaway is generally a bulk phenomenon and the reaction rates normally have an Arrhenius type dependence on temperature (such as doubling for every 10 °C temperature rise). The potential for runaway is generally assessed by comparing adiabatic runaway and characteristic cooling response times to the storage or exposure time.

If the following inequality is satisfied

$$t_{adiabatic} > t_{storage} \quad (2-1)$$

where $t_{adiabatic}$ is the characteristic time of adiabatic runaway and $t_{storage}$ is the storage time, the situation can immediately be judged to be safe, i.e., a thermal runaway reaction cannot occur. Unfortunately, the value of $t_{adiabatic}$ is not known for the materials in the Hanford Site waste tanks and $t_{storage}$ is very large (tens of years). Therefore, inequality (2-1) is of little use.

However, thermal runaway can also be ruled out if the following inequality is satisfied

$$t_{adiabatic} > t_{cooling} \quad (2-2)$$

where $t_{cooling}$ is the characteristic passive cooling response time of the system. In case of the waste tanks, $t_{cooling}$ can be estimated from

$$t_{cooling} = \frac{L^2}{4\alpha} \quad (2-3)$$

where L can be set equal to the total nonconvective waste height in the tank and α is the thermal diffusivity of the waste material. The values of $t_{cooling}$ for the Hanford Site waste tanks are generally less than one year, which is small compared with the time that has already elapsed without runaway having occurred. This provides proof that inequality (2-2) is indeed satisfied at the present time. This conclusion can be made without requiring a knowledge of $t_{adiabatic}$ or the actual chemical composition and water content. For the passively

cooled tanks (decay and reaction heat are removed by natural phenomena such as conduction and free convection) which are clearly cooling down, a thermal chemical runaway reaction, it would have had to occur many years ago when the tanks were at higher temperatures.

2.2 Propagating Reactions

In contrast to homogeneous runaway reactions, a propagating reaction occurs as a reaction zone traveling through the solid or liquid phase (i.e., similar to a flame propagating through a flammable vapor cloud), and the rate shows no simple dependence on temperature. Whether a particular mixture will experience deflagration or propagation depends on the concentration and the temperature.

The potential for a propagating reaction and its initiation temperature or onset temperature can be determined by slowly heating the mixture in an adiabatic calorimeter such as the RSST. An example of transition from a homogeneous or Arrhenius runaway reaction to a propagating reaction is shown in Figure 2-1. Measurements of this type show that the initiation temperature for a ferrocyanide propagating reaction is about 250 °C and above.

Since homogeneous runaway reaction scenarios can be ruled out, the necessary conditions for a propagating reaction through cold ferrocyanide containing waste material becomes of principal interest. Clearly this requires the presence of an ignition source (such as a hot spot, flame, etc.) to locally bring the temperature up to the required initiation temperature. Such ignition sources are not believed to be present in the Hanford Site ferrocyanide wastes.

Given the presence of an adequate ignition source, the lower bound value of the fuel concentration or reaction temperature that will sustain a propagating reaction through cold material, can be related to the basic requirement that the contact or interface temperature, T_i , between the reacted and unreacted cold material, must be greater than the initiation temperature, T_{ig} (Fauske et al. 1995).

$$T_i \geq T_{ig} \quad (2-4)$$

If the interface temperature, T_i , is below the minimum initiation temperature, the reaction will slow down and be quenched by the much colder unreacted solid layer (Fauske et al. 1995).

Figure 2-1. Illustration of Transition to a Propagating Reaction

Based upon inequality (2-4), the adiabatic combustion temperature, T_{ad} , and the fuel concentration, x_f , must be high enough to satisfy the following inequalities (Fauske et al. 1995)

$$(2-5) \quad T_{ad} > 2 \left[T_{ig} + \frac{x_w C_w}{x_w \lambda} \right]$$

and

$$(2-6) \quad x_f > \frac{\Delta H_R}{2 \left[T_{ig} C + x_w \lambda \right]}$$

where λ is the latent heat of water vaporization, C_w is the specific heat for water, C is an effective average specific heat value of the reacting mixture and its products over the temperature range of interest, and ΔH_R is the ideal heat of reaction based on a unit mass of fuel. Inequalities (2-5) and (2-6) are clearly supported by the measured propagation data summarized in Table 2-1 ($T_{ig} = 250^\circ\text{C}$; $C \approx 2000 \text{ J kg}^{-1} \text{K}^{-1}$, and $\Delta H_R = 9.5 \times 10^6 \text{ J kg}^{-1}$). It is noted that inequalities (2-5) and (2-6) are only considered reasonable for $x_w < 0.2$. For values of 0.2 and larger, the sludge water solution will appear as a continuous phase and inequality (2-4) would not be satisfied. That is, propagation is not possible because $T_i \approx T_B = 130^\circ\text{C}$, which is far below T_{ig} ($\sim 250^\circ\text{C}$).

