Sta 4 (3)

0042863

JAN 29 1996

ENGINEERING DATA TRANSMITTAL

1. EDT 602617

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) TWRS Safety Basis	4. Related EDT No.:
5. Proj./Prog./Dept./Div.: TWRS	6. Cog. Engr.: J. E. Meacham	7. Purchase Order No.:
8. Originator Remarks: This document provides the technical basis for the hazard and safety analysis of ferrocyanide bearing waste stored in the Hanford underground storage tanks (Tank Farms).		9. Equip./Component No.: N/A
		10. System/Bldg./Facility: Tank Farms/East & West Areas
11. Receiver Remarks:		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date:

FEB 1996 RECEIVED EDMC

15. DATA TRANSMITTED

(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	(F) Approval Designator	(G) Reason for Transmittal	(H) Originator Disposition	(I) Receiver Disposition
1.	WHC-SD-WM-SARR-038		0	Assessment of the Potential for Ferrocyanide Propagating Reaction Accidents	SQ	1		

16. KEY

Approval Designator (F)	Reason for Transmittal (G)		Disposition (H) & (I)	
E, S, Q, D or N/A (see WHC-CM-3-5, Sec.12.7)	1. Approval 2. Release 3. Information	4. Review 5. Post-Review 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment	4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)

(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.
1	1	Cog.Eng.	J. E. Meacham	1/25/96	87-15	TF East Ops.	R. A. Dodd	1/25/96	H2-52	1	1
1	1	Cog. Mgr.	R. J. Cash	1/25/96	87-15	TF East Eng.	G. N. Hanson	1/25/96	S5-05	1	1
1	1	QA	M. D. Hassebrock	1/26/96	[illegible]	TF West Ops.	J. J. Badden	1/25/96	T4-08	1	1
1	1	Safety	L. M. Calderon	1/25/96	01	TF West Eng.	S. H. Rifae	1/25/96	T4-07	1	1
		Env.				FSAR Proj.	D. S. Leach	1/25/96	H0-34	1	1
						TFTP	J.E. TRVAK	1/29/96			

18.	19.	20.	21. DOE APPROVAL (if required)
J. E. Meacham Signature of EDT Originator — Date 1/29/96	Authorized Representative for Receiving Organization — Date	R. J. Cash Cognizant Manager — Date 1/29/96	Ctrl. No. [] Approved [] Approved w/comments [] Disapproved w/comments

Assessment of the Potential for Ferrocyanide Propagating Reaction Accidents

J. E. Meacham et al
Westinghouse Hanford Company, Richland, WA 99352
U.S. Department of Energy Contract DE-AC06-87RL10930

EDT/ECN: EDT 602617 UC: 2030
Org Code: H4E1000 Charge Code: N2134
B&R Code: EW3120072 Total Pages: 98

Key Words: Tank Farms Safety Analysis, Watch List, Ferrocyanide, Tank Farm Hazard Assessment

Abstract: This report contains safety criteria for the storage of ferrocyanide bearing waste sludges in Hanford underground waste storage tanks. In addition, the tank wastes are categorized with this criteria into SAFE, CONDITIONALLY SAFE, and UNSAFE categories based on available historical records and sample information. 14 tanks are classified as CONDITIONALLY SAFE, while four C-Farm tanks are categorized as SAFE. This report therefore provides a technical basis to resolve the ferrocyanide safety issue for these four tanks and supports their removal from the Watch List. The 14 CONDITIONALLY SAFE tanks will be re-evaluated in a future revision to this report as representative sample data becomes available. It is anticipated that the 14 tanks will be re-categorized as SAFE at that time.

TRADEMARK DISCLAIMER. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof or its contractors or subcontractors.

Printed in the United States of America. To obtain copies of this document, contact: WHC/BCS Document Control Services, P.O. Box 1970, Mailstop H6-08, Richland WA 99352, Phone (509) 372-2420; Fax (509) 376-4989.

DATE:
STA: 4
HANFORD RELEASE
ID:
JAN 29 1996

Release Approval — Date 1/29/96 — Release Stamp

Approved for Public Release

WHC-SD-WM-SARR-038, Rev. 0

Assessment of the Potential for Ferrocyanide Propagating Reaction Accidents

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Westinghouse
Hanford Company Richland, Washington

Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for public release; distribution is unlimited

WHC-SD-WM-SARR-038, Rev. 0

Assessment of the Potential for Ferrocyanide Propagating Reaction Accidents

J. M. Grigsby
A. K. Postma
G&P Consulting, Inc.

R. J. Cash
J. E. Meacham
D. R. Dickinson
Westinghouse Hanford Company

M. A. Lilga
Pacific Northwest National Laboratory

H. K. Fauske
M. Epstein
Fauske and Associates, Inc.

Date Published
January 1996

Prepared for the U.S. Department of Energy
Assistant Secretary for Environmental Management

Westinghouse
Hanford Company Richland, Washington
Management and Operations Contractor for the
U.S. Department of Energy under Contract DE-AC06-87RL10930

Approved for public release; distribution is unlimited

ASSESSMENT OF THE POTENTIAL FOR FERROCYANIDE PROPAGATING REACTION ACCIDENTS

EXECUTIVE SUMMARY

Defense waste operations at the Hanford Site during the 1950's used ferrocyanide to scavenge ^{137}Cs from waste supernates, forming ferrocyanide-containing sludges that settled in layers in a number of waste tanks. As a result of these operations, approximately 140 metric tons of ferrocyanide [as $Fe(CN)_6^{-4}$] were added to 18 single-shell tanks at the Hanford Site. Ferrocyanide, in sufficiently high concentrations and mixed with oxidizing material such as sodium nitrate/nitrate, can be made to react exothermically by heating it to high temperatures.

The risk posed by continued storage of ferrocyanide wastes in Hanford Site underground storage tanks has been studied extensively through theoretical analysis, laboratory experiments, tank monitoring, and waste sampling. A plan to resolve the safety issue has been put in place and is nearing completion. This report provides an assessment of this hazard and provides the technical basis to resolve the safety issue for the four tanks that received the most concentrated ferrocyanide sludges, and supports the removal of these four tanks (241-C-108, C-109, C-111, and C-112) from the Watch List. In addition, this assessment provides the basis for similar, future actions with other ferrocyanide tanks when representative waste sample data become available. For now, the 14 other tanks remain categorized as CONDITIONALLY SAFE pending the completion of ongoing waste analysis and evaluation activities. All ferrocyanide wastes are currently categorized as SAFE or CONDITIONALLY SAFE, and thus cannot burn or explode; therefore, they pose no hazard.

The safety basis for ferrocyanide wastes described in this report is comprised of:

1. Criteria for ranking the relative safety of waste in each ferrocyanide tank. These criteria were developed in 1994 (Postma et al. 1994) and approved to close the Ferrocyanide Unreviewed Safety Question (USQ) (Sheridan 1994a).

2. The classification of tanks into safety categories by comparing available information on tank contents with the safety criteria. Revised classifications from Postma et al. (1994) are provided for the four C Farm tanks listed above based on the evaluation of additional waste sample data.

3. The evaluation of waste storage conditions to define waste management controls that are required to maintain safety.

Safety Categories

Three safety categories were formulated on the basis of answers to two safety questions: (1) Is a propagating reaction possible during interim storage? and (2) Is a propagating reaction possible under present conditions of waste storage, especially considering the waste moisture content?

Numerical criteria for the three safety categories (SAFE, CONDITIONALLY SAFE, and UNSAFE) were selected on the basis of experimental and theoretical information. Conservative values were chosen to provide a safety margin between safe tank conditions and conditions where significant reactions could occur. These criteria were described in Postma et al. (1994) and are reiterated in this report.

The criteria described herein pertain to the hazard posed by sustained, propagating exothermic reactions between ferrocyanide and nitrate/nitrite salts in stored waste. As such, these criteria do not replace or eliminate safety criteria that have been formulated to address other hazards of tank operations.

The approved criteria (Sheridan 1994a) are:

SAFE

- Concentration of fuel $\leq$ 8 wt% sodium nickel ferrocyanide
- Concentration of water - not limiting
- Concentration of oxidizers - not limiting
- Temperature of waste - not limiting

CONDITIONALLY SAFE

- Concentration of fuel $>$ 8 wt% sodium nickel ferrocyanide
- Concentration of water $\geq$ 0 to 24 wt%
- Concentration of oxidizers - not limiting
- Temperature of waste $\leq$ 90 °C

UNSAFE

- Criteria for SAFE and CONDITIONALLY SAFE are not met.

For tanks that fall into the SAFE category, assurance of low fuel content is sufficient to address the ferrocyanide hazard during interim storage. For CONDITIONALLY SAFE tanks, assurance on minimum retained moisture and maximum waste temperature is required. For tanks that are assigned to the UNSAFE category, monitoring and controls are required to avoid conditions that could lead to reaction initiation.

Ferrocyanide Waste Safety Categorization

The ferrocyanide-bearing wastes have been compared to the safety criteria based on available information that was evaluated in a conservative manner. The categorization is based on waste sample data and information where available. When sample data are not yet available, categorization is based on conservative estimates of waste conditions determined by several techniques, including modeling of waste processes and experimental results from waste process simulants. The waste process models and simulants represent ferrocyanide conditions when the wastes were produced in the 1950s. Waste sample data represent the waste as it exists today. The results of waste categorization are shown in Table ES-1 and are summarized below.

C Farm Tanks

The ferrocyanide wastes were all produced by one of three different processes termed U Plant, In Farm and T Plant after the location where the process was performed. The three processes produced wastes with different ferrocyanide contents when the wastes were originally formed.

The ferrocyanide-bearing wastes stored in C Farm resulted from the In Farm process and produced wastes that were the most concentrated in ferrocyanide when originally formed. These wastes, therefore, have received the highest priority for sampling and analysis. Analyses of samples obtained from all four of these tanks conclude that the ferrocyanide concentration is now very low. This is attributed to chemical degradation (aging) of the ferrocyanide during approximately 40 years of storage. The wastes in these four tanks (241-C-108, C-109, C-111, C-112) are categorized as SAFE based on these low measured ferrocyanide concentrations. Based on this SAFE categorization, the ferrocyanide safety issue for these four tanks is resolved, and it is recommended that these tanks be removed from the Ferrocyanide Tank Watch List.

Other Ferrocyanide Wastes (U Plant and T Plant Processes)

Samples have been obtained from selected tanks containing sludges produced by the two other (U Plant and T Plant) processes. Sample analysis and evaluation are underway. Therefore, pending the results of that effort, the tanks with wastes produced by these processes are currently categorized as CONDITIONALLY SAFE. This judgement is based on ferrocyanide concentration estimates from waste process models and simulants; it is a conservative categorization because it does not account for the chemical degradation (aging) of the ferrocyanide over the approximately 40 years of storage. The results of the sample analysis and evaluation is expected to confirm that chemical degradation has occurred sufficiently to recategorize these wastes as SAFE similar to the C Farm tanks. The results of this ongoing evaluation will be provided later in fiscal year 1996 when this report is revised.

Table ES-1. Safety Categorization of Hanford Ferrocyanide Wastes.

Tank	Waste flow sheet[a]	Ferrocyanide concentration (wt%, dry basis)		Water content criteria (wt%)	Current safety category
		Maximum estimated concentration[b]	Tank samples[c]		
241-BY-103	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-104	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-105	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-106	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-107	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-108	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-110	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-111	U Plant	8.3	No data	0.4	Conditionally Safe
241-BY-112	U Plant	8.3	No data	0.4	Conditionally Safe
241-C-108	In Farm 2	22.6	5.2	n/a	Safe
241-C-109	In Farm 2	22.6	2.8	n/a	Safe
241-C-111	In Farm 2	22.6	2.1	n/a	Safe
241-C-112	In Farm 1	25.5	4.0	n/a	Safe
241-T-107	U Plant	8.3	No data	0.4	Conditionally Safe
241-TX-118	U Plant	8.3	No data	0.4	Conditionally Safe
241-TY-101	T Plant	10.7	No data	3.6	Conditionally Safe
241-TY-103	T Plant	10.7	No data	3.6	Conditionally Safe
241-TY-104	T Plant	10.7	No data	3.6	Conditionally Safe

Notes:

[a]The ferrocyanide wastes were all produced by processes that used one of three "flowsheets." The flowsheets produced wastes with different ferrocyanide concentrations.

[b]This is the highest concentration that was produced for the listed flowsheet as estimated by several different techniques including historical records models and waste simulant experiments.

[c]Upper 95% confidence interval values; see Appendix A.

The minimum water content required to maintain these wastes in the CONDITIONALLY SAFE category is shown in Table ES-1; it is a very small amount of moisture. Waste storage conditions have been evaluated to verify that CONDITIONALLY SAFE temperature criterion are met, and to determine that no controls are required to maintain waste moisture above the minimum requirement.

Temperature Control. The waste temperatures in ferrocyanide tanks are well below temperatures of concern relative to initiating or sustaining a ferrocyanide exothermic reaction accident. These low temperatures are maintained through passive means. For the following reasons, it is not credible for temperatures of concern to be reached.

- Decay heat loads are estimated to be 3.0 kW (10,000 British thermal units per hour [Btu/h]) or less for the 23-m (75-ft)-diameter tanks.

- Decay heat loads have been dissipated passively over the four decades of storage history, during which time temperatures have trended downward or are now essentially constant[1].

- Heat loss from the waste and tanks occurs by conduction, convection, and radiation. There are no active cooling systems that can fail. Heat dissipation does not depend on evaporation of water.

Therefore, the conclusion is that the ferrocyanide sludges categorized as CONDITIONALLY SAFE pose no propagating reaction hazard, and because this safety conclusion does not credit or rely on control of waste temperatures, no controls are required.

Waste Moisture Control. Various postulated dryout mechanisms have been analyzed to determine whether any of them could reduce the ferrocyanide moisture content sufficiently to render it reactive. Based on analysis and experiments with ferrocyanide waste simulants, it is concluded that none of the postulated mechanisms are credible under current passive ventilation conditions, for the following reasons.

- Bulk heating of the entire sludge inventory above 90 °C (194 °F) (or to the boiling point of approximately 130 °C [266 °F]) is not credible (see temperature control above).

- Loss of liquid to the atmosphere via sludge surface evaporation is minimal under current passive ventilation conditions. The net rate of evaporation of water from the waste surface is limited by the rate at which air flowing out of the tank can remove moisture. The highest evaporation rate calculated for these tanks amounts to 0.03% of the retained water per year. Evaporative losses under

[1]The temperature of the waste in some of the ferrocyanide tanks is below the average domespace air temperature.

active (forced) ventilation may be higher; these losses have not been analyzed because there are currently no plans to change the ventilation configuration on these tanks.

- Sludge drainage through a leak in the tank wall or by pumping drainable liquid from the tanks with a saltwell pumping system is limited to about 30 to 40 wt% water at the final equilibrium condition. Such a minimum equilibrium would take many years to achieve.

The conclusion that dryout is beyond extremely unlikely[2] has been substantiated by four decades of waste storage history during which sludge temperatures have gradually decreased or remained constant and the sludge moisture content has been retained.

Hazard Assessment Conclusions

Ferrocyanide accidents are ruled out for waste that meets SAFE or CONDITIONALLY SAFE criteria. All ferrocyanide waste in the Hanford Site underground storage tanks meets these criteria, and therefore pose no hazard for propagating chemical reactions. Waste moisture for CONDITIONALLY SAFE ferrocyanide wastes is maintained by inherent physical-chemical properties and passive storage conditions. There is no reliance on active waste management controls (e.g., surveillance and water addition) to maintain waste moisture for these tanks. A key assumption in this analysis, however, is that the tank ventilation configuration is a passive breather system. Moisture loss rates and the minimum equilibrium waste moisture that could be attained under long-term active (forced) ventilation have not been determined. Therefore, modification of the ventilation systems to a forced (active) ventilation configuration would require additional analysis for tanks that contain waste categorized as CONDITIONALLY SAFE.

[2]Event frequency category defined as having a probability of less than 1×10^{-6}/year, per WHC-CM-4-46, March 1995, *Safety Analysis Manual*, Westinghouse Hanford Company, Richland, Washington.

