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# Ferrocyanide Tank Waste Stability

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# FERROCYANIDE TANK WASTE STABILITY

K. D. Fowler

## ABSTRACT

*Ferrocyanide wastes were generated at the Hanford Site during the mid to late 1950s as a result of efforts to create more tank space for the storage of high-level nuclear waste. The ferrocyanide process was developed to remove* $^{137}Cs$ *from existing waste and newly generated waste that resulted from the recovery of valuable uranium in Hanford Site waste tanks.*

*During the course of research associated with the ferrocyanide process, it was recognized that ferrocyanide materials, when mixed with sodium nitrate and/or sodium nitrite, were capable of violent exothermic reaction. This chemical reactivity became an issue in the 1980s, when safety issues associated with the storage of ferrocyanide wastes in Hanford Site tanks became prominent. These safety issues heightened in the late 1980s and led to the current scrutiny of the safety issues associated with these wastes, as well as current research and waste management programs.*

*Testing to provide information on the nature of possible tank reactions is ongoing. This document supplements the information presented in* Summary of Single-Shell Tank Waste Stability, WHC-EP-0347, *March 1991 (Borsheim and Kirch 1991), which evaluated several issues. This supplement only considers information particular to ferrocyanide wastes.*

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| | |
|---|---|
| CASS | Computer Automated Surveillance System |
| CTMS | Continuous Temperature Monitoring System |
| IR | Infrared |
| LANL | Los Alamos National Laboratory |
| SST | Single-Shell Tank |
| TRAC | Track Radionuclide Component |

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# FERROCYANIDE TANK WASTE STABILITY

## 1.0 INTRODUCTION

The Hanford Site ferrocyanide-nitrate reaction issues are complex. Most of the Hanford Site single-shell tanks (SSTs) contain abundant oxidants as sodium nitrate/nitrite salts. Several tanks also contain potential fuels (i.e., ferrocyanide compounds in significant quantities). The safety of the waste stored in these tanks depends on keeping the waste temperature below the onset temperature of a runaway exothermic reaction*. The moisture content of the waste is important because, if the moisture is maintained above a certain level, the temperature cannot approach the onset temperature.

### 1.1 PURPOSE AND SCOPE

This document provides an updated evaluation of the chemical stability of radioactive ferrocyanide wastes stored in Hanford Site underground SSTs. Potentially hazardous reactions are identified and presented along with related information and analyses. This evaluation is based on work performed as of June 1992. Additional work that is ongoing or planned in support of the resolution of ferrocyanide safety issues is also noted.

The Waste Tank Ferrocyanide Stabilization program was established in 1990 to address safety issues concerning SSTs containing ferrocyanide-bearing wastes. Results of this program are presented in four areas: (1) ensuring proper tank monitoring; (2) waste characterization; (3) computer modeling and analysis; and (4) research and development. The most complete reporting of the ongoing and planned work addressing the ferrocyanide safety issue is contained in the *Quarterly Reports on Defense Nuclear Facilities Safety Board Recommendation 90-7*, WHC-EP-0474 through WHC-EP-0474-5.

The purpose and scope of this supplement are limited to updating WHC-EP-0347, *Summary of Single-Shell Tank Waste Stability*, concerning issues particular to ferrocyanide-bearing wastes (Cash and Dukelow 1992a and 1992b).

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*A runaway chemical reaction occurs when the heat generated within a volume exceeds the rate at which heat is lost from the volume.

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# 2.0 SUMMARY

Several efforts are underway to investigate the properties of ferrocyanide compounds and to characterize actual ferrocyanide wastes in support of the Ferrocyanide Safety Program. To date, results of these investigations have not indicated that continued storage of ferrocyanide-bearing wastes will adversely affect safety.

Isothermal studies have been conducted investigating the reaction pathways and kinetics associated with the reaction between sodium nickel ferrocyanide and sodium nitrate. Preliminary interpretation of results shows little reaction below 220 °C (428 °F) and some exothermic behavior at 240 °C (464 °F). Significant reaction rates were observed at higher temperatures, particularly at temperatures above 300 °C (572 °F).

Reaction studies also indicate that, in order to react, ferrocyanide material would have to be dried out first. Wet ferrocyanide material should not react or propagate.

Vapor sampling and core sampling activities thus far have yielded no indication that the continued safe storage of ferrocyanide wastes is in jeopardy.

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# 3.0 TANK MONITORING

## 3.1 TEMPERATURE MONITORING

A Continuous Temperature Monitoring System (CTMS) is being installed for the ferrocyanide-containing tanks. All data is collected automatically at the Computer Automated Surveillance System (CASS) Operator Control Station. This monitoring system is independent of the CASS and capable of displaying data to an operator upon request. Trend data on selected points is available for display in numerical or graphical form (Cash and Dukelow 1992a).