Table 2-1. Comparison of Tube Propagation Test Results with Inequalities

Fuel Concentration (wt%)	Water (wt%)	Measured Temperature ($^\circ\text{C}$)	Temp to Satisfy Inequality (2-5) ($^\circ\text{C}$)	Fuel to Satisfy Inequality (2-6) (wt%)
15.5	0	~ 800	> 500	~ 10
14	0	~ 30	> 500	~ 10
26	8	~ 850	> 584	~ 14
26	12	~ 30	> 626	~ 16
35	15	~ 950	> 657	~ 18
35	20	~ 30	> 709	~ 20

The water concentration that corresponds to this condition can be calculated by considering that part of the oxidizer (NaNO_3 , NaNO_2) is dissolved in the water (equal parts), and is obtained by satisfying that the volume fraction of the liquid phase exceeds 50%

$$\frac{\left[\frac{m_{\text{water}}}{\rho_{\text{water}}} + \frac{m_{\text{nitrate}}}{\rho_{\text{nitrate}}} \right]}{\left[\frac{m_{\text{water}}}{\rho_{\text{water}}} + \frac{m_{\text{nitrate}}}{\rho_{\text{nitrate}}} + \frac{m_{\text{insoluble}}}{\rho_{\text{insoluble}}} \right]} > 0.5 \quad (2-7)$$

Using the following property values including $\rho_{\text{water}} = 1 \text{ g/cm}^3$, $\rho_{\text{nitrate}} = 2.2 \text{ g/cm}^3$, $\rho_{\text{insoluble}} = 2.0 \text{ g/cm}^3$, a water concentration of 20% is calculated. Water concentrations of this magnitude would prevent propagation of all stoichiometric mixtures involving nitrate/nitrite ($\text{NaNO}_3/\text{NaNO}_2$) as the oxidizing agent and this observation is confirmed by the experiments completed to date (see Table 2-1).

3.0 RSST PROPAGATION TESTS WITH IN FARM AND U PLANT SIMULANTS

Previous RSST tests reported in Fauske (1992) subjected In Farm and U Plant simulant samples to a heating rate of about 1 °C/min. using the RSST test cell external heater. This slow external heating rate allows a measure of the initiation temperature for a self-propagating reaction (see Figure 2-1) if one should occur. While a transition to a propagating reaction occurred for the In Farm simulant at a temperature of about 250 °C, the transition to a propagating reaction was absent with the U Plant simulant [see Figure 3-1 in Fauske (1992)]. These flowsheet simulants have been further screened for propagating characteristics by subjected samples to full heater power from the RSST test cell immersion heater (~10 watts). The initial temperature of the samples was about 30 °C and the containment pressure was set at 28 pounds per square-inch absolute. The results are reported below.

3.1 Comparison Between In Farm and U Plant Simulants

Consistent with previous observations (Fauske 1992), the In Farm 1 simulant (~26 wt% fuel) clearly exhibited a propagating reaction characteristic at ambient sample temperature. This is in contrast to the U Plant simulant (~8.3 wt% fuel) which did not exhibit a propagating characteristic even after substantial heating. The difference in behavior is illustrated in Figures 3-1 through 3-3.

3.2 Diluted In Farm Tests

Additional propagation screening tests were carried out with the In Farm simulant diluted with NaNO_2 to produce fuel concentrations of 15.6 and 18.6 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$. These two tests were also repeated using Al_2O_3 as the diluent producing very similar results. The higher fuel concentration sample exhibited a propagation when the sample reach a temperature of about 260 °C. In contrast, the 15.6 wt% fuel sample exhibited a transition at a sample temperature of about 270 °C. Representative data are illustrated in Figures 3-4 through 3-6.

Based on the above observations it can be concluded that (1) the RSST with its immersion heater provides an adequate means for screening propagation characteristics, and (2) a ferrocyanide fuel concentration of at least 15 wt% is required to produce a self-propagating reaction with cold flowsheet simulant.