TABLE OF CONTENTS

1.0 PURPOSE AND SCOPE 1

2.0 BACKGROUND 1
2.1 WATCH LIST AND USQ FORMULATION 2
2.2 BACKGROUND OF SAFETY ASSESSMENTS 2

3.0 HAZARD POTENTIAL AND POSTULATED FERROCYANIDE ACCIDENTS . . 4
3.1 THE FERROCYANIDE SAFETY ISSUE 4
3.2 ACCIDENT SCENARIO 6
3.3 FERROCYANIDE SAFETY CATEGORIES AND SAFETY CRITERIA . . . 9
3.3.1 Reaction Energies and Energy Balance 9
3.3.2 Adiabatic Calorimetry Tests 11
3.3.3 Tube Propagation Rate Tests 11
3.4 WASTE SAFETY CATEGORIES 15
3.4.1 SAFE 15
3.4.2 CONDITIONALLY SAFE 15
3.4.3 UNSAFE 17

4.0 WASTE CONDITIONS SUPPORTING SAFETY ASSESSMENTS 17
4.1 WASTE FLOWSHEET SIMULANT 18
4.2 PROCESS RECORDS 18
4.3 PROPERTIES OF SLUDGE REMOVED FROM TANKS 23

5.0 AGING PROCESSES 23
5.1 DEPENDENCE ON TEMPERATURE 24
5.2 DEPENDENCE ON GAMMA DOSE RATE AND INTEGRATED DOSE . . 25
5.3 DEPENDENCE ON ALKALINITY 26
5.4 AGING CONFIRMED BY FERROCYANIDE AND NICKEL CONTENT OF TANK SAMPLES 29
5.5 CONCLUSION ON WASTE AGING 31

6.0 MOISTURE RETENTION IN FERROCYANIDE SLUDGES 31
6.1 MOISTURE RETENTION AND DRYOUT THEORY AND ANALYSIS . . . 32
6.1.1 Drying by Draining 33
6.1.2 Dryout by Waste Boiling 33
6.1.3 Dryout by Evaporation 34
6.1.4 Local Drying by Boiling Caused by a Hot Spot 36
6.2 CONCLUSION OF DRYOUT ASSESSMENT 38

TABLE OF CONTENTS (Continued)

7.0 FERROCYANIDE WASTES HAZARD POTENTIAL AND ACCIDENT FREQUENCY 39
7.1 TANKS CONTAINING IN FARM SLUDGE 39
7.2 TANKS CONTAINING U PLANT SLUDGE 39
7.3 TANKS CONTAINING T PLANT SLUDGE 40
7.4 HAZARD POTENTIAL AND ACCIDENT FREQUENCY CONCLUSIONS 41
7.4.1 Temperature Control 41
7.4.2 Waste Moisture Control 42

8.0 SAFETY CONCLUSIONS AND REQUIRED CONTROLS 42
8.1 KEY ASSUMPTIONS 42

9.0 REFERENCES 43

APPENDIX A STATISTICAL ANALYSIS OF FUEL AND NICKEL CONCENTRATIONS A-1

APPENDIX B EVALUATION OF SODIUM NICKEL FERROCYANIDE AND NICKEL SAMPLE DATA FOR C FARM TANKS B-1

LIST OF FIGURES

1. Strategy for Safety Issue Resolution 5

2. Ferrocyanide Reaction Accident Event Tree 8

3. Moisture Criterion for Conditional Safety Category as a Function of Ferrocyanide Concentration 17

4. Eyring Plot for Ammonia Production in the Hydrolysis of In Farm Simulant 25

5. Linear Approximation to the Applied Gamma Dose Rate Dependence of Ammonia Production in the Hydrolysis of In Farm Simulant (0.5 g) in 2 M NaOH at 90 °C 27

6. Ammonia Production Rate Constant as a Function of Applied Gamma Dose Rate in the Hydrolysis of In Farm at 90 °C 27

7. Ammonia Production During Hydrolysis of In Farm Simulant at pH 10 and 60 °C with an Applied Gamma Dose Rate of 4.5 x 10^4 rad/h 30

8. Requirements for Dryout 38

LIST OF TABLES

1. Summary of RSST Tests Regarding Propagation 12

2. Summary of Ferrocyanide Tube Propagation Tests 14

3. Comparison of Tank Contents with Criteria 20

4. Hanford Defined Waste Ferrocyanide Sludge Compositions 22

5. Composition of the More Concentrated Layers of Three Simulant Sludges 22

6. Summary of Available Temperature Data for the Four C Farm Ferrocyanide Tanks 25

7. Average Estimated Integrated Beta and Gamma Radiation Dose for the C Farm Ferrocyanide Tanks 26

LIST OF TABLES (Continued)

8. Summary of Available pH and Hydroxide Data for the C Farm Ferrocyanide Tanks 28

9. Current Ferrocyanide and Nickel Concentrations Compared to Original Concentrations (Dry Basis) 32

10. Thermal Characteristics of Ferrocyanide Tanks 35

11. Rate of Water Loss from Ferrocyanide Tanks Caused by Evaporation During Passive Ventilation 37

LIST OF TERMS

DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	data quality objectives
EA	environmental assessment
EBA	evaluation basis accident
FAI	Fauske and Associates, Inc. (Burr Ridge, IL)
HTCE	historical tank content estimate
RSST	reactive system screening tool (a small adiabatic calorimeter)
SA	safety assessment
SST	single-shell tank
TC	thermocouple
UR	uranium recovery
USQ	unreviewed safety question

LIST OF DEFINITIONS

Aging. As used in this report, aging means chemical and radiolytic degradation that reduces the ferrocyanide (fuel) concentration in ferrocyanide-bearing materials.

Bound water content. Bound water in waste is water remaining in waste after free water is removed. Bound water has been calculated to amount to 4.6 molecules of H_2O per molecule of sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] on the basis of tests described in Postma et al. (1994).

Free water content. Free water is water in ferrocyanide waste that can be removed from samples using standard drying methods by drying at 120 °C for 18 hours or by an equivalent laboratory process. As an example, if a 10-gram sample of waste lost 5 grams of water after drying at 120 °C for 18 hours, the free water content of the waste would be assigned a value of 50 wt%.

Total water content. Total water content is the sum of free and bound water contents.

Dry sodium nickel ferrocyanide. Dry sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] is the ferrocyanide compound alone, with no bound water.

Ferrocyanide concentration on an energy equivalent basis. Theoretical analyses described herein indicate that the criterion for reaction propagation is closely related to exothermic reaction energy per unit mass of waste. The energy equivalent concentration of ferrocyanide is a value computed from a measured exotherm in a waste sample using a specific reaction energy of 6 megajoules per kilogram (MJ/kg) of sodium nickel ferrocyanide. For example, if a waste sample exhibited a reaction exotherm of 0.6 MJ/kg of waste on a zero free water basis, the energy equivalent ferrocyanide concentration would be calculated as:

$$\frac{0.6MJ}{kg\ waste} x \frac{1\ kg\ Na_2NiFe(CN)_6}{6\ MJ}\ x\ 100 = 10\%\ Na_2NiFe(CN)_6$$

on a zero free water basis. The technical basis for this definition of ferrocyanide concentration on an energy equivalent basis is described in Postma et al. (1994).

1.0 PURPOSE AND SCOPE

This report updates the technical basis for the safe storage of ferrocyanide-bearing waste sludges in Hanford Site underground waste storage tanks.

An updated ferrocyanide program plan was submitted to the Defense Nuclear Facilities Safety Board (DNFSB) in December 1994 (O'Leary 1994). The program plan outlines activities planned to meet the Wyden Amendment requirements (Public Law 101-510, Section 3137 [1990]) and to provide the safety basis for removing the remaining ferrocyanide tanks from the Watch List. Theoretical analysis, laboratory experiments, and monitoring have been completed for all ferrocyanide tanks. Sampling and analysis have been completed for four C Farm tanks. This report is part of the ferrocyanide program activities (O'Leary 1994) that are scheduled to be completed by the end of fiscal year (FY) 1997. This report provides the technical basis to resolve the safety issue for four C Farm tanks and provides a foundation for updating the safety evaluation of the 14 other ferrocyanide tanks pending completion of sampling and analysis activities. More specifically, this report's purpose is as follows:

1. Provide a technical basis for and resolving the safety issue for four C Farm tanks (241-C-108, C-109, C-111, C-112). This technical basis is supported by the results of waste sampling and analysis efforts which conclude that the sludges in all four of these tanks can be recategorized from CONDITIONALLY SAFE to SAFE.

2. Present the results of experiments and waste sample results that indicate that the ferrocyanide hazard has been eliminated as a result of radiolytic and chemical degradation (aging) over the many years of waste storage. This provides the foundation for resolving the safety issue for all ferrocyanide sludges stored in Hanford Site underground storage tanks.

This report addresses only the hazard posed by ferrocyanide sludges and does not address other hazards that may be posed by these tanks, such as organic-nitrate condensed-phase reactions or flammable gas deflagrations.

2.0 BACKGROUND

Radioactive waste from defense operations has accumulated in the Hanford Site's waste storage tanks since the early 1940's. During the 1950's, additional tank storage space was required to support the defense mission. To obtain this additional storage space quickly, while minimizing the construction of additional storage tanks, Hanford Site scientists developed a process to remove (scavenge) radiocesium and other soluble radionuclides from

tank waste liquids through precipitation processes. After the radionuclide concentrations in the supernatant were reduced below established limits, the liquid was decanted to cribs and trenches. The solids that precipitated in the tank contained ferrocyanide, which accumulated in various settling tanks as a waste sludge. Some of the settled sludges were transferred to accumulation tanks for storage.

As a result of the scavenging process, approximately 140 metric tons (154 tons) of ferrocyanide [as $Fe(CN)_6^{-4}$] were added to waste now residing in 18 of the single-shell tanks (SSTs).

2.1 WATCH LIST AND USQ FORMULATION

In March 1989 (Nguyen 1989), based on process knowledge, process records, transfer records, and log books, 22 Hanford Site tanks were originally identified as containing 1,000 gram-moles (g-moles)[3] (211 kg [465 lb]) or more of ferrocyanide [as the $Fe(CN)_6^{-4}$]. Two additional ferrocyanide tanks were identified in January 1991 (Borsheim and Cash 1991), increasing the number of ferrocyanide tanks to 24. To avert possible injury to personnel and damage to the facility or environment, strict controls were identified for these and other safety issue tanks in *Operating Specifications for Watch List Tanks* (WHC 1990). Tanks identified by this document (see WHC 1996 for the latest revision) have been commonly referred to as Watch List tanks.

Originally, little was known about the potential hazards of a ferrocyanide-nitrate/nitrite reaction in Hanford Site SSTs. Because the safety envelope was not adequately defined by the existing analyses, an inadequacy existed in the authorization basis. Specifically, the existing safety analysis report (Smith 1986) and subsequent analyses such as the 1987 environmental impact statement (DOE 1987) did not adequately define the conditions necessary to preclude propagating reactions in the ferrocyanide waste; therefore, an unreviewed safety question (USQ) was declared (Deaton 1990).

In November 1990, the Wyden Amendment (Public Law 101-510, Section 3137 [1990]) was enacted. This law required the identification of Hanford Site tanks that may have a serious potential for release of high-level waste. In February 1991 (Harmon 1991), 24 ferrocyanide tanks were among the tanks identified and included in the July 1991 report to Congress (Watkins 1991) that responded to the Wyden Amendment. However, a re-examination of the historical records (Borsheim and Simpson 1991) indicated that six of the 24 tanks did not contain the requisite 1,000 g-moles of ferrocyanide, and should not have been included on the Watch List nor identified in the response to the Wyden Amendment. The six tanks were subsequently removed from the Watch List (Anttonen 1993, Sheridan 1994b).

[3]The 1,000 g-moles criterion has since been replaced with a 115 calories per gram (cal/g) fuel concentration criterion (Meacham et al. 1995).

2.2 BACKGROUND OF SAFETY ASSESSMENTS

In response to the USQ designation and DNFSB Recommendation 90-7 (FR 1990), the ferrocyanide hazard has been studied extensively. The chemical and physical nature of ferrocyanide and the condition of the waste in the underground storage tanks have been investigated extensively through theoretical analysis, laboratory experiments, tank monitoring, and waste sampling. Safety documentation concerning the ferrocyanide hazard has been updated a number of times to reflect new information, as described below.

Hazard Assessment. A report assessing the ferrocyanide waste tank hazards was issued in July 1992 (Grigsby et al. 1992). The report reviewed the understanding of the ferrocyanide hazard at that time, and presented an integrated evaluation and interpretation of historical data and then-available information.

Safety and Environmental Assessments. Safety Assessments (SAs) were prepared to assess the safety of proposed activities (e.g., upgrading temperature monitoring and waste sampling) and to provide proper controls to maintain safety. The SAs and the accompanying environmental assessments (EA) for operations provided the basis for DOE authorization of the proposed activities used to manage the waste while the ferrocyanide hazard was under investigation. SAs have been approved for headspace sampling of all ferrocyanide tanks, waste surface sampling, push-mode and rotary-mode core sampling, thermocouple (TC)/instrument tree installation in sound and assumed leaker tanks, and removal of pumpable liquid (interim stabilization). A generic EA covering all proposed operations in the tank farms was approved and a Finding of No Significant Impact issued by DOE (Gerton 1994). Approval of the generic EA provides adequate National Environmental Policy Act coverage for the planned Ferrocyanide Safety Program activities.

USQ Closure. A strategy for closing the Ferrocyanide Unreviewed Safety Question (USQ) and resolving the Safety Issue was developed by DOE and Westinghouse Hanford Company and presented to the DNFSB in August 1993 (Grumbly 1993). The strategy uncoupled USQ closure from the final resolution of the Safety Issue. The strategy contains two key steps: (1) development of criteria for safety categories that rank the hazard for each tank and hence allow closure of the USQ; and (2) confirmation and final placement of each tank into one of the categories based on core sampling and analyses of the tank contents.

Based on the knowledge gained from simulant studies, theoretical analyses, and analyses of actual waste samples, safety criteria were defined for the ferrocyanide waste (Postma et al. 1994). These criteria were reviewed and accepted by external oversight panels and the U.S. Department of Energy (DOE). The USQ was closed on March 1, 1994 by the DOE Assistant Secretary for Environmental Restoration and Waste Management (Sheridan 1994a).

Resolving the Safety Issue. A ferrocyanide program plan was submitted to the DNFSB in December 1994 (O'Leary 1994) that outlines planned activities to complete the requirements of DNFSB Recommendation 90-7, meet the Wyden Amendment requirements (Public Law 101-510, 1990) and remove the remaining ferrocyanide tanks from the Watch List. These

activities include theoretical analysis, laboratory experiments, waste monitoring, and tank sampling. The results are used to categorize the tank contents and evaluate the risk. Theoretical analyses, laboratory experiments, and tank monitoring have been completed for all ferrocyanide tanks. As described in *Strategy for [Ferrocyanide] Safety Issue Resolution* (Grumbly 1993), resolution of the safety issue is based on knowledge of waste conditions obtained through characterization studies, including representative waste samples. This strategy is shown in Figure 1. Sample analysis results are available for tanks that originally contained the most concentrated ferrocyanide wastes; that is, those stored in four C Farm tanks (241-C-108, C-109, C-111, and C-112). This report completes the evaluation of the ferrocyanide hazard for these four tanks.

Samples have been obtained from tanks representative of the other 14 ferrocyanide tanks. Following completion of sample analysis and characterization evaluations, these 14 tanks will receive final categorization. It is expected that these tanks will also meet SAFE criteria and that the safety issue will be resolved on this basis.

3.0 HAZARD POTENTIAL AND POSTULATED FERROCYANIDE ACCIDENTS

3.1 THE FERROCYANIDE SAFETY ISSUE

Ferrocyanide is a complex of ferrous and cyanide ions that is considered stable in aqueous solutions. However, *Sax's Dangerous Properties of Industrial Materials* (Lewis 1992) indicates that "fusion of mixtures of metal cyanides with metal chlorates, perchlorates, nitrates, or nitrites may cause violent explosions." Testing of ferrocyanide-bearing waste simulants has shown no evidence of explosive waste behavior, but the waste will support energetic exothermic reactions under special conditions in the laboratory. Laboratory studies of ferrocyanide waste simulants have been used to define the conditions under which energetic reactions might occur, and likewise to define conditions under which such reactions are not possible. Conditions that are necessary to support rapid, sustained exothermic reactions are:

- sufficient fuel concentration
- sufficient oxidizer concentration
- relatively dry material
- an initiator that can heat a portion of the material above the ignition temperature.

These conditions are described in more detail below and are used to judge the likelihood and severity of postulated ferrocyanide exothermic reaction accidents.