The CTMS became operational in September 1991 and has the capability to assign alarms for change in value of any temperature point. Five BY Farm tanks were connected to the system in September 1991 and an additional five in December 1991. The tanks in the system include 241-BY-101, -103, -104, -105, -106, -107, -108, -110, -111, and -112. The work to connect three tanks in TY Farm and one in TX Farm was completed in April 1992. Future plans include the expansion of the system to four tanks in C Farm and two in T Farm (Cash and Dukelow 1992a).

Temperature data from the ferrocyanide tanks are presented in Table 3-1.

## 3.2 INFRARED MONITORING

Infrared (IR) scanners could be an aid for the detection of hypothetical localized hot spots in the waste tanks. The detection error band applied to IR scanning was determined to be approximately 1.1 °C (2 °F), based upon laboratory calibration experiments. An evaluation of the 24 ferrocyanide tanks indicates that all but 8 of the tanks contain a relatively shallow waste depth, and would exhibit a detectable surface temperature pattern to indicate the presence of a hot spot of concern.*

It is expected that even the ferrocyanide tanks with larger amounts of low thermal conductivity waste can be scanned for hot spot indications with a high degree of confidence because of the good IR scanning sensitivity. For comparison of relative temperature changes across a surface, a temperature differential discrimination of 0.28 °C (0.5 °F) could routinely be resolved.

The IR scanning system will not allow an exact hot spot size and temperature determination, but could provide information needed to determine the worst-case hot spot causing a detected temperature pattern.

## 3.3 GAMMA SCANNING

Ferrocyanide waste tank neutron and gamma scan interpretation work using data analysis and available surveillance techniques is underway to identify a method for determining in situ moisture content of waste. Several techniques

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*A hot spot of concern is one where the temperature exceeds 220 °C (425 °F).

Table 3-1. Temperature Data for Ferrocyanide Watchlist Tanks.

| Tank | Maximum Temperature (°F) | Date | Probe |
|---|---|---|---|
| BX-102 | 67 | 08/07/92 | TC (thermocouple tree) |
| BX-106 | 65 | 08/07/92 | TC |
| BX-110 | 74 | 08/07/92 | TC |
| BX-111 | 67 | 08/07/92 | TC |
| BY-101 | 72 | 08/07/92 | TC |
| BY-103 | 76 | 08/07/92 | TC |
| BY-104 | 124 | 08/07/92 | TC |
| BY-105 | 114 | 08/07/92 | TC (2 trees) |
| BY-106 | 124 | 08/07/92 | TC |
| BY-107 | 94 | 08/07/92 | TC |
| BY-108 | 105 | 08/07/92 | TC |
| BY-110 | 119 | 07/18/92 | TC |
| BY-111 | 85 | 08/07/92 | LOW[a] |
| BY-112 | 80 | 08/07/92 | LOW[a] |
| C-108 | 77 | 08/09/92 | TC |
| C-109 | 87 | 08/09/92 | TC |
| C-111 | 76 | 08/09/92 | TC |
| C-112 | 90 | 08/09/92 | TC |
| T-101 | 70 | 08/09/92 | TC |
| T-107 | 68 | 08/06/92 | TC |
| TX-118 | 74 | 08/07/92 | TC |
| TX-101 | 60 | 08/07/92 | TC |
| TY-103 | 68 | 08/02/92 | TC |
| TY-104 | 67 | 08/07/92 | TC |

[a] Dedicated TC in liquid observation well.

are being developed to determine the potential for obtaining new information about moisture levels, material density, and other waste characteristics from the existing tank scans. The techniques could then be used in a monitoring system to determine the axial moisture profile within the wastes of ferrocyanide tanks in their present state and during remediation (Cash and Dukelow 1992b).

Gamma scans of the core sample segments from Tank 112-C show multiple peaks of various heights along the vertical axis of the segments. These results are consistent with the scavenged ferrocyanide sludge settling as layers in the tank. Each layer would have a different $^{137}$Cs concentration, as did the feed tank being scavenged*.

## 3.4 VAPOR SPACE MONITORING

An effort is now underway to conduct flammable and toxic gas monitoring and analyses in the 24 ferrocyanide tanks. Results from Tank BY-104 indicate no significant levels of flammable gas. Detected levels of ammonia were, however, above the threshold limit value for personnel exposure. Results from Tanks BY-104 and 112-C, and preliminary results from Tanks 109-C and BY-110, indicate no significant levels of flammable gas. This is not surprising because past sampling conducted by Industrial Hygiene and Safety has indicated no flammable gas content above 6 percent of the lower flammability limit. Samples of the two BY Farm tanks did, however, contain concentrations of ammonia which are well above the threshold limit value**.