Figure 3-1. Self-Heat Rate as a Function of Time for U Plant Simulant

Figure 3-2. Temperature as a Function of Time for U Plant Simulant

Figure 3-3. Pressure as a Function of Time for U Plant Simulant

Figure 3-4. Self-Heat Rate as a Function of Time for In Farm Simulant

Figure 3-5. Temperature as a Function of Time for In Farm Simulant

Figure 3-6. Pressure as a Function of Time for In Farm Simulant

4.0 TUBE PROPAGATION TESTS WITH IN FARM SIMULANT

Several one-inch tube propagation tests were completed with In Farm simulant. The material was received from Westinghouse Hanford Company and was reported to contain 16 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ on a wet basis with a free water content of 44.6 wt% (see Appendix). This translates to 28.9 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ on a dry basis. The noted free water content was verified in separate drying experiments completed at the FAI laboratory.

The first sample tested included a 15.5 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ dry mixture preheated to 30 °C. The 15.5 wt% concentration was obtained by diluting the In Farm simulant with NaNO_3 . The use of the thermite (barium oxide and aluminum) ignition source, as well as the hot wire, resulted in sustained propagation, but the propagation velocity was measured to be only about 2 cm/min.

In view of the above result, the flowsheet material was further diluted with NaNO_3 to yield a 12 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ concentration on a dry basis. Tests with this concentration were carried out at both 30 °C and 130 °C. Both tests resulted in non-propagating events.

In view of the above results, the In Farm simulant was diluted with NaNO_3 in order to produce 14 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ samples. Preheating to 30 °C again did not produce a propagating event. When the sample was preheated to 130 °C, a partial propagation event took place. The above observations are summarized in Table 4-1.

Based on the above results, it was concluded that a fuel concentration of about 15 wt% is required to support self-propagation at ambient waste temperatures given a credible initiator.

Finally; it should be noted that the 15 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ sample was also tested in the RSST using the immersion heater at full power. Consistent with the tube propagation test, the RSST test indicated a propagating reaction starting at about 280 °C. As such, it should be noted that previous RSST tests with the older In Farm simulant [~ 26 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ on a dry basis] reported in Section 3.0, clearly indicated a propagating event at 260 °C when the sample was diluted to 18.6 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$, while a sample diluted to 15.6 wt% $\text{Na}_2\text{NiFe}(\text{CN})_6$ exhibited a propagating event at about 270 °C. It is interesting to note that the 15 wt% and the 18.6 wt% samples resulted in almost identical results when tested for propagating events in the RSST.

In summary, fuel concentrations less than 15 wt% will not produce a propagating event given a credible initiator.

Table 4-1. Summary of Tube Propagation Tests With In Farm Flowsheet Simulant

Ignition Source	Fuel Concentration (wt%)	Initial Temperature (°C)	Propagation Velocity (cm/min)
Hot Wire	15.5	30	~2.5
Thermite	15.5	30	~1.5
Thermite	12	30	0
Thermite	12	130	0
Thermite	14	30	0
Thermite	14	130	Partial Burn

5.0 TUBE PROPAGATION TESTS WITHOUT DILUENTS

Several 1-inch tube propagation tests have been completed with the dried "standard ferrocyanide material (pure $\text{Na}_2\text{NiFe}(\text{CN})_6$)" received from Westinghouse Hanford Company. The composition of this material is provided in the Appendix. The testing procedures are similar to that described in Fauske (1992). The results are summarized in Table 5-1.

Table 5-1. Summary of Tube Propagation Tests With Stoichiometric Fuel-Oxidizer

Fuel Concentration wt%	Water Concentration wt%	Propagation Velocity cm/min
35	0	~20
35	15	~2.8
35	20	~0

The retarding effect of moisture is clearly illustrated. Note that 20 wt% moisture inhibits propagation altogether for an otherwise stoichiometric mixture of $\text{Na}_2\text{NiFe}(\text{CN})_6$ and NaNO_3 .

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APPENDIX

COMPOSITION OF SODIUM NICKEL FERROCYANIDE TEST MATERIAL

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Westinghouse
Hanford Company

P.O. Box 1970 Richland, WA 99352

August 18, 1994

9455562

Dr. H. K. Fauske, President
Fauske and Associates, Inc.
16W070 West 83rd Street
Burr Ridge, Illinois 60521

Dear Dr. Fauske:

FERROCYANIDE PROPAGATION TESTS WITHOUT SOLID DILUENTS

- References: (1) Kawamura, S., S. Shibata, and K. Kurotaki, *Analytica Chimica Acta*, 81: 91, (1976).
- (2) Purchase Order No. MRS-SIV-296845 to Fauske and Associates, "Provide Technical Support and Perform Experiments to Characterize Ferrocyanide Simulant Material Behavior"

Please complete ferrocyanide propagation tests to 1) identify the moisture content which prevents the propagation of a stoichiometric mixture of "standard ferrocyanide material" and sodium nitrate, and 2) determine the effect, if any, of upward propagation on the ferrocyanide concentration limit of propagation using 25 mm diameter propagation tests. The "standard ferrocyanide material" sent to you in June 1994 should be used for these tests. It is also requested that you perform propagation tests to determine the effect of increasing diameter from 25 to 50 mm on propagation initiation for a given test material concentration. It is suggested that a plug ignition source be used for these tests instead of a point source. Westinghouse Hanford Company requests that you transmit the test procedures for performing the upward propagation tests for review and approval before these tests commence.