The potential for a sustained, rapid exothermic reaction involving ferrocyanide in stored waste is presented within this discussion. The analysis is based on process knowledge obtained from historical records, experiments performed with process waste simulants that represent the wastes as originally produced from the scavenging process flowsheets, and

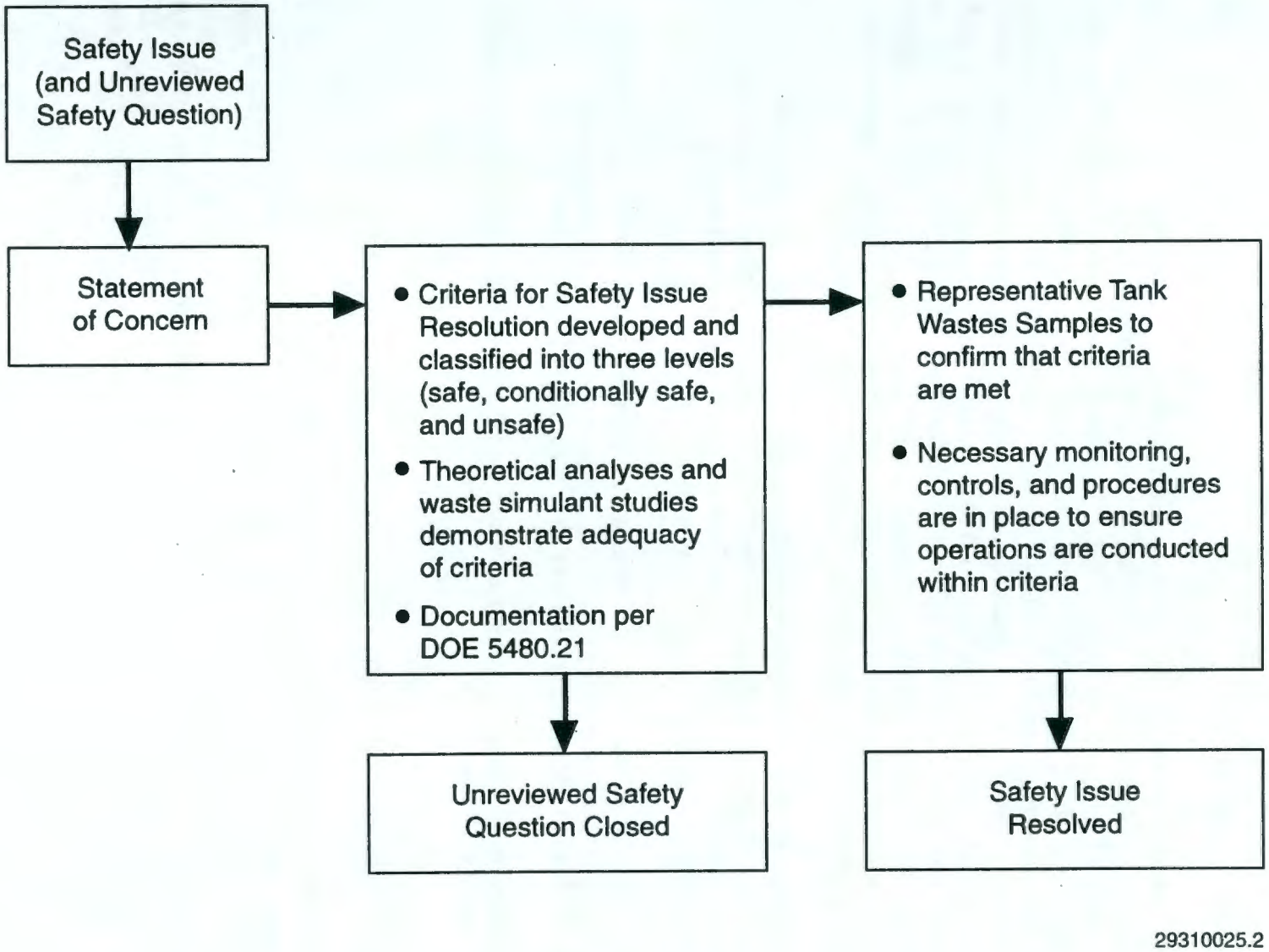


Figure 1. Strategy for Safety Issue Resolution (Grumbly 1993).

analyses of chemical and physical processes that might affect waste conditions to exacerbate or ameliorate the ferrocyanide hazard. The hazard posed by the ferrocyanide-bearing wastes can differ depending on the waste's composition. The composition of the ferrocyanide sludges, as they were originally formed, varied as a result of the different processes that were used to produce them.

Three treatment processes were conducted in separate facilities to treat three different types of waste. The corresponding flowsheets are termed U Plant, T Plant, and In Farm flowsheets (Borsheim and Simpson 1991). In general, the aqueous waste was pumped to process tanks where precipitating agents were added. The slurry was then transferred to an underground storage tank for settling of the solids and disposal of the supernatant liquid to the ground. The precipitated solids formed a sludge that constitutes the ferrocyanide waste. The U Plant flowsheet material is named such because the processing was performed at the U Plant facility and then transferred to the tank farms for settling. Likewise, the T Plant flowsheet material was originally processed at the T Plant facility. In Farm flowsheet was used to treat waste liquids recovered from the underground tanks. These liquid wastes were treated in the CR Vault facility, which is adjacent to the C Farm tanks.

U Plant and T Plant flowsheets produced precipitates that contained relatively large percentages of inert diluents and thus produced sludge that contained relatively low concentrations of ferrocyanide. Some 74% (by mass) of ferrocyanide consumed at the Hanford Site was used by these two flowsheets.

The In Farm flowsheets contained lower concentrations of inert diluents, and therefore resulted in sludge that contained relatively higher concentrations of ferrocyanide. Roughly 26% of the total ferrocyanide consumed was used in the In Farm flowsheet.

The following evaluation assesses the hazard by focusing on these three different types of ferrocyanide sludges.

3.2 ACCIDENT SCENARIO

The postulated accident of concern arising from the ferrocyanide hazard is the occurrence of a sustainable, rapid exothermic ferrocyanide-nitrate reaction in the stored waste. A sustainable reaction is one that can spread beyond a local ignition source. A rapid reaction is one that generates heat faster than it can be removed; it excludes the slow aging (degradation) reactions believed to occur over a period of years. Such a sustainable, rapid exothermic reaction could produce sufficient heat and evolved gases to pressurize the tank headspace, releasing aerosolized waste from tank vents and potentially damaging the tank's structure.

For a propagating reaction accident to occur, several conditions would be necessary. The specific limits for these conditions that define when a reaction may or may not be possible are discussed later. All of these conditions must be met or exceeded to have a propagating reaction:

- Tank waste would need a ferrocyanide (fuel) concentration sufficient to support a sustainable rapid exothermic reaction (propagating reaction)
- Sufficient oxidizer would need to be well mixed and in contact with the fuel
- The water (moisture) content of the sludge would need to be sufficiently low (the sludge must be relatively dry) that initiated reactions would not be quenched by wet material
- The reaction would need to be initiated by heating a portion of the waste to the reaction ignition temperature.

If all of these conditions were met, a reaction could propagate through additional reactive sludge until materials not meeting these conditions were encountered. Thus, a postulated accident scenario is as follows (as shown in Figure 2).

- Ferrocyanide-bearing waste settled or was transferred to an SST for storage. The settled sludge had a sufficiently high ferrocyanide (fuel) concentration to support a propagating reaction. The ferrocyanide concentration was not reduced, through aging processes over approximately 40 years of storage, below the minimum required value.
- The sludge contains sufficient nitrate and/or nitrite mixed sufficiently with the ferrocyanide to provide the oxidizer for the propagating combustion reaction.
- The water content of the settled sludge was reduced by draining or evaporation until the sludge is relatively dry.
- A portion of the sludge is heated to ignition temperatures of 250 °C to 270 °C (482 °F to 518 °F) (Epstein et al. 1994, Postma et al. 1994) by in-tank activities and equipment (such as electrical equipment malfunctions), or by a lightning strike that arcs from suspended in-tank equipment to the waste surface, or by a hot spot that develops by concentrating waste ^{137}Cs in a small portion of the waste.

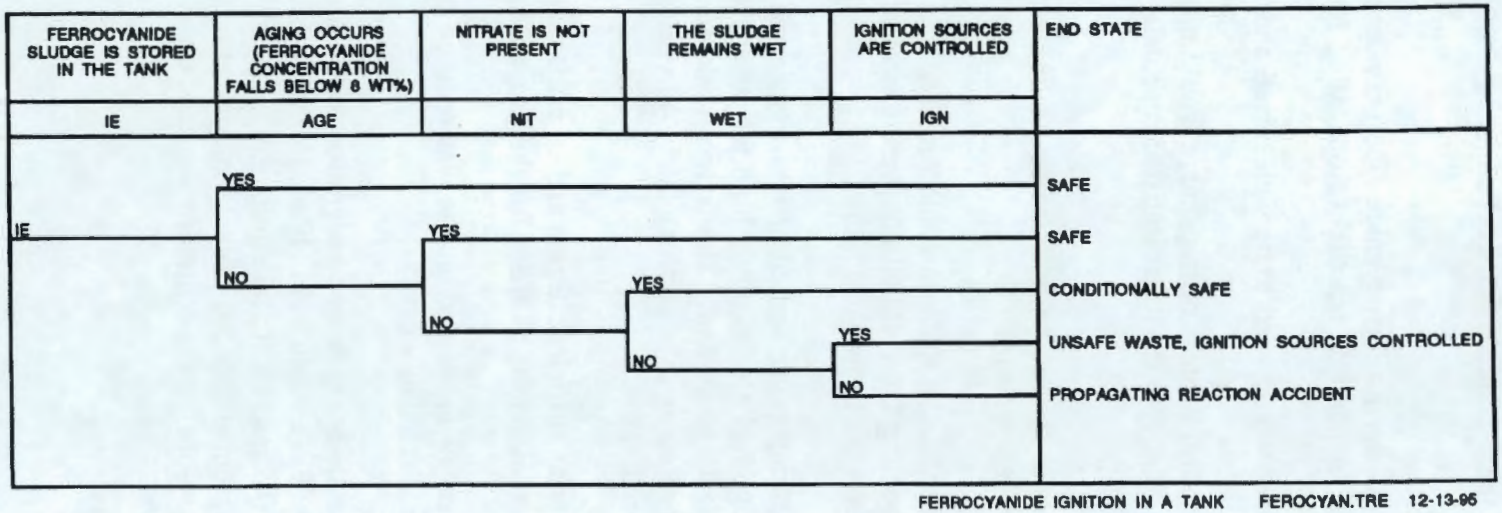


Figure 2. Ferrocyanide Reaction Accident Event Tree.

- Once initiated, the reaction propagates through surrounding reactive sludge. This reaction is not explosive; the measured reaction propagation velocities are quite low, on the order of 10 cm/min (Table 2). The hot gases produced can pressurize the tank headspace and vaporize volatile radionuclides that condense as aerosols when mixed into the cooler headspace gas. These radioactive aerosols are released from tank vents, including ruptured high-efficiency particulate air filters. If the reaction is sufficiently rapid and consumes sufficient material, the tank structure can be damaged by the pressurization.

The following discussion shows that the wastes stored in Hanford Site waste tanks are sufficiently dilute in ferrocyanide (SAFE) or sufficiently wet (CONDITIONALLY SAFE) that the ferrocyanide is not a hazard and such a postulated accident is not possible.

3.3 FERROCYANIDE SAFETY CATEGORIES AND SAFETY CRITERIA

The derivation and bases of the ferrocyanide safety categories and safety criteria are described more fully in Postma et al. (1994) but summarized here. A combination of theoretical analysis and experimental measurements is used.

3.3.1 Reaction Energies and Energy Balance

The theoretical approach used to identify waste compositions that could or could not support a propagating reaction was based on an energy balance. A necessary condition for propagation is that the reaction generate enough energy to heat unreacted fuel to its ignition temperature. The criteria were therefore defined as the condition when the potential reaction energy is less than the endotherms that would accompany the heating of a waste from ambient temperature to a reaction threshold temperature. By this means, a ferrocyanide concentration criterion level was calculated as a function of waste moisture content.

The oxidation of ferrocyanide by nitrate and/or nitrite can result in a variety of reaction products with different reaction energies. The most energetic, for a given amount of fuel, is one that produces nitrogen and carbon dioxide (or carbonate salt if there is sufficient hydroxide available to form it). A representative equation with nitrate is

$$Na_2NiFe(CN)_6 + 6NaNO_3 \rightarrow FeO + NiO + 4\ Na_2CO_3 + 6N_2 + 2CO_2. \qquad (1)$$

The calculated energy (ΔH) for this reaction is approximately -9.52 megajoules (exothermic) per kilogram (MJ/kg) of ferrocyanide at 25 °C (298 °K).

Observations indicate that oxides of nitrogen are formed in slow, low temperature reactions between ferrocyanide and nitrate-nitrite mixes. Calculated reaction energies are much lower for reactions that produce nitrogen oxides. The theoretical energy available from the reaction decreases to -6.6 MJ/kg when N_20 is the product. If NO is produced, a reaction endotherm of 0.73 MJ/kg is calculated.

For this assessment the reaction energy was assigned a value of -6 MJ/kg of $Na_2NiFe(CN)_6$ on the basis of three independent experimental determinations carried out with simulated waste (Postma et al. 1994). This amounts to 63% of the theoretical value given above for Equation (1) and 90% of the calculated energy with N_2O as the product gas.

Conservative estimates of exothermic energy density required for propagating reactions can be made on the basis of a simplistic model that largely ignores kinetic factors. The criteria for preventing propagation may be described in terms of an energy balance expressed as:

$$\Delta H_M + \Delta H_R \geq 0 \qquad (2)$$

where:

ΔH_M = Change in enthalpy of waste upon heating from initial temperature to reaction onset temperature (positive term)

ΔH_R = Reaction enthalpy (negative term).

The energy balance represented by Equation (2) indicates that propagation is impossible if the reaction energy is insufficient to heat unreacted material to the reaction onset temperature (ignition temperature). The endotherms that are accounted for are those attributable to sensible heat and changes in phase (water to steam and melting of nitrates and nitrites).

The model will yield conservative results because it assumes that the reaction goes to completion at temperatures below the ignition temperature and that the reaction takes place adiabatically. A more realistic estimate of minimum reaction energy may be made by accounting for heat transfer between reacted and unreacted material. This method estimates the interface temperature between solid slabs initially at different temperatures. The criterion for propagation is that the interface temperature must be heated to the reaction threshold temperature. Because interface temperature is approximated by the average between unreacted and reacted material, the threshold can be reached only when the temperature of reacted material is appreciably higher than the threshold temperature. A rough estimate of required energy density for this model is a factor of two greater than that expressed in Equation (2)[4].

[4]This method is described in *The Contact Temperature Ignition (CTI) Criteria for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste*, (Fauske et al. 1995) and is expected to be implemented following verification as described in *Test Plan for Samples From Selected Hanford Waste Tanks* (Meacham 1995).

The theoretical approach used for this assessment was verified to be conservative through testing of ferrocyanide sludge simulants in adiabatic calorimeters and with tube propagation tests as described below.

3.3.2 Adiabatic Calorimetry Tests

A number of compositions containing ferrocyanide and $NaNO_3/NaNO_2$ were tested in the reactive system screening tool (RSST)(Fauske and Leung 1985). In these tests, sizeable samples (10 grams and 70 grams) were heated under low heat loss conditions. A summary of the tests is shown in Table 1. As the sample was heated to above the reaction onset temperature, the thermal energy produced by the reaction caused the sample to self-heat. The rate and extent of this self-heating provides direct evidence of the character of the reaction that has taken place. Two distinct types of behavior were seen depending on sample reactivity (i.e., ferrocyanide concentration):

- A relatively slow heat-up rate that is typical of an Arrhenius or runaway reaction (any material that contains chemicals that react exothermically will exhibit this behavior)

- A sharp transition to a very high self-heating rate indicating a characteristic ignition temperature as the sample is heated. For materials that exhibit this behavior, a propagating reaction is possible, given an appropriate initiator.

Based on adiabatic calorimetry (i.e., RSST) tests (Postma et al. 1994), it was found that propagating reactions were not observed for sodium nickel ferrocyanide concentrations below 15 weight percent (wt%) on a zero free water basis. The RSST cannot measure the effect of water on reactivity because all samples are heated to dryness before reaching the ignition temperature.

3.3.3 Tube Propagation Rate Tests

The potential for ferrocyanide waste simulants to sustain a propagating reaction was also evaluated with tube propagation tests. Test compositions, test conditions, and results are summarized in Table 2. The test apparatus for measuring the propagation velocity of a chemical reaction through the ferrocyanide sludge consisted of a thin, insulated stainless-steel cylinder, 25 mm in diameter and 100 mm tall, that was filled with the test material (Fauske 1992). The reaction was ignited at the top by a BaO_2-Al mixture. The progress of the reaction, if any, was monitored by four thermocouples spaced 20 to 30 mm apart. These show sharp temperature rises as the reaction front passes. Again, one of two distinct behaviors was observed. The reaction proceeded to the bottom of the cylinder in samples capable of supporting a propagation reaction. If the reaction was not ignited or if it fizzled out in a short distance, the sample did not support a propagating reaction.

Table 1. Summary of RSST Tests Regarding Propagation.

$Na_2NiFe(CN)_6$ (wt%, dry basis)	Sludge type	Ignition temperature (°C)	Propagation observed	Notes
4.6	U Plant-1	--	No	a
6.3	U Plant-2 top	--	No	a
8.2	U Plant-2 bottom	--	No	a
8.8	T Plant	--	No	b
18.2	In Farm 1 top	254	Yes	a
18.6	In Farm 2 top	278	Yes	a
27.6	In Farm 2 bottom	244	Yes	a
25.5	In Farm 1 bottom	250	Yes	a
50	Mixtures of pure $Na_2NiFe(CN)_6$	280	Yes	a, d
40	Mixtures of pure $Na_2NiFe(CN)_6$	245	Yes	a
31	Mixtures of pure $Na_2NiFe(CN)_6$	275	Yes	a, d
20	Mixtures of pure $Na_2NiFe(CN)_6$	240	Yes	a
10	Mixtures of pure $Na_2NiFe(CN)_6$	--	No	a
5	Mixtures of pure $Na_2NiFe(CN)_6$	--	No	a
2.5	Mixtures of pure $Na_2NiFe(CN)_6$	--	No	a
26	In Farm 1	250 °C	Yes	c
18.6	In Farm + $NaNO_2$	260 °C	Yes	c
15.6	In Farm + $NaNO_2$	270 °C	Yes	c
8.3	U Plant	--	No	c

Notes:

[a]Fauske (1992)
[b]Fauske (1993)
[c]Fauske et al. (1995). RSST heater at full power.
[d]These tests used $Cs_2NiFe(CN)_6$

Several compositions (as shown in Table 2) were tested by this method, where both ferrocyanide and water concentrations were varied. The basic test conclusions were the following: For dry sludge (zero free water), $Na_2Ni\ Fe(CN)_6$ concentrations of 15 wt% and higher supported propagation; those with 12 wt% or less did not. The ferrocyanide content required to support propagation increases with the water content of the sludge. With 26 wt% ferrocyanide on a dry basis (the most concentrated of the flowsheet simulants) propagation was observed with 8 wt% water, but not with 12 wt%.