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*Cs$^{137}$ contributes almost all of the gamma activity for Tank 112-C.

**The threshold limit value time-weighted average is the time-weighted average concentration for a normal 8-hour workday and a 40-hour workweek, to which nearly all workers may be repeatedly exposed without adverse effect.

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# 4.0 WASTE CHARACTERIZATION

## 4.1 FERROCYANIDE INVENTORY FROM MODELS

One estimate on the amount of ferrocyanide within the SSTs was documented by Nguyen (1989) using the track radionuclide components (TRAC) (Jungfleisch 1984) composition database (baseline value). More recent estimates of ferrocyanide concentration in the tanks are obtained from the spreadsheet model of the scavenging program from historical records (model value) calculated by Borsheim and Simpson (1991). These are considered to be the best available to date.

The two estimates (Table 4-1) were developed from a thorough review of the operating records. Both the TRAC computer program and the Borsheim and Simpson Model values assume that, during the scavenging program, the ferrocyanide sludge remained in the settling tanks unless special efforts were made to transfer sludge. The ferrocyanide tanks also remained in use after the scavenging program and were used for the receipt, storage, and processing of waste until the SSTs were removed from active service in 1980. Figure 4-1 illustrates a simplified material balance for ferrocyanide additions to the scavenging process, estimated inventories remaining in the SSTs, and the losses to the cribs (ground).

Overall, the results of the model (Borsheim and Simpson 1991) agree well with the other information about the ferrocyanide tanks. The model results provide reasonable estimates as to the location and distribution of ferrocyanide precipitates. For the purposes of this model it is assumed that all the ferrocyanide that is added precipitates as a metal-$Fe(CN)_6^{-2}$ complex. Because the exact precipitates are not known, the number of gram-moles of ferrocyanide ion presented in Table 4-1 was calculated as $Fe(CN)_6^{4-}$.

Based on evidence presented by Borsheim and Simpson (1991) a strong case can be made that 6 of the 24 tanks (241-BX-102, -106, -110, -111, -BY-101, -T-101) designated as ferrocyanide tanks do not belong on the Watchlist because they are estimated to have less than the 1,000 g-mol threshold amount of ferrocyanide. This conclusion is based on the model taken from the tanks' process histories, and the likely physical and chemical interaction between the sludge and supernate.

## 4.2 CHARACTERIZATION EFFORTS

Characterization of ferrocyanide tank contents is necessary to (1) guide chemical reaction studies; (2) apply the study results to mitigation and/or remediation of these tanks; (3) provide a basis for estimating the consequences of a runaway ferrocyanide reaction; and (4) determine how the ferrocyanide waste can be safely stored until mitigation or remediation actions are completed.