The dried "standard ferrocyanide material" composition has been determined for use in preparing test mixtures. Chemical analyses of this material have been completed by X-ray diffraction (XRD), X-ray fluorescence (XRF), inductively coupled plasma (ICP) - (LiBO₂ fusion) and ICP - (elixer plus nitric acid dissolution), reverse ion chromatography (RIC), and simultaneous thermogravimetric analysis (TG), differential thermal analysis (DTA), and evolved gas analysis (EGA).

For dried (in vacuum at 60°C for 48 hrs.) "standard ferrocyanide material" the water content was determined to be 17.0 wt% by simultaneous TG, DTA, and EGA as determined by Dr. G. S. Barney of Westinghouse Hanford Company. The water remaining after drying under vacuum did not completely leave the

Dr. H. K. Fauske
Page 2
August 18, 1994

9455562

ferrocyanide until heated to 300°C in an argon atmosphere. Tightly bound water was determined to be about 3.76 moles of water per hexacyanoferrate gram atom on the average. The cation composition of the "standard ferrocyanide material" by elixir plus nitric acid solution ICP analysis and XRF is listed in the table below as provided by Dr. K. H. Pool of Pacific Northwest Laboratory. The concentrations of all other cations were less than detectable by ICP and XRF. The cyanide content was determined to be all in the form of ferrocyanide (i.e. no ferricyanide or free cyanide was found). These analyses provided close agreement on balance of charge between anions and cations (1.53 vs. 1.54, respectively) and on total sample accounted for (98.3 wt%). The iron and cyanide analyses were in very good agreement for the expected presence of stable hexacyano-ferrate (II).

Composition of Ferrocyanide "Standard Material"		
Analyte	Method of Analysis	wt% after vacuum drying
Iron	ICP (dissolution)	14.0
Nickel	ICP (dissolution)	17.1
Sodium	ICP (dissolution)	9.1
Cyanide $[\text{Fe}(\text{CN})_6]^{4-}$	RIC [RIC+ICP dissolution]	39.7 [53.7]
Water	Simultaneous TG, DTA, and EGA	17.0
Potassium	XRF	0.79
Boron	ICP (dissolution)	0.48
Sulfur	XRF	<0.15
Calcium	XRF	0.016
Chromium	XRF	0.005
Lead	XRF	0.001
TOTAL		98.2 to 98.4

The mole ratios of the cations and cyanide anion are such that the average chemical composition of the ferrocyanide with balanced anions is $\text{Na}_{1.6}\text{Ni}_{1.2}\text{Fe}(\text{CN})_6 \cdot 3.76 \text{ H}_2\text{O}$. It should be noted that the sulfur content is very low indicating that the sulfate content is low. The potassium concentration is greater than expected and amounts to only about 0.02 gram atoms per gram atom of iron. Any potassium is expected to behave like

Dr. H. K. Fauske
Page 3
August 18, 1994

9455562

sodium and amounts to an equivalent of 0.02 of the 1.58 gram atoms of sodium as part of the sodium nickel ferrocyanide. The XRD results of the "standard ferrocyanide material" suggest the presence of two uncertain phases of ferrocyanide. Reference 2 indicates that for preparations in which 1:1 ferrocyanide to nickel is used (as in the case of the preparation of the "standard ferrocyanide material") the product consists of two phases, $\text{Ni}_2\text{Fe}(\text{CN})_6$ and $\text{Na}_2\text{NiFe}(\text{CN})_6$. The "standard ferrocyanide material" could consist of these two phases at a mole ratio of about 1:4, respectively, and satisfy the ICP analysis. Further XRD evaluations are being made to support or refute this conclusion.

The exact stoichiometric quantity of sodium nitrate to react with the "standard ferrocyanide material" is not known but 6 moles per gram atom of ferrocyanide is a generally accepted value for disodium mononickel ferrocyanide and should be used for these test purposes.

This work should be conducted within the scope of the Reference 2 purchase order. Please address any questions of a technical nature to Mr. Dave Jeppson at (509) 376-6058.

Very truly yours,

R. J. Cash, Manager
Ferrocyanide Safety Technology Program
Tank Waste Remediation System

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