A key finding of these tests is that propagation ceased when the free water content was 12 wt% or more and the simulant contained less than 25.5 wt% ferrocyanide, which is the highest concentration of ferrocyanide-bearing waste originally put in the tanks.

This 12 wt% moisture threshold determined experimentally is only 43% of the threshold indicated by the thermodynamic calculations. This difference is expected because the thermodynamic calculations are inherently conservative.

Table 2. Summary of Ferrocyanide Tube Propagation Tests.

$NaNiFe(CN)_6$ (wt%, dry basis)	Free water (wt %)	Initial temperature (°C)	Propagation observed	Propagation velocity (cm/min)	Notes
29.5	0	60	Yes	4, 9	b
26	0	26	Yes	10	c
26	8	26	Yes	5.3	c
26	12	26	No	-	c
26	14.6	26	No	-	c
26	0	26	Yes	7.5	d
26	50	26	No	-	c
35	0	~25	Yes	20	a
35	15	~25	Yes	7.8	a
35	20	~25	No	-	a
15.5	0	30	Yes	2	e
12	0	30	No	-	e
12	0	130	No	-	e
14	0	30	No	-	e
14	0	130	Partial	-	e

Notes:

[a]Stoichiometric mixture of pure $Na_2NiFe(CN)_6$ with $NaNO_3$ (Fauske et al. 1995)
[b]Mixture of 30% $Na_2NiFe(CN)_6$ with 70% $NaNO_3/NaNO_2$ oxidizer (Fauske 1992)
[c]Mechanical mixture representing In-Farm-1 flowsheet material (Fauske 1992)
[d]In-Farm-1 (bottom) simulant (Fauske 1992)
[e]In-Farm simulant (Fauske et al. 1995)

3.4 WASTE SAFETY CATEGORIES

3.4.1 SAFE

Based on the experiments and theoretical analysis summarized above, the conservative criteria that define the SAFE category are as follows (Postma et al. 1994):

- Concentration of fuel ≤ 8 wt% sodium nickel ferrocyanide[5]
- Concentration of water - not limiting
- Concentration of oxidizers - not limiting
- Temperature of waste - not limiting

The safety category SAFE defines waste that cannot burn or explode because it contains too little ferrocyanide as fuel. This conclusion is valid even for waste that contains optimum concentrations of oxidizer and/or no free water. A small amount of tightly bound water (4.6 molecules of H_2O per molecule of sodium nickel ferrocyanide) has been identified through testing and is credited as being present in ferrocyanide waste that meets SAFE criteria (Postma et al. 1994). A further conservative assumption is that the prevention of reaction initiation is not credited for preventing accidents for the SAFE category.

3.4.2 CONDITIONALLY SAFE

Based on experiments and theoretical analysis, the conservative criteria that define the CONDITIONALLY SAFE category are as follows:

- Concentration of fuel > 8 wt% sodium nickel ferrocyanide[5]
- Concentration of water ≥ 0 to 24 wt%
- Concentration of oxidizers - not limiting
- Temperature[6] of waste ≤ 90 °C

The safety category CONDITIONALLY SAFE defines waste that cannot burn or explode because, although it may contain sufficient fuel and oxidizer, it contains sufficient water (moisture) to quench any reaction that may be initiated, and thus propagating reactions are prevented. This safety category is valid even for waste that contains optimum concentrations of oxidizer. The prevention of reaction initiation is also not credited for preventing accidents for the CONDITIONALLY SAFE category. Waste temperature limits are specified, however, to provide assurance that waste moisture, which is credited, is not lost through

[5] $Na_2NiFe(CN)_6$ on an energy equivalent basis, calculated on a zero free water basis.

[6] Temperature is not an independent criterion; it is implicit in the moisture criterion.

high evaporation rates. A key assumption in this temperature limit is that the ventilation rate in the tanks where CONDITIONALLY SAFE waste is stored, is low and evaporation losses are very slow.

Water Limit

Thermodynamic calculations using Equation (2) above and described in detail in Postma et al. (1994) showed that 24 wt% water would prevent the propagation of reactions in the In Farm simulant that contained 26 wt% $Na_2NiFe(CN)_6$.

Experiments (Table 2) showed that 12 wt% water was sufficient to quench propagating reactions in In Farm simulant waste. A conservative moisture criterion equal to the rounded theoretical value (24%) and equal to twice the experimental value, 2(12%) = 24 wt%, was specified for sludge having ferrocyanide concentrations of 26 wt% on a dry basis. Thus the moisture criterion applicable to 26 wt% $Na_2NiFe(CN)_6$ on an energy equivalent basis is

Moisture criterion = 24 wt% free water.

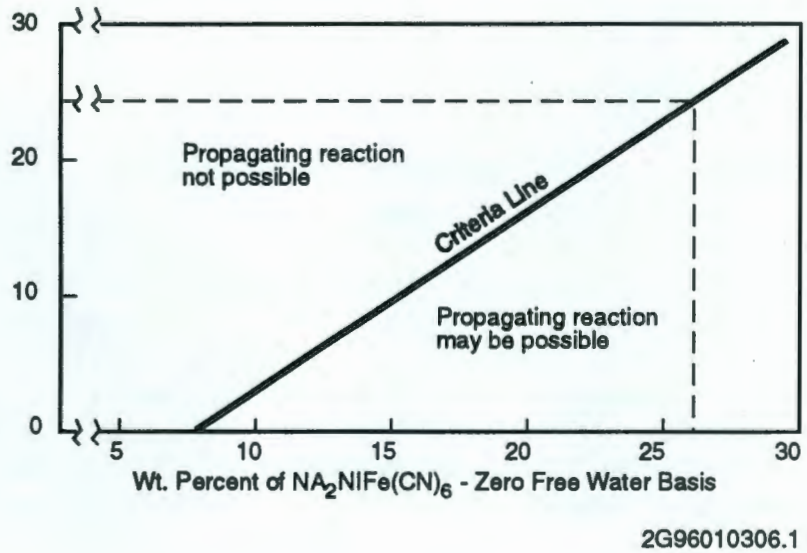
Because this minimum required water content was based on the In Farm simulant sludge (26 wt% ferrocyanide), it will be overly conservative for sludge that has ferrocyanide concentrations close to the SAFE fuel criterion, 8 wt%.

To more realistically account for the lower exothermic energy potential of sludge that contains less than the maximum fuel concentration, the water criterion can be relaxed for tanks known to contain less than 26 wt% ferrocyanide. The thermodynamic calculations indicate that the mass of free water (grams water/grams dry waste) required to quench reactions increases linearly with ferrocyanide concentration (Postma et al. 1994). This relationship was shown to be approximated by a linear moisture relationship that increases from zero at 8 wt% $Na_2NiFe(CN)_6$ to 24 wt% water at a ferrocyanide concentration of 26 wt% (zero free water basis) to stay within a conservative safety envelope.

The 24 wt% free water criterion cited above is applicable to the In Farm simulant, which contained the highest concentration of $Na_2NiFe(CN)_6$ found in any waste simulant. It is recognized that higher ferrocyanide concentrations are theoretically possible, and as illustrated in Figure 3, the criterion line extends beyond 26 wt% $Na_2NiFe(CN)_6$. While it is unlikely that waste will be found to contain ferrocyanide concentrations higher than 26 wt%, the moisture criterion line allows for this possibility. For example, for a stoichiometric mixture of $Na_2NiFe(CN)_6 \bullet 4.6H_20 + 6NaN0_3$, the ferrocyanide concentration is 34.8 wt% (zero free water basis). Based on the criterion line of Figure 3, the required free moisture concentration is computed to be 35.7 wt% for this mixture of pure reactants.

The water content referred to in the water criterion above is free water. This is water in excess of the bound water. The bound water is assumed to amount to 4.6 molecules per molecule of $Na_2NiFe(CN)_6$. At 8 wt% $Na_2NiFe(CN)_6$, this bound water amounts to 2.1 wt% of the total waste.

Figure 3. Moisture Criterion for Conditional Safety Category as a Function of Ferrocyanide Concentration.



Temperature Limit

The criterion of 90 °C (194 °F) is specified as the upper temperature limit for ferrocyanide waste because the limit provides a margin of approximately 30 °C (86 °F) between peak waste temperature and the boiling temperature of interstitial liquid, at which point relatively rapid moisture loss could occur.

3.4.3 UNSAFE

The safety category UNSAFE defines waste that does not meet the criteria for the SAFE or CONDITIONALLY SAFE categories. For waste in this category, it is assumed that a reaction initiated at a local site could propagate through a significant quantity of waste. Accidents would only be prevented by avoiding conditions that could initiate a reaction.

4.0 WASTE CONDITIONS SUPPORTING SAFETY ASSESSMENTS

The potential for an exothermic reaction in stored waste depends on the relative concentrations of the reactants, inert solid diluents, and water. Process knowledge, obtained from historical records and from waste simulants produced from the original ferrocyanide scavenging process flowsheets, has been used to predict the major constituents and some general physical properties of the waste matrix. The ferrocyanide scavenging processes were

well documented, and records for most of the campaigns still exist (e.g., GE 1958). The 18 tanks where ferrocyanide is stored are listed in Table 3 along with process record estimates of ferrocyanide concentrations and other key information that is developed in the following discussions.

4.1 WASTE FLOWSHEET SIMULANT

Simulants have been prepared based on the flowsheets, without the radioactive constituents. The precipitates were centrifuged to simulate approximately 40 years of settling. Typically, two or three layers of precipitates (discernable by color) were formed at the bottom of the settling and centrifuging containers. These layers were separated and sampled to gain a better understanding of the potential ferrocyanide concentrations. The bottom layer of the U Plant and In Farm simulants and the top layer of the T Plant simulant contained the higher ferrocyanide concentrations. Compositions of the more concentrated layers of sludge (maximum simulant) for each flowsheet are listed in Table 5. The simulants are expected to overpredict current ferrocyanide concentrations as they do not account for the degradation of ferrocyanide over approximately 40 years of storage; nor do they account for dilution by mixing with other waste.

The simulant sludges were composed of small particles and had rheological properties similar to those of clay, mayonnaise, or toothpaste. Stoichiometric calculations based on the ferrocyanide and nitrate/nitrite concentrations shown in Table 5 indicated that nitrate and nitrite concentrations were in excess of the ferrocyanide concentrations. In addition, the total water content of the simulant sludge was very large.

4.2 PROCESS RECORDS

Two models were developed from historical records and used to determine where the ferrocyanide was stored, to predict how much ferrocyanide was placed in the tanks, and to estimate original ferrocyanide concentrations.

The first model estimates ferrocyanide concentrations based on process records, and was derived on the basis of material balance calculations that traced waste transfers in the tank farms. Details of this model are provided in Borsheim and Simpson (1991).

The model predictions also use sludge volume data derived from simulant studies. This model predicts average concentrations in the sludge for each tank by dividing the ferrocyanide mass (material balance calculations) in a tank by the mass of the sludge in the tank.

The second model is described in *Historical Tank Content Estimate Reports* (HTCE), (Brevick 1995a and 1995b) and is based on tank fill records that define solids layers in each tank. Each layer is attributed to a particular waste addition or process. Based on a

combination of a knowledge of the chemicals used, the process used, and analyses of characteristic wastes, a composition is provided for each "defined waste" as described in *Hanford Defined Wastes: Chemical and Radionuclide Compositions*, (Agnew 1995). Agnew predicts compositions for four different "defined" ferrocyanide sludges. Key ferrocyanide sludge waste composition estimates are included in Table 4 for these four "defined" sludges.

- PFeCN1: Ferrocyanide scavenged uranium recovery (UR) supernates in plant using 0.005 molar (*M*) ferrocyanide (U Plant flowsheet)

- PFeCN2: Ferrocyanide scavenged UR supernates in plant using 0.0025 *M* ferrocyanide (U Plant flowsheet)

- TFeCN: Ferrocyanide scavenged in the CR vault (in Farm flowsheet)

- 1CFeCN: Ferrocyanide scavenged first cycle (1C) supernatants (T Plant flowsheet).

Based on waste transfer records as used in the historical tank contents estimates, TFeCN is applicable to the sludges in the C Farm flowsheet. The ferrocyanide sludges stored in the BY Farm are comprised of a combination of PFeCN1 and PFeCN2 sludges (U-Plant flowsheet). Finally, the ferrocyanide sludges in the TY Farm are 1CFeCN (T-Plant flowsheet). The highest predicted ferrocyanide concentration for the sludges in each tank is shown in Table 3.

Table 3. Comparison of Tank Contents with Criteria. (2 sheets)

Tank	Waste flow sheet	Concentration of $Na_2NiFe(CN)_6$ (wt%, on a zero free water basis)				Safety category	Control requirements
		Process records	HTCE defined waste	Maximum simulant[a]	Tank sample[b]		
241-BY-103	U Plant	6.0	c	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-104	U Plant	6.0	4.0	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-105	U Plant	7.4	4.0	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-106	U Plant	5.2 - 5.5	7.0	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-107	U Plant	5.0 - 5.9	7.0	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-108	U Plant	5.0 - 5.8	7.0	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-110	U Plant	5.7 - 6.2	7.0	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-111	U Plant	6.6	c	8.3	No data	Conditionally safe	Maintain passive ventilation
241-BY-112	U Plant	3.5	4.0	8.3	No data	Conditionally safe	Maintain passive ventilation
241-C-108	In Farm 2	10.4 - 15.6	18.8	22.6	5.2	Safe	none
241-C-109	In Farm 2	14.0 - 20.9	18.8	22.6	2.8	Safe	none
241-C-111	In Farm 2	8.9 - 12.1	18.8	22.6	2.1	Safe	none
241-C-112	In Farm 1	16.1 - 24.2	18.8	25.5	4.0	Safe	none
241-T-107	U Plant	7.3	c	8.3	No data	Conditionally safe	Maintain passive ventilation

Table 3. Comparison of Tank Contents with Criteria. (2 sheets)

Tank	Waste flow sheet	Concentration of $Na_2NiFe(CN)_6$ (wt%, on a zero free water basis)				Safety category	Control requirements
		Process records	HTCE defined waste	Maximum simulant[a]	Tank sample[b]		
241-TX-118	U Plant	d	c	8.3	No data	Conditionally safe	Maintain passive ventilation
241-TY-101	T Plant	7.6	10.7	8.8	e	Conditionally safe	Maintain passive ventilation
241-TY-103	T Plant	6.9	10.7	8.8	f	Conditionally safe	Maintain passive ventilation
241-TY-104	T Plant	10.7	c	8.8	No data	Conditionally safe	Maintain passive ventilation

Notes:

[a]Ferrocyanide concentration of flowsheet simulant for the most concentrated waste added to the tank (does not account for aging).

[b]Upper 95% confidence limit (see Appendix A).

[c]The HTCEs predict that no ferrocyanide sludge is stored in these tanks.

[d]Process records do not show that a significant quantity of ferrocyanide sludge is stored in this tank (Borsheim and Simpson 1991). The tank was erroneously identified as ferrocyanide tanks because of earlier track radioactive components (TRAC) calculations (Jungfleisch 1984).

[e]Composite sample yielded concentrations of 1.2 - 1.4 wt%. Data are insufficient to rank tank (Winters 1988).

[f]Composite sample yielded concentration of 1.0 - 1.3 wt%. Data are insufficient to rank tank (Winters 1988).

Table 4. Hanford Defined Waste Ferrocyanide Sludge Compositions (Agnew 1995).

Ferrocyanide sludge type	Solids volume %	Water content (wt%)	Ferrocyanide concentration (wt%, dry basis)
PFeCN1	3.7	62	7.0
PFeCN2	3.2	62	4.0
TFeCN	1.4	65	18.8
1CFeCN	4.8	78	10.7

Table 5. Composition of the More Concentrated Layers of Three Simulant Sludges (Jeppson and Wong 1993).

Wt% for stated sludge (dry basis)			
Constituent	U Plant	In Farm 1	T Plant
Bound water	2.5	5.8	~3
Sodium nitrate	45.2	39.8	27.1
Sodium nitrite	10.9	11.4	6.1
$Na_2NiFe(CN)_6$	8.3	25.5	~8.8
Nickel sulfide	0.0	2.7	0.0
Inert solids	~33	~15	~55
Free water[a]	64	48	69

Note:

[a]This value applies to the as-prepared, centrifuged sludge before drying.

Note that the ferrocyanide concentration estimates based on the process models and simulants as shown in Tables 3, 4, and 5 do not account for the aging of ferrocyanide over the approximately 40 years of storage, nor do they account for dilution by mixing with other waste. For these reasons, the models and simulants are expected to overpredict current ferrocyanide concentrations.

4.3 PROPERTIES OF SLUDGE REMOVED FROM C FARM TANKS

Core samples have recently been removed from four C Farm tanks (241-C-108, C-109, C-111, and C-112) that received waste generated using the In Farm flowsheet. The analysis of the samples provides data representative of the material currently in the tanks. Key properties of the retrieved waste are summarized as follows.