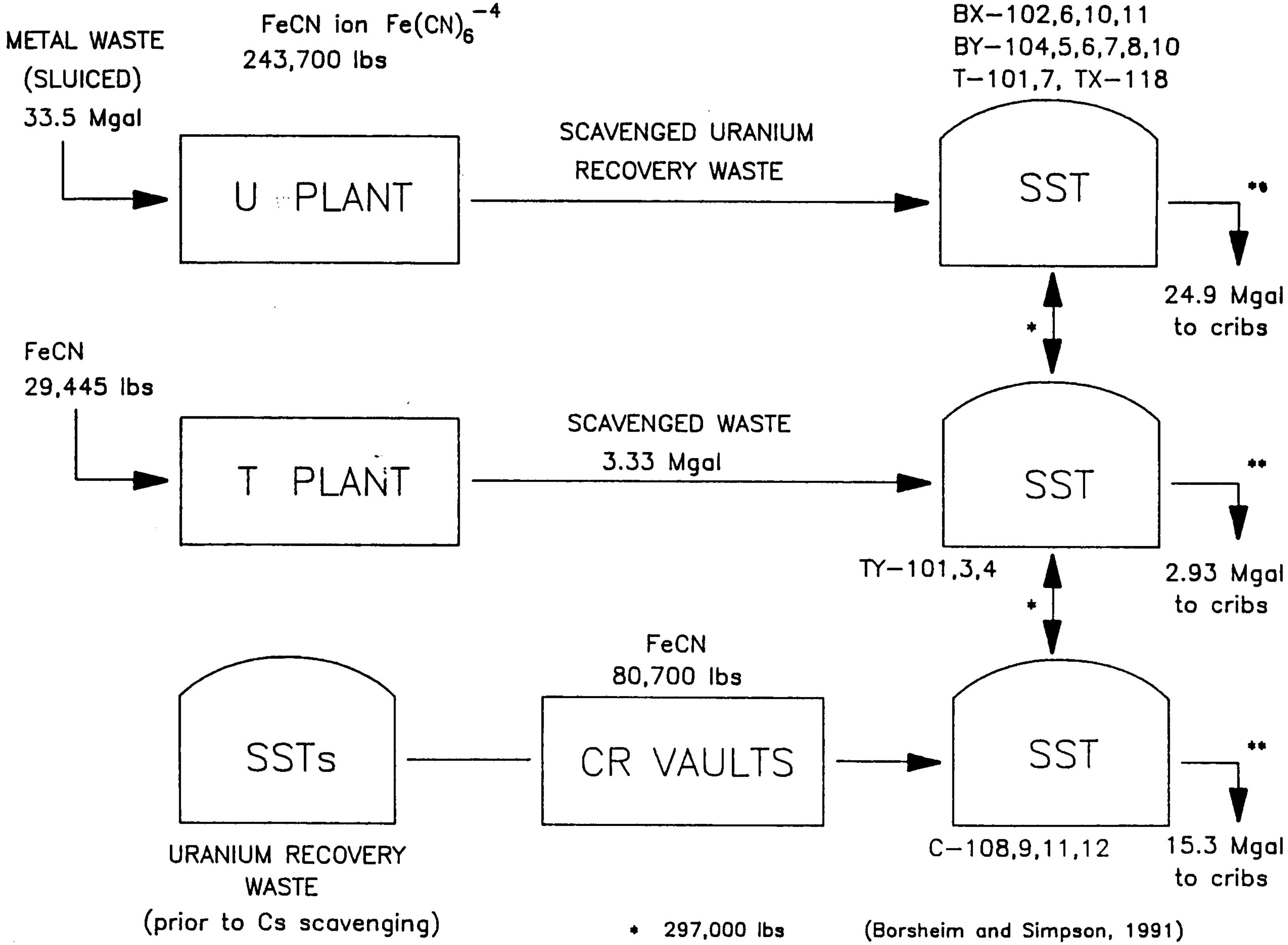
Table 4-1. Comparison of Model Results with Baseline Values: Ferrocyanide at the End of Scavenging.

| Tank | Date year-quarter | Model value[a] | Baseline value[b] |
|---|---|---|---|
| | | Amount-$Fe(CN)_6^{-4}$ (g-mol) | Amount-$Fe(CN)_6^{-4}$ (g-mol) |
| BX-102 | 1956-4 | <1,000 | 0-3,000 |
| BX-106 | 1956-1 | <1,000 | 0-1,000 |
| BX-110 | 1958-1 | <1,000 | 0-1,000 |
| BX-111 | 1958-1 | <1,000 | 0-1,000 |
| BY-101 | 1951-1 | <1,000 | 0-1,000 |
| BY-103 | 1955-3 | 65,900 | 0-2,000 |
| BY-104 | 1957-3 | 83,200 | 100,000-200,000 |
| BY-105 | 1957-3 | 36,200 | 70,000-100,000 |
| BY-106 | 1956-4 | 70,000 | 30,000 |
| BY-107 | 1957-1 | 42,400 | 30,000-80,000 |
| BY-108 | 1957-3 | 58,000 | 30,000-70,000 |
| BY-110 | 1957-3 | 70,700 | 50,000-90,000 |
| BY-111 | 1956-4 | 5,500 | 0-3,000 |
| BY-112 | 1957-4 | 2,000 | 2,000-3,000 |
| C-108 | 1958-1 | 25,000 | 9,000-20,000 |
| C-109 | 1958-1 | 30,000 | 30,000-50,000 |
| C-111 | 1957-4 | 33,000 | 10,000-30,000 |
| C-112 | 1958-1 | 31,000 | 50,000-70,000 |
| T-101[c] | 1953-4 | <1,000 | 0-10,000 |
| T-107 | 1953-4 | 5,000 | 0 (TRAC) |
| TX-118 | 1958-1 | N.E. | 0-3,000 |
| TY-101 | 1956-4 | 22,900 | 0-30,000 |
| TY-103 | 1956-4 | 28,000 | 0-30,000 |
| TY-104 | 1955-3 | 12,000 | 0 (TRAC) |

[a] Reference: Borsheim and Simpson 1991, Table 3-7

[b] Reference: Nguyen 1989

[c] After cribbing half of the supernate, 50 percent of the solids from T-101 were transferred to T-107. The tank was refilled with bismuth-phosphate process metal waste and subsequently sluiced for uranium recovery.



* 297,000 lbs (Borsheim and Simpson, 1991)
** Approx total to cribs 57,000 lbs

Figure 4-1. Material Balance.