- The consistency of the high nickel-bearing sludge samples varied from a thin slurry to a moist, paste-like sludge to a thick, chunky, clay-like sludge.
- Free moisture content varied from 16 wt% to 57 wt% on a mass basis.
- Cyanide concentrations varied with vertical position as expected and ranged from zero to 1.6 wt% (reported as $Na_2NiFe(CN)_6$ on a zero free water basis). These values are much less than values expected on the basis of the simulants (see Table 5 for comparison).
- Reaction exotherms were consistently small (less than 120 joules per gram [J/g] on a zero free water basis) and correspond reasonably to those calculated on the basis of the measured cyanide concentrations.

The low ferrocyanide concentration and small reaction exotherms are attributable to chemical aging of the sludges, which is described below.

5.0 AGING PROCESSES

Aging of ferrocyanide waste is broadly defined as the thermal or radiolytic degradation of the ferrocyanide molecules. The resulting materials have a lower potential for ferrocyanide propagating reactions (Babad et al. 1993).

Insoluble sodium nickel ferrocyanide, the major component of the ferrocyanide sludges formed during the radioisotope scavenging campaign, will dissolve in a caustic solution containing 0.01 M or higher hydroxide. Dissolution of sodium nickel ferrocyanide results in soluble sodium ferrocyanide and a nickel hydroxide precipitate as shown by Equation 3.

$$Na_2NiFe(CN)_6(s) + 2\ NaOH \rightarrow Na_4Fe(CN)_6 + Ni(OH)_2. \quad (3)$$

Under tank waste conditions, the ferrocyanide complex will then hydrolyze to form formate, ferric oxide, and ammonia (see Equation 4).

$$6\ Fe(CN)_6^{-4} + 12\ OH^- + 66\ H_2O + O_2 \rightarrow 36\ HCOO^- + 2\ Fe_3O_4 + 36\ NH_3. \quad (4)$$

It should be noted that this aging process does not need the tank environment to proceed. However, the available literature (MacDiarmid and Hall 1953, Masri and Haissinsky 1963, Hughes and Willis 1962, Ohno and Tsuchihasi 1965, Robuck and Luthy 1989) and recent experiments on ferrocyanide waste simulants (Lilga et al. 1993, 1994, and 1995) indicate that three parameters strongly affect the rate of aging: temperature, solution pH, and radiation dose rate.

5.1 DEPENDENCE ON TEMPERATURE

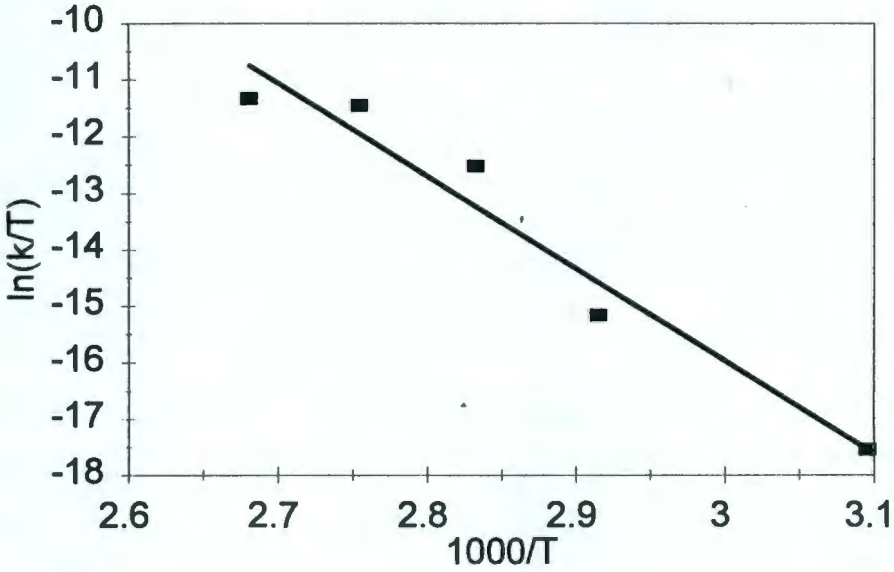
Experiments investigating the aging of In Farm waste simulant were conducted at 50 °C, 70 °C, 80 °C, 90 °C, and 100 °C in 2 M NaOH solutions over the last three years (Lilga et al. 1993, 1994, and 1995). Waste simulant solutions were exposed to ^{60}Co gamma radiation at a dose rate of about 1×10^5 rad per hour (rad/h). The control solutions were not irradiated, but were otherwise prepared and treated identically. The concentrations of ammonia, formate ion, and other species produced upon hydrolysis of ferrocyanide ion in the dissolved simulant were measured at various times over about a three-week period of reaction.

Overall, the generation of ammonia at each temperature was approximately linearly with hydrolysis time. The rate of hydrolysis, however, increased with temperature. As an approach toward building a mathematical model, the generation of ammonia was assumed to be linear with time, and global rate constants were calculated from the slopes. The Eyring plot of these rate data (Figure 4) was linear, and an activation energy of $\Delta H = 32.5$ kilocalories per mole was calculated. Rate constants for ammonia production at a given temperature (°K) and a gamma dose rate of 1×10^5 rad/h may be calculated using Equation (5). This equation is conservative in that the calculated rate constants do not include the subsequent ammonia radiolysis. Rate constants predicted from this equation are generally within a factor of about 2 of the observed rate constants.

$$\ln(k_T/T) = 33.1 - 1.64 \times 10^4 \cdot 1/T. \qquad (5)$$

The temperature history of the four C Farm ferrocyanide tanks is shown in Table 6. Tanks C-109, C-111, and C-112 have experienced relatively high temperatures during ferrocyanide sludge storage, with temperatures recorded in the 1960's in the mid-70 °C to high-80 °C range. Temperature data for C-108 were not found for these earlier periods when these tanks were warmer. However, a review of the operating history and management of waste materials indicates that tank C-108 should have experienced temperatures similar to tank C-109. Tank C-108 materials and waste levels were almost identical to tank C-109 with nearly identical contents and times (Brevick 1995a). The temperatures in these tanks were sufficient to enhance ferrocyanide aging as discussed above.

Figure 4. Eyring Plot for Ammonia Production in the Hydrolysis of In Farm Simulant.



5.2 DEPENDENCE ON GAMMA DOSE RATE AND INTEGRATED DOSE

Experiments on ferrocyanide waste simulants (Lilga et al. 1993, 1994, and 1995) show that gamma radiation promotes ferrocyanide aging. Simulants that were irradiated aged up to one order of magnitude faster than non-irradiated samples under similar conditions of time, pH, and temperature.

Table 6. Summary of Available Temperature Data for the Four C Farm Ferrocyanide Tanks.

Tank	Temperature (°C)	Month/year	Tank	Temperature (°C)	Month/year
C-108	32 24 21	01/75 01/84 03/90	C-109	77 54 27	01/63 09/64 01/83
C-111	88 27 27	09/64 01/77 01/83	C-112	75 54 24	12/61 04/63 01/76

Experiments to investigate the influence of incident gamma dose rate on the rate of hydrolysis of In Farm ferrocyanide simulant were conducted at 90 °C in 2 *M* NaOH solutions. Figure 5 shows the production of ammonia as a function of hydrolysis time in experiments conducted with applied dose rates varied over about one order of magnitude. Ammonia production is again approximately linear with exposure time. The slopes of the lines give rate constants at each applied dose rate, which show that the rate of ammonia production increases with increasing dose rate. The rate constant for ammonia production is linearly related to applied dose rate, as shown in Figure 6. The gamma dose rate dependence of hydrolysis, therefore, can be described by Equation (6), where γ is the incident gamma dose rate and $k_{\gamma,90}$ is the predicted hydrolysis rate constant at 90 °C.

$$k_{\gamma,90} = 2.8 \times 10^{-8} \cdot \gamma + 7.88 \times 10^{-4} \qquad (6)$$

The estimated integrated beta and gamma doses for the ferrocyanide waste tanks (Parra 1994) are presented in Table 7. These data show that the C Farm tanks have experienced a relatively high integrated gamma dose of between 2.4×10^8 rad to 5.3×10^8 rad. In the aging experiments, the maximum incident integrated dose was about 5×10^7 rad, which was less than that experienced by C Farm tank waste by up to one order of magnitude. Based on these aging experiments, the radiation exposure in the tanks was sufficient to significantly age the ferrocyanide waste.

Table 7. Average Estimated Integrated Beta and Gamma Radiation Dose for the C Farm Ferrocyanide Tanks.

Tank	Total beta (rad*10^8)	Total gamma (rad*10^8)	Tank	Total beta (rad*10^8)	Total gamma (rad*10^8)
C-108	2.6	4.3	C-109	2.9	5.3
C-111	2.3	4.4	C-112	0.1	2.4

5.3 DEPENDENCE ON ALKALINITY

Aging of ferrocyanide wastes by a dissolution and hydrolysis process is increased under highly alkaline conditions because sodium nickel ferrocyanide dissolves more readily at high pH. As discussed below, experiments show that hydrolysis also occurs in pH 10 solution, in which sodium nickel ferrocyanide has a low solubility.

In cesium scavenging operations, precipitation of sodium nickel ferrocyanide was done at slightly alkaline conditions (pH = 8.0 - 10). Later, the ferrocyanide tanks were used for a variety of waste management operations that introduced highly alkaline waste to the tanks (Anderson 1990). Table 8 presents a summary of the available historical pH and hydroxide data collected for the four C Farm ferrocyanide tanks (Wodrich et al. 1992).

Figure 5. Linear Approximation to the Applied Gamma Dose Rate Dependence of Ammonia Production in the Hydrolysis of In Farm Simulant (0.5 g) in 2 M NaOH at 90 °C.

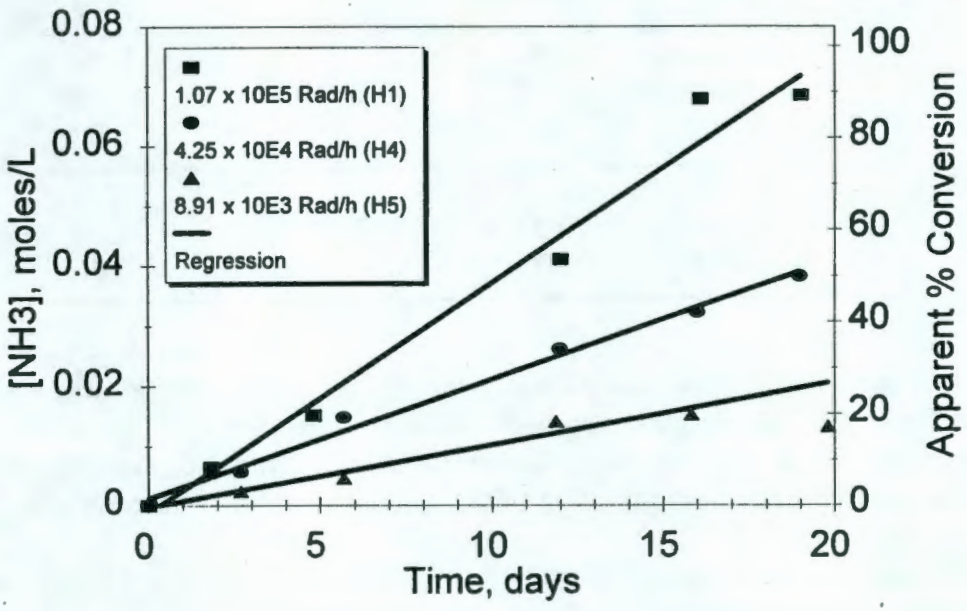


Figure 6. Ammonia Production Rate Constant as a Function of Applied Gamma Dose Rate in the Hydrolysis of In Farm at 90 °C.

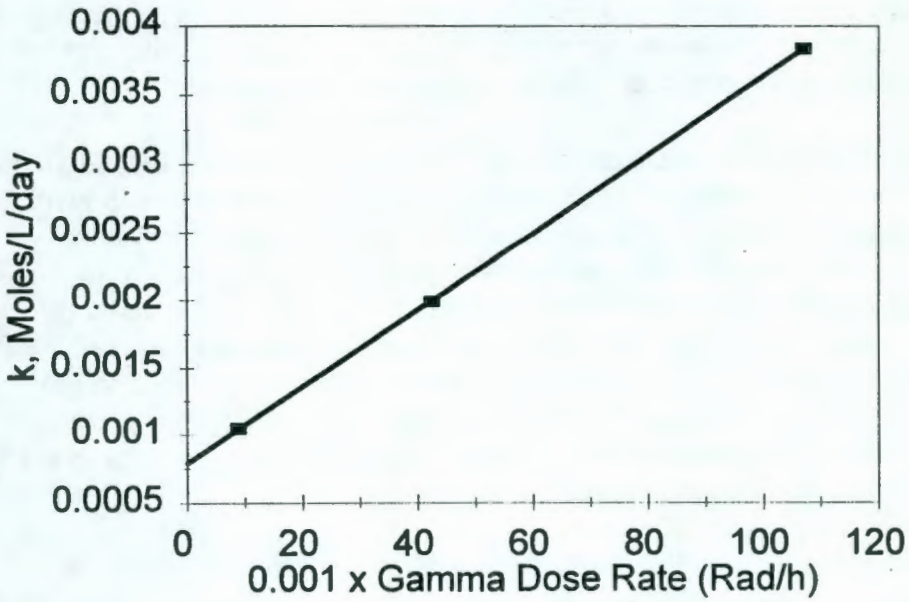


Table 8. Summary of Available pH and Hydroxide Data for the C Farm Ferrocyanide Tanks.

Tank	pH	OH^- (Molar)	Date (mo/yr)	Tank	pH	OH^- (Molar)	Date (mo/yr)
	9.8	---	05/56		11.9	---	12/71
C-108	11.8	---	12/71	C-109	12.5	0.8	06/75
	11.8	0.5	09/75		13.7	0.5	11/90
	12.2	---	05/55		10.1	---	01/56
C-111	8.6	---	10/57	C-112	11.7	---	12/71
	13.9	0.8	02/75		11.9	0.5	06/75

Values for pH presented in Table 8 are only estimates because the solutions tested had a high ionic strength (most of the samples exceeded 4 *M* sodium, making a direct correlation between hydrogen ion activity and concentration difficult). Hydroxide concentrations were measured by direct potentiometric titration of the solutions with a standardized acid.

Historical pH and hydroxide data show that all the ferrocyanide tanks contained, subsequent to the ferrocyanide campaigns, enough caustic to promote aging. Tank BY-111 had no data later than June 1956 when the pH was 9.6, but this tank was used for the same operations that transferred high-pH waste into the other BY farm ferrocyanide tanks. Consequently, waste pH should not be a limiting factor for ferrocyanide waste aging in Hanford Site tanks. However, although modeling indicated that added caustic waste could penetrate sludge at a rate of 3 meters per yr (McGrail et al. 1993), there was a question whether ferrocyanide sludge at greater depths, or that otherwise would not come into contact with high pH waste, would age. Therefore, aging under less alkaline conditions was studied.

Aging of In Farm simulant was investigated at 60 °C in a gamma-irradiated pH 10 solution. The change in ammonia concentration over the course of this experiment is shown in Figure 7. The concentration in the 161-day sample indicates an apparent cyanide decomposition of about 18 mole%. The actual decomposition is higher because ammonia radiolysis decreases the concentration with time. If it is assumed that ammonia production is linear with time, as assumed above, a global rate constant for ammonia production of 8.0×10^{-5} M/day is calculated. The fit of the data to the linear model is not very good, but this rate constant is similar to the rate constant determined for the 70 °C experiment conducted in 2 M NaOH. Considering the low solubility of In Farm simulant in pH 10 solution, the magnitude of this rate is remarkable.

It is possible that direct gamma radiolysis of ferrocyanide in the solid phase forms ferricyanide (Box et al. 1977), which may have a higher solubility (Bácskai et al. 1995), thus promoting aging. The difference in pH may not greatly affect the hydrolysis reaction itself,

because it is reported that thermal hydrolysis is unaffected by pH above pH 9 (Kuhn and Rice 1977). These results suggest that even if ferrocyanide sludge did not come into direct contact with highly basic wastes, it may have aged significantly over the decades of storage.

5.4 AGING CONFIRMED BY FERROCYANIDE AND NICKEL CONTENT OF TANK SAMPLES

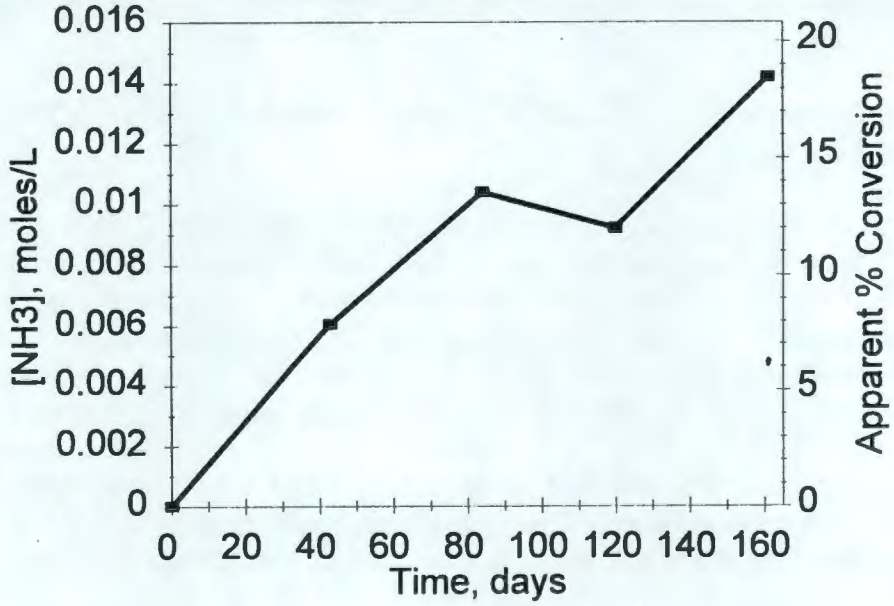
Characterization strategies developed by the Data Quality Objectives (DQO) process allow ferrocyanide tanks to be categorized as SAFE, CONDITIONALLY SAFE, or UNSAFE based on fuel and moisture concentrations and temperature. The characterization approach for ferrocyanide described in *Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives Process* (Meacham et al. 1995) also allows historical data and aging models to be corroborated by measuring fuel and nickel concentrations.

The logic used to evaluate the effects of aging first considers the fuel concentration. If the waste contains a fuel concentration less than predicted by the process flowsheets, then aging may be the reason. This aging hypothesis is evaluated by considering the nickel content of the waste.

Data on nickel concentration are used to confirm historical information and ferrocyanide aging models because nickel is a signature analyte of the nickel ferrocyanide scavenging campaigns. This is the only source of high nickel concentrations in Hanford Site underground waste tanks. Experiments that replicated the original process flowsheets (Jeppson and Simpson 1994) show that the nickel concentrations ranged between 0.8 to 4.8 wt% on a dry-weight basis. Based on these experiments, a lower bound of 0.8 wt% or 8,000 μg/g (dry-weight basis) was selected as a minimum value needed to confirm that the tank originally contained ferrocyanide sludge (Meacham et al. 1995).

Based on nickel concentration, logic leads to one of two conclusions about a ferrocyanide tank: (1) The waste has a sufficiently high nickel concentration to conclude that it originally did contain ferrocyanide sludge. This confirms waste aging has occurred and additional sampling of ferrocyanide waste is not required. (2) The waste has a low nickel concentration; therefore, the tank has been erroneously identified as containing ferrocyanide waste, and the historical model will require reevaluation.

Figure 7. Ammonia Production During Hydrolysis of In Farm Simulant at pH 10 and 60 °C with an Applied Gamma Dose Rate of 4.5 x 10^4 rad/h.



The combined data for the total cyanide, energetics, and nickel analyses confirm that the ferrocyanide in the four C Farm tanks has aged. Table 9 shows the concentrations from recent sampling results (Kelly 1995, Sasaki 1995, Simpson et al. 1993a and 1993b) and the original concentrations indicated by process flowsheets and experiments (Jeppson and Wong 1993).

Table 9 shows that the average ferrocyanide concentrations in the four C Farm tanks' waste are at least a factor of ten less than the original concentrations. The nickel analyses (the ferrocyanide scavenging campaigns were the only source of high nickel concentrations) confirm that the ferrocyanide was once present.

The sample data have been evaluated using statistical techniques to confirm that ferrocyanide has degraded to SAFE levels. Two statistical techniques were used. The first consisted of an analysis of the waste layers and is described in Appendix A. This analysis tested the hypothesis that the waste layers had concentrations ≥ 8 wt% sodium nickel ferrocyanide, or ≤ 0.8 wt% nickel. The statistical evaluation concluded that the probability that the sodium nickel ferrocyanide concentration in the waste was ≥ 8 wt% for the layers in the four C Farm tanks is very low, ranging from 0.001 to 0.03. In addition, the probability that the nickel concentration in the waste was below 0.8 wt% was less than 0.2 for all layers with two exceptions. A review of these two exceptions concluded that the low nickel results are explained by the waste sample not being from the ferrocyanide sludge. The statistical evaluation in Appendix A also estimated the upper 95% confidence level ferrocyanide concentrations that are shown in Table 9.

An alternate statistical evaluation of the sample data is described in Appendix B. In this evaluation, the sample data were used to generate a model probability density function for sodium nickel ferrocyanide and nickel concentrations in the tanks' waste. From these distributions the probability that the sodium nickel ferrocyanide concentration in the waste exceeds 8 wt%, or that the nickel concentration is less than 0.8 wt% nickel, is calculated. The evaluation concluded that, for all four of the C Farm tanks, there is a very low probability ($< 1 \times 10^{-6}$) that the sodium nickel ferrocyanide concentration exceeds 8 wt%. In addition, there is a reasonable probability (above 0.96 for tanks C-109, C-111, and C-112, and 0.75 for C-109) that the tank waste has a nickel concentration above 0.8 wt%.

The large differences between the current measured ferrocyanide and the original concentrations confirm that the ferrocyanide sludges in these tanks have aged and can be categorized as SAFE.

5.5 CONCLUSION ON WASTE AGING

Based on tank histories and laboratory experiments with simulated ferrocyanide flowsheet materials, it has been shown that conditions existed within the tanks that would promote ferrocyanide aging. Caustic solutions, high temperature, and the presence of gamma radiation, all increase the hydrolysis rate of ferrocyanide ions.

It is likely that ferrocyanide was dissolved from sludge that contacted high pH evaporator or cladding wastes and was subsequently hydrolyzed. Modeling predicts that sludges not initially exposed could eventually contact caustic waste through convection (McGrail et al. 1993), thereby causing dissolution and aging.

Other experiments (Hallen 1996) indicate that aging also could occur in sludges that were never exposed to high pH wastes. These experimental results are consistent with analytical results from actual tank samples that show the expected amount of nickel but very low cyanide and energy content, verifying that aging occurred in the waste tanks.

6.0 MOISTURE RETENTION IN FERROCYANIDE SLUDGES

Physical-chemical properties and storage conditions both foster the retention of moisture in ferrocyanide sludge. Because moisture is an effective diluent in preventing reaction propagation for waste categorized as CONDITIONALLY SAFE, current levels of moisture in waste tanks have been estimated and an analysis performed to predict how much water could be lost as a result of various potential drying mechanisms.

The ferrocyanide sludge was formed by the precipitation of small particles in aqueous solution. After settling and consolidation into a sludge layer, moisture is retained by the following mechanisms:

- Interstitial liquid held by physical-chemical forces in the sludge
- Water held as hydrates in waste salts and caustic in waste
- Water bound in hydrous metal oxides found in sludge.

A high moisture concentration is confirmed by measurement on simulants and on real waste samples. The water content (free water plus bound water) of each of the ferrocyanide settled sludge simulants prepared according to the three flow sheets was greater than 45 wt%. In addition, the moisture contents of ferrocyanide tank waste samples (high-nickel-bearing sludges) are reported in Kelly (1995), Sasaki (1995), and Simpson et al. (1993a and 1993b) and range from a low of 16 wt% to a high of 57 wt%. The low moisture samples were always the lowest in energy content, indicating that other waste had mixed with the ferrocyanide layers during subsequent tank operations.

Table 9. Current Ferrocyanide and Nickel Concentrations Compared to Original Concentrations (Dry Basis).

Tank	Original $Na_2NiFe(CN)_6$ wt%, dry	Waste sludge layer[a]	Average $Na_2NiFe(CN)_6$ wt%, dry	$Na_2NiFe(CN)_6$ upper 95% confidence limit[b] wt%, dry	Original nickel wt%, dry	Average nickel wt%, dry
C-108	22.6	Top Bottom	1.1 0.3	5.2 1.0	3.5 - 4.2	1.0 2.9
C-109	22.6	1 2 3	1.4 1.6 0.7	1.9 2.8 1.0	3.5 - 4.2	1.0 3.9 3.2
C-111	22.6	1 2 3	0.04 0.05 0.02	2.1 2.1 2.1	3.5 - 4.2	2.5 4.3 2.0
C-112	25.5	1 2 3 4 5	1.3 1.2 1.2 1.5 1.5	2.5 4.0 3.2 4.0 4.0	3.2 - 4.7	1.0 3.7 2.6 3.9 3.7

Notes:

[a]Waste sludge layers are described in Appendix A.
[b]Statistical estimations are described in Appendix A.

6.1 MOISTURE RETENTION AND DRYOUT THEORY AND ANALYSIS

Experiments and theoretical calculations have been performed to help quantify the moisture content and moisture retention capability of stored waste sludges (Postma et al. 1994, Epstein et al. 1994). The results indicate that sludge may be viewed as a concentrated

aqueous suspension of fine precipitate particles produced from a dilute chemical suspension by gravitational settling. Sludge is a material similar to silty soil, mud, clay, or even toothpaste. In such suspensions, strong physical-chemical forces act between fluid and particles to hold these materials together. As such, force must be applied to expel liquid from the matrix of micrometer-sized sludge particles. Experiments (gravity drainage tests and centrifuge tests) have been performed to determine the stress-strain relationships (or consolidation curves) for ferrocyanide sludge simulants. This consolidation model was used as part of an analysis of potential drying mechanisms. The analysis is summarized below.

Various sludge dryout mechanisms have been analyzed to determine whether any could dry out ferrocyanide sludge and render it chemically reactive:

- Bulk heating of the entire sludge inventory to its boiling point
- Loss of liquid to the atmosphere via sludge surface evaporation
- Local drying by boiling in a hot-spot region
- Sludge drainage through a leak in the tank wall or by pumping drainable liquid from the tanks with a saltwell pumping system
- Local drying by evaporation from a warm segment of surface sludge.

These analyses are reported in Epstein et al. (1994) and are summarized below.

6.1.1 Drying by Draining

Based on tests performed on sludge simulants and on analysis using a consolidation model, water retention following drainage caused by either tank leaks or interim stabilization by saltwell pumping was evaluated. The evaluation concluded that sludge drainage in a waste tank would not dry waste below about 30 to 40 wt% water at the final equilibrium condition (Epstein et al. 1994). Such a minimum equilibrium would take many years to achieve.

6.1.2 Dryout by Waste Boiling

The potential for wastes in tanks containing ferrocyanide to heat up to boiling temperatures has been analyzed and shown to be impossible based on the following considerations (Epstein et al. 1994).

- The peak measured sludge temperatures (54 °C [129.2 °F] or less) are well below the boiling point (see Table 10).

- Historic temperature data show that sludge temperatures are slowly decreasing with time in a manner consistent with the decay of ^{137}Cs and ^{90}Sr, each with approximately 30-year half lives.

- The tank decay heat loads are low; the maximum is 3.0 kilowatts (kW) (10,000 Btu/h) in 241-BY-106 (see Table 10). These heat loads are distributed over a tank 23 meters (75 feet) in diameter, so heat fluxes are very low.

- Heat removal is entirely by the passive mechanisms of conduction through the sludge and soil and natural convection and radiation through the headspace. There is no forced coolant flow or any active cooling mechanism that could fail and thereby allow a rise in temperature.

- Evaporation of water is not required to remove the decay heat, and evaporation plays only a minor role in heat dissipation. Thermal analyses of selected tanks show good agreement with measured tank temperature profiles using an analytical model that neglected cooling by evaporation and included only conduction, natural convection, and radiation. Because the ferrocyanide tanks are not actively ventilated, the net evaporation and evaporative cooling are low. The upper-bound evaporation rate for tank 241-BY-106 of 480 kilograms per year (kg/yr) (1,050 pounds mass/yr) (discussed in the next section) would absorb 35 watts (120 Btu/h) of heat. This is only 1.2% of the total heat load.

6.1.3 Dryout by Evaporation

The net rate of evaporation of water from the waste surface will be limited by the rate at which air flowing out of the tank can remove moisture.

While the ferrocyanide tanks are not actively ventilated, they can exchange air with the outside through the riser pipes and high-efficiency particulate air (HEPA) filter by means of atmospheric pressure fluctuations, instrument air flow and by natural convection. The air in the tank has a temperature and water vapor composition different from that of the air outside, and as a result, the density of the tank atmosphere is less than that of the air outside. Thus, buoyancy forces may cause a flow of air out of the tank and a corresponding flow of air into the tank.

These moisture loss rates have been analyzed in Epstein et al. (1994). The results indicate that the evaporation rate caused by tank breathing is very small, on the order of 0.005% of the sludge water content per year, while the evaporation rate from natural convection is 0.04% per year. The water loss rates were calculated for each ferrocyanide tank and are shown in Table 11. The evaporation rates range from 160 to 500 kg (350 to 1,100 lb) of water per year. The fraction of the total water present that is evaporated per year ranges from 0.0003 to 0.0033, with the highest rate in 241-C-109. These rates of water loss are much lower than the rate of decay of the tank heat generation, which is 0.023 per year for

^{137}Cs and ^{90}Sr. Thus, the tanks are losing their heat source much faster than they are losing water by evaporation. It is concluded that it is extremely unlikely that ferrocyanide waste can be dried out to below about 24 wt% water by surface evaporation during passive ventilation.

Table 10. Thermal Characteristics of Ferrocyanide Tanks.

Tank	Depth of solids[a] (meters)	Maximum temperature[b] (°C)	Estimate of heat load	
			kW[c]	Watts/meter^3
241-BY-103	3.9	28	1.6	1.0
241-BY-104	3.9	54	2.6	1.5
241-BY-105	4.8	50	2.6	1.2
241-BY-106	6.1	54	3.0	1.1
241-BY-107	2.7	35	2.6	2.3
241-BY-108	2.3	43	2.7	2.8
241-BY-110	3.9	48	2.0	1.2
241-BY-111	4.4	30	1.6	0.8
241-BY-112	2.9	32	1.8	1.5
241-C-108	0.8	22	1.8	6.4
241-C-109	0.8	26	2.1	7.9
241-C-111	0.7	21	1.9	7.9
241-C-112	1.2	26	2.2	5.0
241-T-107	1.8	18	0.9	1.2
241-TX-118	3.4	25	1.3	0.9
241-TY-101	1.3	18	0.9	1.8
241-TY-103	1.7	16	1.2	1.7
241-TY-104	0.6	17	0.9	4.9

Notes:

[a]Grigsby et al. (1992)
[b]Hanlon (1993)
[c]Crowe et al. (1993)

6.1.4 Local Drying by Boiling Caused by a Hot Spot

This mechanism would require that the heat-generating material become highly concentrated in a hot spot, sufficient to raise the temperature of some local region above the boiling point of the sludge liquid, and that this event actually results in dryout of a significant volume of sludge.

If these conditions could be met, such a hot spot would be highly significant to ferrocyanide tank safety. A hot spot capable of heating some volume above the boiling point (120 °C [250 °F]) might also heat the center of the dry volume to the ignition temperature (about 250 °C [480 °F]). Furthermore, the dry region would be at an elevated temperature (120 to 250 °C [250 to 480 °F]), and propagation might occur with lower fuel concentrations than were measured in tests with initial temperatures of 25 °C to 60 °C (77 °F to 140 °F). Chemical reactivity could also be increased by removal of bound water at these elevated temperatures. Thus, such a hot spot might act as a common-mode initiator of dry fuel, ignition temperature, and reactivity at lower ferrocyanide concentrations.

Such an event, however, is ruled out because any one of the following three analysis conclusions render dryout of sludge caused by temperatures above boiling to be impossible (Epstein et al. 1994).

- Analysis based primarily on conduction heat transfer shows that the concentration of heat generators required, or the fraction of the total tank heat load that must be placed in the hot spot, to heat even a single point to 120 °C (250 °F) is too large to be credible (see Figure 8). This argument is independent of sludge rheology and of data from simulants.

- Experiments have shown that the rheology of the sludge is such that steam formation would push aside the sludge and form a bubble of pure steam without expelling the liquid from the solid sludge constituents. Furthermore, the expansion from steam formation would move the heat-generating sludge into a more coolable geometry and would thus tend to be self-limiting; bubble formation reduces the hot spot density.

- Rheology experiments have shown that when ferrocyanide sludge is heated locally to boiling at high heat flux, a network of cracks develops that provides cooling by convection of liquid and steam and limits local temperatures to the boiling point. There is no local dryout.

Local Surface Evaporation. Evaporation of water from warmer regions of the waste surface (e.g., above a hot spot) and condensation on cooler portions of the surface is another postulated mechanism of locally removing the water content from ferrocyanide sludge.

However, experimental work and analyses reported in Epstein et al. (1994) show that waste material suspensions cannot dry out in this manner, because the liquid return flow induced by sludge shrinkage that results from consolidation is capable of keeping the evaporation surface wet.