The important reaction materials present in the ferrocyanide tanks are fuel (ferrocyanides, sulfides, and reduced carbon species, such as organic complexants), oxidants (nitrates and nitrites), and inerts or diluents (phosphates, aluminates, sulfates, carbonates, oxides, and hydroxides). The location of fission products, such as $^{137}Cs$ and $^{90}Sr$, is important because they are sources of heat that can raise and maintain the temperature of the tank contents. The water content of the waste is important because the high heat capacity and the heat of vaporization of water make it an effective inerting material and can prevent a sustained combustion or an explosion. Also, wet ferrocyanide material should neither react nor propagate; it would have to be dried first.

### 4.2.1 Theoretical Characterization

The potential for a propagating reaction depends on several factors, especially the concentration of fuel and oxidant present and the concentration of diluents. No exothermic reaction will be sustained if there is a sufficient proportion of water or other substances that do not take part in an exothermic reaction. If the energy available is not sufficient to permit the mixture to reach the ignition temperature, propagation cannot occur. Therefore, it is possible by thermodynamic calculations to define compositions for which a sustained chemical reaction is possible (Grigsby et al. 1991).

Grigsby et al. (1991) analyzed the reactivity limits for ferrocyanide mixtures. For the thermodynamic analysis, components of the waste were considered to belong to one of three general categories, based on their function as either heat producers, mixtures of ferrocyanide and nitrate/nitrite, or heat absorbers, water and other diluents. The conditions considered were whether the reaction was confined (without venting) or unconfined (vented).

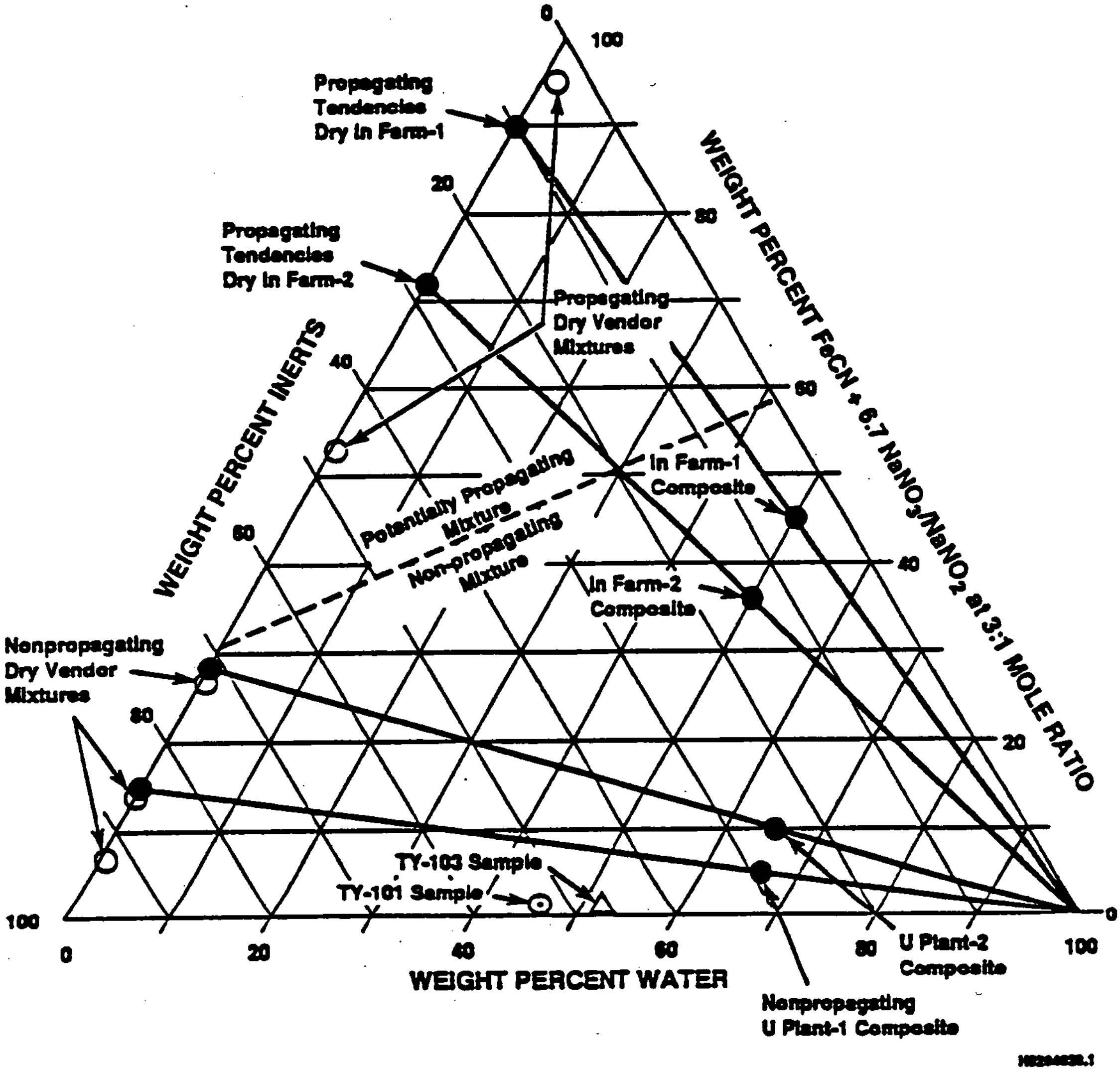
The theoretical range of combinations of ferrocyanide fuel and nitrate oxidant, water and other inert compounds for which a reaction is thermodynamically possible was plotted by Grigsby et al. (1991) in a triangular diagram (Figure 4-2) using the following parameters:

- **Heat of reaction - 3,025 kJ/mol of ferrocyanide:** This is the theoretical estimate calculated for the most energetic of the possible reactions involving sodium nitrate as the oxidant.

- **Initial temperature - 55 °C (131 °F):** This is approximately the maximum temperature measured in any ferrocyanide tank.

- **Temperature to which the fuel must be heated to support propagation (ignition temperature) - 275 °C (527 °F):** This is the temperature at which a stoichiometric mixture of ferrocyanide and sodium nitrate shows an abrupt increase in self-heating rate during adiabatic calorimetry testing.

Figure 4-2. Thermodynamic Analysis Results.



The reactivity limits for both the confined and the vented burn are represented as lines on the diagram. The composition above the line can possibly sustain a propagating reaction; the compositions below the line cannot.

The shaded area of Figure 4-2 shows the estimated in-tank concentration of fuel plus oxidant as ranging from near zero to 6 percent, as indicated by the composition estimates. The water concentration in the sludge is estimated to range from a minimum of 40 percent to approximately 70 wt%. The ferrocyanide concentration and water content is expected to be most representative of waste provided by the U Plant and T Plant process. These wastes contain approximately 80 percent of the total ferrocyanide. Waste produced by the In Farm process may be more concentrated in ferrocyanide and contain fewer solid diluents. Additional information on In Farm produced waste is needed before its combustibility can be appropriately evaluated. The U Plant and T Plant waste composition fall in the nonreactive region for both confined and vented burns (Grigsby et al. 1991).

Grigsby et al. (1991) tentatively concluded that the Hanford Site U Plant and T Plant ferrocyanide sludge cannot sustain a propagating exothermic reaction. Key waste properties supporting this conclusion include a dilute ferrocyanide concentration and insignificant organic carbon concentration; the remainder of the ferrocyanide sludge is composed of oxidant, water, and other inert diluents.

### 4.2.2 Vapor Sampling

Because the ferrocyanide tanks have been classified as an unresolved safety question, it is necessary to sample the tank vapor spaces before any intrusive activity to be sure the vapor space is noncombustible.

Vapors of concern that have been targeted in the vapor sampling effort include hydrazine, hydrogen cyanide, and nitrous fumes (e.g., nitrous oxide and nitrogen dioxide). Results from the vapor sampling of Tank BY-104 and preliminary results from the sampling of Tanks C-112 and C-109 show no significant concentrations of these compounds.

As a part of the vapor monitoring effort, combustible gas meter readings, gas chromatograph monitoring for hydrogen gas, and cryogenic sampling are being used in an attempt to characterize tank vapors. Small quantities of organic compounds (e.g., normal paraffin hydrocarbon) have been found. However, no concentration of any component was identified that would jeopardize the continued safe storage of the waste.

### 4.2.3 Auger Sampling

Auger samples were taken from Tank BY-104 to determine fuel values for the safety assessment for rotary mode core sampling. Analysis of the auger samples has not been completed. Results, however, should yield valuable information for the study of ferrocyanide wastes.

### 4.2.4 Core Sampling

Tank C-112 was push-mode core sampled in March 1992. Preliminary results from core analyses indicate that the fuel value of the waste is low. Total organic carbon, total inorganic carbon, and total carbon values are presented in Table 4-2.