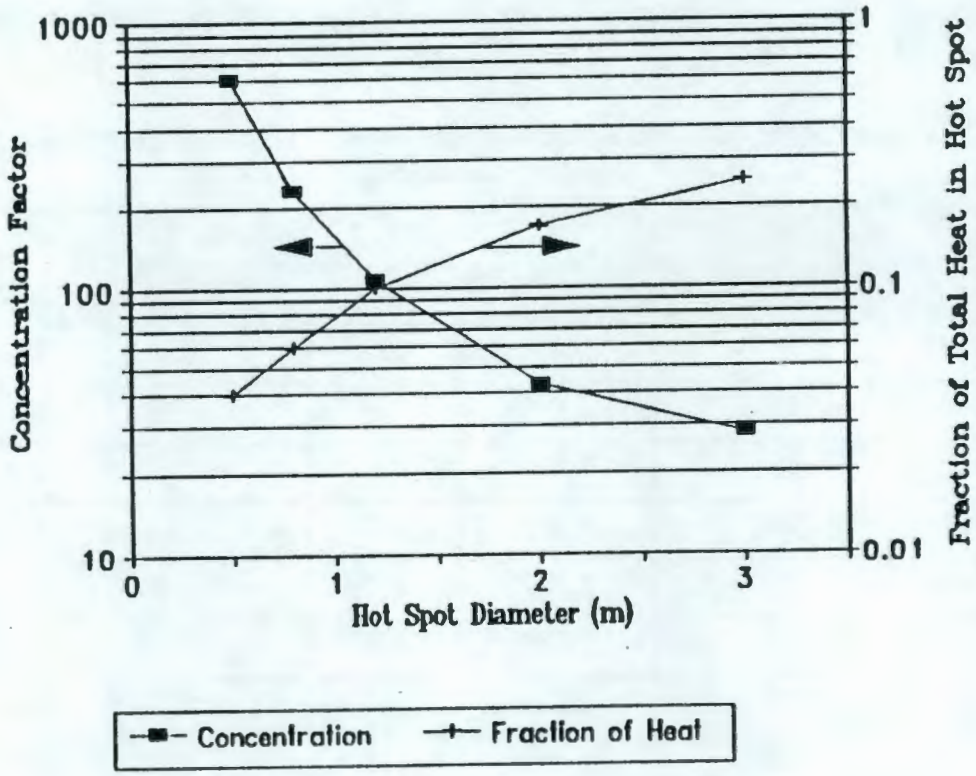
Table 11. Rate of Water Loss from Ferrocyanide Tanks Caused by Evaporation During Passive Ventilation.

Tank	Gas temperature[a] (°C)	Gas volume[b] (m^3)	Rate of Water Loss[c]		
			kg/yr	$kg/m^2/yr$	Fraction/yr
241-BY-103	21	2,420	223	0.55	2.6 E-04
241-BY-104	26	2,640	429	1.05	4.7 E-04
241-BY-105	26	2,110	403	0.98	5.9 E-04
241-BY-106	27	1,460	483	1.18	4.1 E-04
241-BY-107	26	2,920	460	1.12	8.2 E-04
241-BY-108	27	3,080	496	1.21	6.8 E-04
241-BY-110	23	2,870	305	0.74	3.8 E-04
241-BY-111	21	2,290	216	0.53	8.0 E-04
241-BY-112	22	2,810	264	0.64	24.0 E-04
241-C-108	23	3,050	361	0.88	20.3 E-04
241-C-109	24	3,060	453	1.10	32.8 E-04
241-C-111	23	3,080	396	0.97	25.7 E-04
241-C-112	25	2,910	490	1.19	20.8 E-04
241-T-107	18	2,610	203	0.50	4.8 E-04
241-TX-118	20	2,830	223	0.54	14.0 E-04
241-TY-101	18	3,480	218	0.53	6.8 E-04
241-TY-103	19	3,320	258	0.63	4.8 E-04
241-TY-104	18	3,530	216	0.53	14.0 E-04

Notes:

[a]Crowe et al. (1993)
[b]Klem (1991)
[c]Based on conservative assumptions. Actual water loss is probably less.

Figure 8. Requirements for Dryout (120 °C [248 °F])(Epstein et al. 1994).



The experiments subjected sludge materials to immersed heaters, and moisture and temperature gradients produced were observed. The temperature and moisture remained very uniform throughout the sludge, indicating that local dryout in waste tank sludges is not credible. Water contained in surrounding sludge quickly replenishes any water lost at a locally heated waste surface area.

6.2 CONCLUSION OF DRYOUT ASSESSMENT

Based on the analysis, it was concluded that global loss of water from bulk heating of the sludge to its boiling point or from surface evaporation and vapor transport to the outside air is not credible. In addition, the analysis concluded that the formation of a dry local or global regions of sludge as a result of tank leakage (draining of interstitial liquid) is not possible. Finally, it was concluded that formation of dry local regions in the ferrocyanide sludge by local hot spots or warm surface regions is not possible.

As a result of a rather extensive laboratory program and present knowledge of water migration and water retention behavior in sludge-like materials (concentrated suspensions of fine particles), it has been concluded that none of these postulated mechanisms are credible to reduce the sludge moisture content sufficiently to render it reactive.

This conclusion, that local or global dryout is beyond extremely unlikely, is substantiated by four decades of waste storage history during which sludge temperatures have gradually decreased or are now essentially constant and the sludge moisture content has been retained. Current measurements from ferrocyanide sludge waste samples show a consistently high moisture content.

7.0 FERROCYANIDE WASTES HAZARD POTENTIAL AND ACCIDENT FREQUENCY

Based on conservative estimates of the maximum expected ferrocyanide concentration, and analysis and experiments for water retention, the ferrocyanide wastes have been compared to the safety criteria and categorized as shown in Table 3. As indicated, all ferrocyanide wastes meet SAFE or CONDITIONALLY SAFE criteria as summarized below.

7.1 TANKS CONTAINING IN FARM SLUDGE

The four tanks containing the highest projected ferrocyanide concentrations (241-C-108, C-109, C-111, and C-112) are put into the SAFE category on the basis of sample data for all four tanks. Multiple core and auger samples, taken from opposite tank quadrants, were divided into vertical subsegments. Statistical evaluations of the sample results are described in Appendixes A and B and summarized in Table 9. The statistical analysis in Appendix A concludes that the 95% confidence level estimate for fuel is no higher than 5.2 wt%, on a dry weight basis. This is below the 8 wt% criterion for SAFE waste; therefore, the wastes in the four C Farm ferrocyanide tanks are categorized as SAFE.

Appendix B treats the same sample data from the four C Farm tanks in a slightly different manner, but also concludes that there is a very low probability ($< 1 \times 10^{-6}$) that the ferrocyanide exceeds 8 wt%.

7.2 TANKS CONTAINING U PLANT SLUDGE

Until analytical analyses are completed on selected BY Farm tanks, all of the tanks with U Plant sludge (Table 3) were conservatively assumed to contain ferrocyanide at the original concentrations, which are greater than 8 wt%. This judgment is based on the U Plant 2 bottom fraction simulant sludge, which, as indicated in Table 3, contained 8.3 wt% $Na_2NiFe(CN)_6$. This approach is conservative, because actual waste is expected to have aged to lower ferrocyanide concentrations.

According to ferrocyanide safety criteria, ferrocyanide sludge with concentrations >8 wt%, temperature and water content criteria must be met. The highest measured temperature in any ferrocyanide tank is 54 °C (129.2 °F) (Table 11). This is well below the temperature criterion of 90 °C (194 °F).

Although moisture concentrations in most U Plant tanks have not been measured, experiments and analyses of waste simulants lead to the conclusion that ferrocyanide sludge has a moisture content greater than the criterion. The conservatively estimated 8.3 wt% ferrocyanide would require minimal moisture to remain CONDITIONALLY SAFE. The minimum criterion value for the free moisture content required at the 8.3 wt% level can be obtained from Figure 3 or calculated as follows:

$$\text{moisture limit} = \frac{(8.3 - 8.0)(24)}{(26 - 8)} = 0.4 \text{ wt\%}.$$

This moisture concentration is small compared to values that are retained in sludges, and is even small compared to waste moisture if it is in equilibrium with ambient air (Epstein et al. 1994, Postma et al. 1994), and it is concluded that actual moisture levels will exceed this low requirement. Therefore, all tanks containing U-Plant sludge are currently categorized as CONDITIONALLY SAFE.

Note that the ferrocyanide concentrations based on process records are all lower than the 8 wt% criterion. These estimated concentrations are judged to overestimate actual concentrations, and confirmatory data from tank samples would likely put the tanks into the SAFE category.

7.3 TANKS CONTAINING T PLANT SLUDGE

The three tanks containing T Plant sludge (Table 3) have been put into the CONDITIONALLY SAFE category. Reasons for this assignment parallel those discussed above for U Plant sludge and are briefly restated as follows (Postma et al. 1994).

- The maximum simulant ferrocyanide concentration is 8.8 wt%, which is just slightly higher than the 8 wt% criterion, so the SAFE category is not applicable.

- The maximum process record model for the tanks' original ferrocyanide concentration is 10.7 wt%, which is higher than the 8 wt% criterion also.

- A moisture concentration of only 1.1 wt% is required at the 8.8 wt% $Na_2NiFe(CN)_6$ level, and 3.6 wt% at the 10.7 wt% level, to meet the moisture criterion. Experiments and analyses on moisture retention provide a high level of confidence that actual moisture concentrations are well above the 3.6 wt% criterion.

- Ferrocyanide concentrations measured in samples taken from two tanks (241-TY-101 and 241-TY-103) fall in the range 1.0 to 1.4 wt%. These values apply to composited samples of entire cores and therefore may not represent maximum concentrations in the sludge layer. The sample data do not meet the quarter-segment analysis called for in the data quality objectives protocol (Meacham et al. 1995) and therefore are insufficient to categorize the tanks as SAFE.

- The low measured concentrations of ferrocyanide in sampled tanks provide evidence that the tanks can be put into the SAFE category after confirmatory sample data are obtained.

7.4 HAZARD POTENTIAL AND ACCIDENT FREQUENCY CONCLUSIONS

The ferrocyanide wastes for all ferrocyanide Watch List tanks meet either SAFE or CONDITIONALLY SAFE criteria and therefore cannot support a sustained rapid exothermic (propagating) reaction. Ferrocyanide wastes meet these criteria through inherent waste properties; that is, without any reliance on active waste management such as temperature management/control as recapped below.

7.4.1 Temperature Control

The waste temperatures in ferrocyanide tanks are well below temperatures of concern relative to ferrocyanide exothermic reaction accident considerations. These low temperatures are maintained through passive means. For the following reasons, it is not credible for temperatures of concern to be reached.

- Decay heat loads are estimated to be 3.0 kW (10,000 Btu/h) or less for the 23-meter (75-foot) diameter tanks.

- Decay heat loads have been dissipated passively during four decades of storage history during which temperatures have trended downward or remained constant.

- Heat loss occurs by conduction, convection, and radiation. There are no active systems that can fail. Heat dissipation does not depend on evaporation of water.

- Significant changes in waste storage configuration (the filling of headspace with insulating materials or increasing soil overburden) would be required to significantly diminish heat dissipation capabilities. Such changes would not be permitted without additional analysis and are beyond the scope of this analysis.

This conclusion, that the ferrocyanide sludges pose no propagating reaction hazard and that ferrocyanide accidents are beyond extremely unlikely, does not credit or rely on control of waste temperatures, and therefore no temperature control is required.

7.4.2 Waste Moisture Control

Ferrocyanide accidents are ruled out for waste that meets the SAFE criteria with no credit or reliance on the free water content of the waste. Waste moisture for CONDITIONALLY SAFE ferrocyanide wastes is maintained by inherent physical-chemical properties and passive storage conditions. There is no reliance on active waste management controls to maintain waste moisture for these tanks. Therefore, no control for moisture is required.

Therefore, it is concluded that the potential hazard and postulated accident of initiating and sustaining a rapid exothermic reaction is not credible.

8.0 SAFETY CONCLUSIONS AND REQUIRED CONTROLS

The above analysis shows that all ferrocyanide wastes in the Hanford Site underground storage tanks meet SAFE or CONDITIONALLY SAFE criteria. These wastes cannot support a sustained, rapid exothermic (propagating) reaction. Ferrocyanide wastes meet these criteria through inherent waste properties; that is, without any reliance on active waste management. Therefore, no controls are required.

8.1 KEY ASSUMPTIONS

A key assumption in this analysis is that the tank ventilation configuration is a passive breather system. Moisture loss rates and the minimum equilibrium waste moisture that could be attained under long-term active (forced) ventilation have not been determined. Therefore, modification of the ventilation systems to a forced (active) ventilation configuration would require additional analysis for tanks that contain waste categorized as CONDITIONALLY SAFE.

9.0 REFERENCES

Agnew, S. F., 1995, *Hanford Defined Wastes: Chemical and Radionuclide Compositions*, LA-UR-94-2657, Rev. 2, Los Alamos National Laboratory, Los Alamos, New Mexico.

Anderson, J. D., 1990, *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington.

Anttonen, J. H., 1993, *Resolution of Unreviewed Safety Question (USQ) for Four Ferrocyanide Tanks*, (letter 9304645B/93-CAB-223 to T. M. Anderson, President, Westinghouse Hanford Company, July 9), U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Babad, H., J. E. Meacham, B. C. Simpson, and R. J. Cash, 1993, *The Role of Aging in Resolving the Ferrocyanide Safety Issue*, WHC-EP-0599, Westinghouse Hanford Company, Richland, Washington.

Bácskai, K. M., E. Czirók, G. Inzelt, P. J. Kulesza, and M. A. Malik, 1995, "Polynuclear Nickel Hexacyanoferrates: Monitoring of Film Growth and Hydrated Counter-Cation Flux/Storage During Redox Reactions," *J. Electroanal. Chem.*, vol. 385, pp. 241-248.

Borsheim, G. L., and R. J. Cash, 1991, *Unusual Occurrence - Addition of Two Tanks to List of Unreviewed Safety Question Tanks Containing Ferrocyanide*, WHC-91-0096-TFARM, February 13, Westinghouse Hanford Company, Richland, Washington.

Borsheim, G. L., and B. C. Simpson, 1991, *An Assessment of the Inventories of the Ferrocyanide Watch List Tanks*, WHC-SD-WM-ER-133, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Box, H. C., K. T. Lilga, and E. E. Budzinski, 1977, "Radiation-Induced Oxidation and Reduction of Iron-Cyanide Complexes," *J. Chem. Phys.*, vol. 66, pp. 2135-2138.

Brevick, C. H., 1995a, *Historical Tank Contents Estimates for the Northeast Quadrant of the Hanford 200 East Areas*, WHC-SD-WM-ER-349, Rev. 0A, March 1995, Westinghouse Hanford Company, Richland, Washington.

Brevick, C. H., 1995b, *Historical Tank Contents Estimates for the Northwest Quadrant of the Hanford 200 West Area*, WHC-SD-WM-ER-351, Rev. 0, March 1995, Westinghouse Hanford Company, Richland, Washington.

DOE, 1987, *Final Environmental Impact Statement - Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes*, Vols. 1-5, DOE/EIS-0113, U.S. Department of Energy, Washington, D.C.

Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, *Ferrocyanide Safety Program: Estimate of Heat Load in Waste Tanks Using Average Vapor Space Temperature*, WHC-EP-0709, Westinghouse Hanford Company, Richland, Washington.

Deaton, D. E., *Unusual Occurrence - Unreviewed Safety Questions Regarding Tanks Containing Ferrocyanide*, WHC-90-B003-R1, Update 10-22-90, Westinghouse Hanford Company, Richland, Washington.

Epstein, M., H. K. Fauske, D. R. Dickinson, M. D. Crippen, J. D. McCormack, R. J. Cash, J. E. Meacham, and C. S. Simmons, 1994, *Ferrocyanide Safety Program: An Assessment of the Possibility of Ferrocyanide Sludge Dryout*, WHC-EP-0816, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1992, *Adiabatic Calorimetry and Reaction Propagation Tests with Synthetic Ferrocyanide Materials Including U Plant 1, U Plant 2, In Farm 1, In Farm 2, and Vendor-Procured Sodium Nickel Ferrocyanide*, WHC-SD-WM-RDT-054, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., 1993, *Adiabatic Calorimetry (RSST and VSP) Tests with Synthetic T Plant Flow Sheet Material*, (letter to R. J. Cash, Westinghouse Hanford Company, July 28), Fauske and Associates, Inc., Burr Ridge, Illinois.

Fauske, H. K., M. Epstein, D. R. Dickinson, R. J. Cash, D. A. Turner, and J. E. Meacham, 1995, *The Contact-Temperature Ignition (CTI) Criteria for Propagating Chemical Reactions Including the Effect of Moisture and Application to Hanford Waste*, WHC-SD-WM-ER-496, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Fauske, H. K., and J. C. Leung, 1985, "New Experimental Techniques for Characterizing Runaway Chemical Reactions," *Chemical Engineering Progress*, vol. 81, p. 39 (August).

FR, 1990, "Implementation Plan for Recommendation 90-3 at the Department of Energy's Hanford Site, Washington," *Federal Register*, Defense Nuclear Facilities Safety Board Recommendation 90-7, Vol. 55, No. 202, pp. 42243-42244.

GE, 1958, *Record of Scavenged TBP Waste*, General Electric Company, Richland, Washington.

Gerton, R. E., 1994, *Environmental Assessment (EA) and Finding of No Significant Impact (FONSI) for the Waste Tank Safety Program at the Hanford Site*, (DOE/EA-0915), (letter 9402034B/94-SST-053 to President, Westinghouse Hanford Company, March 8), U.S. Department of Energy, Richland, Washington.

Grigsby, J. M., D. B. Bechtold, G. L. Borsheim, M. D. Crippen, D. R. Dickinson, G. L. Fox, D. W. Jeppson, M. Kummerer, J. M. McLaren, J. D. McCormack, A. Padilla, B. C. Simpson, and D. D. Stepnewski, 1992, *Ferrocyanide Waste Tank Hazard Assessment--Interim Report*, WHC-SD-WM-RPT-032, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Grumbly, T. P., 1993, *Strategy for [Ferrocyanide] Safety Issue Resolution*, (letter to J. T. Conway, Chairman, Defense Nuclear Facilities Safety Board, August 25), U.S. Department of Energy, Washington, D.C.