Table 4-2. Tank C-112 Total Organic Carbon/Total Inorganic Carbon/Total Carbon Preliminary Results.[a]

| Sample ID | Total organic carbon (%) | Total inorganic carbon (%) | Total carbon (%) |
|---|---|---|---|
| 92-06761-C-1 | 0.77 | 0.35 | 1.12 |
| 92-06761-C-2 | 0.86 | 0.45 | 1.31 |
| 92-06761-C-3[b] | 0.13 | 0.021 | 0.15 |
| 92-06762-C-1 | 0.48 | 0.54 | 1.02 |
| 92-06762-C-2 | 0.50 | 0.54 | 1.04 |
| 92-06763-C-1 | 0.39 | 0.43 | 0.82 |
| 92-06763-C-2 | 0.38 | 0.48 | 0.86 |
| 92-06764-C-1 | 0.27 | 0.25 | 0.52 |
| 92-06764-C-2 | 0.27 | 0.25 | 0.52 |
| 92-06765-C-1 | 0.31 | 0.36 | 0.67 |
| 92-06765-C-2 | 0.28 | 0.32 | 0.60 |
| 92-06765-C-3[b] | 0.14 | 0.03 | 0.17 |
| 92-06766-C-1 | 0.21 | 0.29 | 0.50 |
| 92-06766-C-2 | 0.25 | 0.29 | 0.54 |

[a] Determinations performed by the hot persulfate method with an estimated error of ±10 percent. The method is applicable to organic carbon species and inorganic carbonates, but not to other forms of carbon such as elemental graphite. It may also be poorly applicable to cyanide.

[b] Indicates methanol blank.

Thermal analyses were performed on waste from the core sampling of Tank C-112 and three transitions were observed. The first transition began at the lower temperature limit of the analysis (30 °C) and was essentially complete by 140 °C. This was most likely the release of bulk and interstitial water in the sample. The second significant transition region was an exotherm over the temperature range from 265 °C to 300 °C with an onset temperature of 275 °C. A weight gain appeared to be associated with the third significant transition that had an onset temperature of 350 °C.

Table 4-3 compares thermal analysis data from quarter segments 2B, 2C, 2D and the segment 2 composite of core 34 with thermal analysis data from In Farm 1 and In Farm 2 simulants.

Table 4-3. Comparison of Thermal Analysis Data from Quarter Segments 2B, 2C, 2D and the Segment 2 Composite of Core 34 with Thermal Analysis Data from In Farm 1 and In Farm 2 Simulants.

| Sample | Temperature range (°C) | Results |
|---|---|---|
| 2B | 47 - 91 | Release of bulk and interstitial water |
| | 276 - 283 | Exotherm -11.7 Joules/gram of sample (J/g) |
| | 349 - 373 | Exotherm -63 J/g |
| 2C | 43 - 81 | Release of Bulk and interstitial water |
| | 267 - 280 | Exotherm -13.1 J/g |
| | 360 - 390 | Exotherm -35 J/g |
| 2C | 49 - 91 | Release of bulk and interstitial water |
| | 289 - 307 | Exotherm -16.9 J/g |
| | 347 - 376 | Exotherm -47 J/g |
| Composite | 58 - 103 | Release of bulk and interstitial water |
| | 276 - 287 | Exotherm -10.8 J/g |
| | 257 - 387 | Exotherm -75 J/g |
| In Farm 1 (top layer) | 20 - 140 | Endotherm, free water evaporation |
| | 140 - 200 | Endotherm, free and bound water loss |
| | 200 - 250 | Endotherm, $NaNO_3/NaNO_2$ reaction w/FeCN |
| | 250 - 280 | Endotherm, $NaNO_3/NaNO_2$ melting |
| | 340 - 350 | Exotherm, oxidation of FeCN w/$NO_3$ - $NO_2$ |
| | 350 - 430 | Exotherm, oxidation of FeCN w/$NO_3$ - $NO_2$ |
| In Farm 1 (bottom layer) | 20 - 130 | Endotherm, free water evaporation |
| | 130 - 180 | Endotherm, free and bound water loss |
| | 240 - 290 | Endotherm, $NaNO_3/NaNO_2$ melting |
| | 340 - 350 | Exotherm, oxidation of FeCN w/$NO_3$ - $NO_2$ |
| In Farm 2 (top layer) | 20 - 140 | Endotherm, free water evaporation |
| | 140 - 210 | Endotherm, free and bound water loss |
| | 210 - 250 | Endotherm, $NaNO_3/NaNO_2$ reaction w/FeCN |
| | 250 - 280 | Endotherm, $NaNO_3/NaNO_2$ melting |
| | 320 - 350 | Exotherm, oxidation of FeCN w/$NO_3$ - $NO_2$ |
| In Farm 2 (bottom layer) | 20 - 130 | Endotherm, free water evaporation |
| | 220 - 250 | Exotherm, $NaNO_3/NaNO_2$ reaction w/FeCN |
| | 250 - 290 | Endotherm, $NaNO_3/NaNO_2$ melting |
| | 330 - 350 | Exotherm, oxidation of FeCN w/$NO_3$ - $NO_2$ |

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# 5.0 COMPUTER MODELING AND ANALYSIS

A hot spot must reach an exothermic reaction onset temperature before heating from chemical reactions is a contributor. Based on conservative simulant mixtures of ferrocyanide waste (stoichiometric mixes of fuel and oxidant) an onset temperature of 200 °C is used. Waste temperatures approaching 200 °C are considered incredible for the following 3 reasons: (1) measured temperatures in the tanks are all well below 200 °C; (2) thermal modeling performed using the HEATING7 computer code indicates that slab-shaped hot spots can not reach 200 °C; and (3) bounding (spherical) hot spot geometries will not run away (considered to be the worst case for it has the lowest surface to volume ratio). (For complete description of each reason see Grigsby et al. 1991, pg 1-11 to 1-13.)

Because temperature measurements in Watchlist tanks are an important issue, additional work is being undertaken to determine the validity of the current measurements (Cash and Dukelow 1992a). This includes the following:

- Analyses of expected measurement uncertainties for the measurement system
- The CTMS (refer to Section 3.1)
- Installation of calibrated thermocouple trees in ferrocyanide tanks without operable thermocouple trees.

One option in the monitoring of potential hot spots and supplementation of thermocouple readings is the use of IR scanners. The IR scanners have been proven to detect temperature changes of ±0.5 °C (±1 °F) on the waste surface. The sensitivity of the IR system may prove to be beneficial mapping surface temperature profiles in the ferrocyanide tanks (Cash and Dukelow 1992b).

Thermal modeling performed on Tank 241-BY-104 shows that, if hot spots with temperatures of concern are possible, surface temperature differences might be great enough to be detected by IR mapping; however, it is currently believed a hot spot would be very marginally detected. Besides the limited life of the IR camera there are several drawbacks to the IR modeling; for example, the detection of a hot spot could take 5 to 6 months to appear on the surface of the waste (Efferding et al. 1992), thereby limiting the time detection of the hot spot. In addition, surface irregularities may cause inaccurate readings.

Results from an IR scanning system installed in a non-Watchlist tank indicated that a hot spot, if one exists, can probably be detected by surface mapping using the IR system, especially in the tanks containing shallow waste depths (Cash and Dukelow 1992b).

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# 6.0 RESEARCH AND DEVELOPMENT

Reactive mixtures can possibly be initiated by mechanisms other than increasing temperatures (i.e., sensitivity to friction, electric spark, shock, and impact in addition to heat). The Los Alamos National Laboratory (LANL) performed nonthermal sensitivity tests on $Cs_2Ni[Fe(CN)_6] * xH_2O$ mixed with stoichiometric amounts of oxidizers ($NaNO_3/NaNO_2$). The LANL report indicated that their ferrocyanide/oxidant test mixture does not react to impact or friction and has a low spark sensitivity. The LANL report did not address the question of shock and the ease with which high-order detonation can be established in the studied mixture (Grigsby et al. 1991).

Fauske and Associates, Inc. completed adiabatic calorimetry tests on dried and pulverized U Plant 2 simulants (FAI 1992). These tests indicated that, when dry, this material, if heated, could produce limited quantities of aerosol but would not produce an explosive reaction.

Development of waste analysis with Laser Raman Spectroscopy is being investigated to quantify measurements of ferrocyanide and ferricyanide in Hanford Site high-level waste tanks. A secondary objective is to extend any methodology to the analysis of other anions of interest, such as sulfate, nitrate, nitrite, phosphate, and aluminate, and to organic compounds such as the sodium salts of ethylenediaminetetraacetic acid, and hydroxydiaminetriacetic acid.

Florida State University is conducting the Raman Investigation task. Initial results with In Farm and U Plant simulants indicate that there is essentially no pH* impact on the Raman peak width for ferro- and ferricyanide materials. Initial limits of detection measurements made for selected In Farm and U Plant waste species are presented in Table 6-1 (Cash and Dukelow 1992b).

Table 6-1. Limits of Raman Spectroscopy Detection in $NaNO_3$ Solutions.

| Matrix: 1 M $NaNO_3$ in $H_2O$ | |
|---|---|
| Species | LOD[a], M |
| $NH_4^+$ | $2 \times 10^{-2}$ |
| $SO_4^{2-}$ | $1 \times 10^{-3}$ |
| $Fe(CN)_6^{4-}$ | $4 \times 10^{-4}$ |
| $Fe(CN)_6^{3-}$ | $3 \times 10^{-4}$ |

[a]LOD = Limits of Detection

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*Wodrich et al. (1992) states that there is no impact to the ferrocyanide safety issue because of "low pH".

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