Hallen, R. T., 1996, *Ferrocyanide Safety Project - December Monthly Report*, (letter to R. J. Cash, Westinghouse Hanford Company, January 15), Pacific Northwest National Laboratory, Richland, Washington.

Hanlon, B. M., 1993, *Tank Farm Surveillance and Waste Tank Summary Report for June 1993*, WHC-EP-0182-63, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Harmon, H. D., 1991, *Safety Measures for Waste Tanks at Hanford Site, Richland, Washington*, (letter 9059124.1 to R. E. Gerton, DOE-RL, February 8), Westinghouse Hanford Company, Richland, Washington.

Hughes, G. and C. Willis, 1962, "The Radiolysis of Ferro- and Ferri-cyanide Solutions," *J. Chem. Soc.*, 4848-4853.

Jeppson, D. W., and J. J. Wong, 1993, *Ferrocyanide Waste Simulant Characterization*, WHC-EP-0631, Westinghouse Hanford Company, Richland, Washington.

Jeppson, D. W., and B. C. Simpson, 1994, *Characterization and Reaction Behavior of Ferrocyanide Simulants of Hanford Site High-Level Ferrocyanide Waste*, WHC-SA-2190-FP, Westinghouse Hanford Company, Richland, Washington.

Jungfleisch, F. M., 1984, *TRAC: A Preliminary Estimation of the Waste Inventories in Hanford Tanks through 1980*, WHC-SD-WM-TI-057, Rockwell Hanford Operations, Richland, Washington.

Kelly, S. E., 1995, *Tank Characterization Report for Single-Shell Tank 241-C-111*, WHC-SD-WM-ER-475, Rev. 0-B, Westinghouse Hanford Company, Richland, Washington.

Klem, M. J., 1991, *Vapor Space Sampling Criteria for Single-Shell Tanks Containing Ferrocyanide Waste*, WHC-EP-0424, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Kuhn, A. and C. Rice, 1977, "Alkaline Hydrolysis of Cyanates, and Dicyan," *Oberflache-Surface*, vol. 18, pp. 119-123.

Lewis, R. J., Sr., 1992, *Sax's Dangerous Properties of Industrial Materials*, Van Nostrand Reinhold, New York, New York.

Lilga, M. A., M. R. Lumetta, and G. F. Schiefelbein, 1993, *Ferrocyanide Safety Project, Task 3: Ferrocyanide Aging Studies - FY 1993 Annual Report*, PNL-8888, Pacific Northwest Laboratory, Richland, Washington.

Lilga, M. A., E. V. Alderson, D. J. Kowalski, M. R. Lumetta, and G. F. Schiefelbein, 1994, *Ferrocyanide Safety Project, Task 3: Ferrocyanide Aging Studies - FY 1994 Annual Report*, PNL-10126, Pacific Northwest Laboratory, Richland, Washington.

Lilga, M. A., E. V. Alderson, R. T. Hallen, M. O. Hogan, T. L. Hubler, G. L. Jones, D. J. Kowalski, M. R. Lumetta, G. F. Schiefelbein, and M. R. Telander, 1995, *Ferrocyanide Safety Project: Ferrocyanide Aging Studies - FY 1995 Annual Report*, PNL-10713, Pacific Northwest Laboratory, Richland, Washington.

MacDiarmid, A. G. and N. F. Hall, 1953, "Illumination-pH Effects in Solutions of Complex Cyanides," *J. Amer. Chem. Soc.*, vol. 75, pp. 5204-5207.

Masri, E. and M. Haissinsky, 1963, "Radiolytic Transformations. Gamma-Radiolysis of Potassium Ferro- and Ferricyanide Solutions," *J. Chim. Phys.*, vol. 60, pp. 397-401.

McGrail, B. P., D. S. Trent, G. Terrones, J. D. Hudson, and T. E. Michener, 1993, *Computational Analysis of Fluid Flow and Zonal Deposition in Ferrocyanide Single-Shell Tanks*, PNL-8876, Pacific Northwest Laboratory, Richland, Washington.

Meacham, J. E., 1995, *Test Plan for Samples from Hanford Waste Tanks 241-BY-103, BY-104, BY-105, BY-106, BY-108, BY-110, TY-103, U-105, U-107, U-108, and U-109*, WHC-SD-WM-TP-378, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Meacham, J. E., R. J. Cash, B. A. Pulsipher and G. Chen, 1995, *Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives Process*, WHC-SD-WM-DQO-007, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Nguyen, D. M., 1989, *Data Analysis of Conditions in Single-Shell Tanks Suspected of Containing Ferrocyanide*, (internal memorandum 13314-89-025 to N. W. Kirch, March 2), Westinghouse Hanford Company, Richland, Washington.

Ohno, S. and E. Tsuchihasi, 1965, "The Photochemistry of Hexacyanoferrate(II) Ions in Aqueous Solutions," *Bull. Chem. Soc. Japan*, vol. 38, pp. 1052-1053.

O'Leary, H. R., 1994, *[Transmittal of "Program Plan for Evaluation of the Ferrocyanide Waste Tank Safety issue at the Hanford Site," DOE/RL-94-110]*, (letter to J. T. Conway, Chairman, Defense Nuclear Facilities Safety Board, December 2), U.S. Department of Energy, Washington, D.C.

Parra, S. A., 1994, *Integrated Beta and Gamma Radiation Dose Calculations for Ferrocyanide Waste Tanks*, WHC-SD-WM-TI-634, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Peach, J. D., 1990, *Consequences of Explosion of Hanford's Single-Shell Tanks are Understood*, (letter B-241479 to C. N. Synar, Chairman of Environment, Energy and Natural Resources Subcommittee, Committee on Government Operations, House of Representatives, October 10), GAO/RCED-91-34, General Accounting Office, Washington, D.C.

Postma, A. K., J. E. Meacham, G. S. Barney, G. L. Borsheim, R. J. Cash, M. D. Crippen, D. R. Dickinson, J. M. Grigsby, D. W. Jeppson, M. Kummerer, J. M. McLaren, C. S. Simmons, and B. C. Simpson, 1994, *Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks*, WHC-EP-0691, Westinghouse Hanford Company, Richland, Washington.

Public Law 101-510, Section 3137, 1990, *Safety Measures for Waste Tanks at Hanford Nuclear Reservation*, U.S. Congress, Washington, D.C. [Also referred to as the Wyden Amendment]

RHO, 1986, *Single-Shell Tank Isolation Safety Analysis Report*, SD-WM-SAR-006, Rev. 2, Rockwell Hanford Operations, Richland, Washington.

Robuck, S. J., and R. G. Luthy, 1989, "Destruction of Iron-Complexed Cyanide by Alkaline Hydrolysis," *Wat. Sci. Tech.*, vol. 21, pp. 547-558.

Sasaki, L. M., 1995, *Tank Characterization Report for Single Shell Tank 241-C-108*, WHC-SD-WM-ER-503, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Sheridan, T. R., 1994a, *Closure of the Ferrocyanide Unreviewed Safety Question*, (letter 9401180/94-SST-052 to A. L. Trego, President, Westinghouse Hanford Company, March 4), U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Sheridan, T. R., 1994b, *Approval to Remove Two Ferrocyanide Tanks, 241-BX-102 and 241-BX-106, from the Watch List*, (letter 9406684/94-SST-205 to A. L. Trego, President, Westinghouse Hanford Company, November 17), U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Data Report: Tank 241-C-112,* WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Washington.

Smith, D. A., 1986, *Single-Shell Tank Isolation Safety Analysis Report*, WHC-SD-WM-SAR-006, Rev. 2, Westinghouse Hanford Company, Richland, Washington.

Watkins, J. D., 1991, *Report to United States Congress on Waste Tank Safety Issues at the Hanford Site*, (letter to D. Quayle, President of the Senate, July 16), U.S. Department of Energy, Washington, D.C.

WHC, 1990, *Operating Specifications for Watch List Tanks*, OSD-T-151-00030, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

WHC, 1996, *Operating Specifications for Watch List Tanks*, OSD-T-151-00030, Rev. B-16, Westinghouse Hanford Company, Richland, Washington.

Winters, W. I., 1988, *Analysis of Archive Samples from Tanks 241-TY-101 and 241-TY-103 for Total Cyanide* (internal memo 12715-ASL88-067 to D. M. Nguyen, December 29), Westinghouse Hanford Company, Richland, Washington).

Wodrich, D. D., G. S. Barney, G. L. Borsheim, D. L. Becker, W. C. Carlos, M. J. Klem, R. E. Van der Cook, and J. L. Ryan, 1992, *Summary of Single-Shell Waste Tank Stability*, WHC-EP-0347, Supplement, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

STATISTICAL ANALYSIS OF FUEL AND NICKEL CONCENTRATIONS

This page intentionally left blank.

APPENDIX A

STATISTICAL ANALYSIS OF FUEL AND NICKEL CONCENTRATIONS

A.1 BACKGROUND

All four of the C Farm tanks (241-C-108, C-109, C-111, and C-112) received waste from the In Farm process flowsheet (Borsheim and Simpson 1991). During scavenging, aqueous waste was pumped to process tanks where precipitating agents were added. The slurry was then transferred to an underground storage tank for settling of the solids and disposal of the supernatant liquid to the ground. The precipitated solids formed layers of ferrocyanide sludge. The statistics in this appendix are applied to 12-cm layers of sludge.

Experiments on waste simulants indicate that ferrocyanide is not a hazard in Hanford Site tanks because of aging (Babad et al. 1993, Lilga et al. 1993, 1994, and 1995). As part of resolution of the Ferrocyanide Safety Issue, aging is being confirmed via sampling of selected ferrocyanide tanks. This appendix examines the statistical confidence derived from the data for the four ferrocyanide C Farm tanks.

Data on fuel and nickel concentrations are necessary to confirm aging (Meacham et al. 1995). Fuel measurements allow a comparison of the original and current ferrocyanide concentrations. Nickel is a signature analyte of the nickel ferrocyanide scavenging campaigns, the only source of high nickel concentrations. Nickel measurements confirm that the waste once contained high concentrations of ferrocyanide.

The four ferrocyanide C Farm tanks have been sampled and analyzed. Two augers were taken from C-108, three push cores were taken from C-109, one auger was taken from C-111, and two push cores were taken from C-112 (Sasaki 1995, Simpson et al. 1993b, Kelly 1995, Simpson et al. 1993a). The approximate location of the subsegments analyzed are shown in Figure A-1.

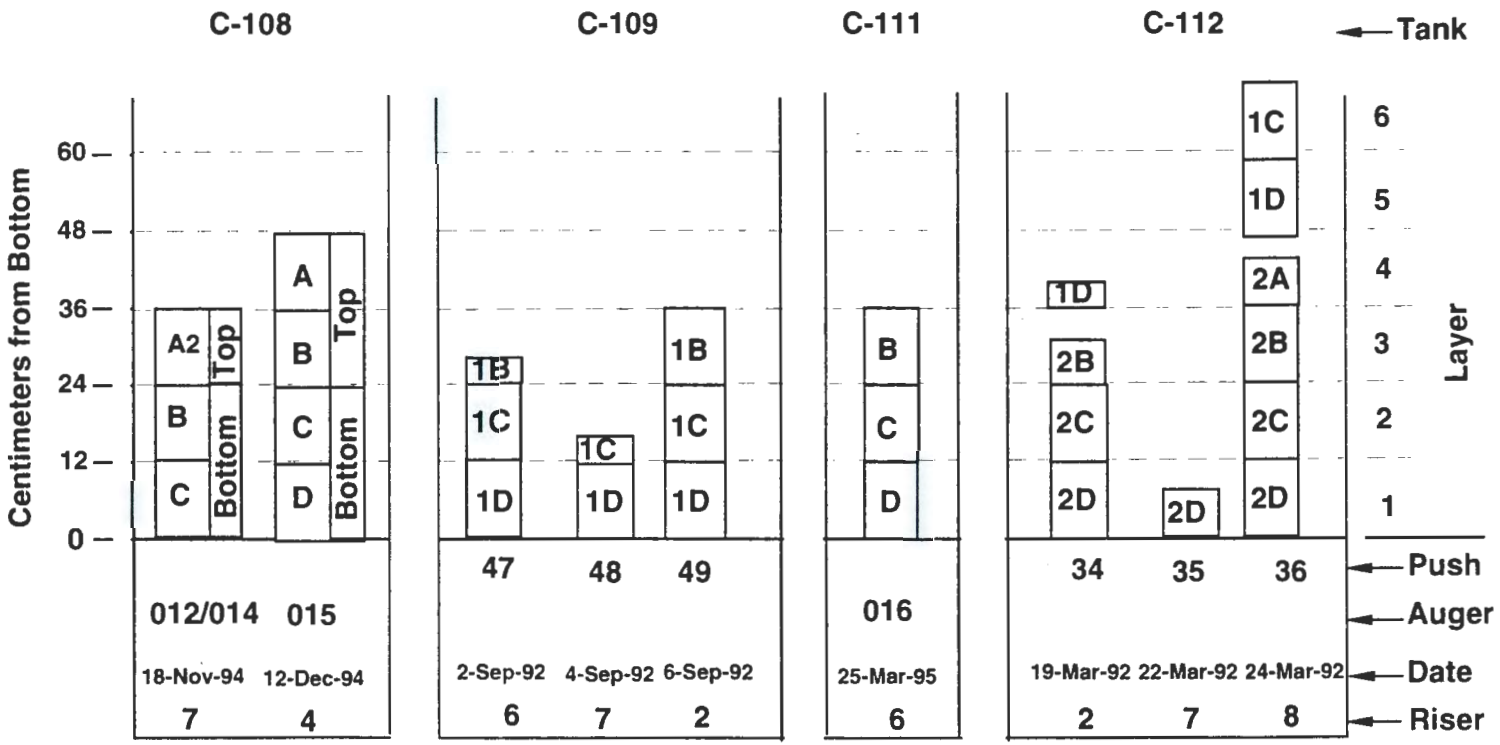


Figure A-1. Approximate Elevations of Quarter Segment Samples From Tanks C-108, C-109, C-111, and C-112.

A.2 STATISTICAL TESTS

From the ferrocyanide Data Quality Objectives document (Meacham et al. 1995), two questions must be answered to resolve the Ferrocyanide Safety Issue:

(1) Does the waste contain a fuel concentration less than 8 wt% $Na_2NiFe(CN)_6$? If so, then proceed to nickel analyses to confirm the historical and aging models.

(2) Does the waste have a sufficiently high nickel concentration (> 0.8 wt%) to conclude that it originally did contain ferrocyanide sludge? If so, waste aging is confirmed and the tank is categorized as SAFE.

A statistical analysis was used to address these questions. In both cases it was assumed (null hypothesis) that the opposite condition was true (i.e., fuel concentration $\geq$ 8%, nickel concentration $\leq$ 0.8%). A one-sided t-test was run with the index of importance being the resulting p-value, or probability of seeing the resulting t-statistic if the sampling results had been taken from a layer with average contents equal to the null hypothesis value. In addition, a one-sided confidence interval on the layer average was calculated, indicating what range of values the true layer average content is probably within.

Several steps were necessary to use the raw data (see Section A.3) for the t-statistic test on fuel and nickel concentrations:

(1) Duplicate moisture measurements were averaged for each subsegment

(2) Total cyanide and nickel measurements were converted to a dry basis by dividing by the average moisture concentration

$$\text{wt\% dry} = (100 \times \text{wet wt\%}) / (100 - \text{\% water})$$

(3) μg/g measurements were converted to wt% by dividing by 10,000

(4) Total cyanide (CN) concentrations were converted to sodium nickel ferrocyanide concentrations [molecular weight of $Na_2NiFe(CN)_6$ = 316.64, $(CN)_6$ = 156.11]

$$Na_2NiFe(CN)_6 = (316.64/156.11) \times CN$$

(5) The layer each subsegment represents was identified (Figure A-1)

(6) Simple summary statistics (mean, standard deviation, relative standard deviation, and standard error of the mean) were calculated for layers in each tank

(7) A statistical hypothesis test was run against the null hypothesis for each layer in a tank using a one-sided t-test

(8) A one-sided confidence interval was estimated for each layer in a tank. For $Na^2NiFe(CN)_6$ a 95% upper limit was used. For nickel, an 80% lower limit was used as required by the Data Quality Objectives (Meacham et al. 1995).

A.3 TANK DATA

Each subsegment is typically a quarter-segment and represents about 12 cm. Exceptions to this are the total cyanide analyses for tank C-108, where the cyanide analyses were done on composites of quarter-segments and represent a 24-cm (half-segment) layer. Total cyanide, nickel, and moisture data used in the analyses are shown in Tables A-1 through A-4.

The appropriate moisture is the average of the subsegment duplicates (because duplicate number is not a meaningful commonality identifier across these analytical samples). In addition, for C-108, further averaging was done over the subsegment samples that were used to make the half-segments that cyanide was measured on, because no moisture measurements were made on these half-segments (see Figure A-1).

Table A-1. Cyanide, Nickel, and Moisture Data for C-108 (Sasaki 1995).

Auger	Subsegment	Cyanide (μg/g)		Nickel (wt%)		Water (wt%)
		Sample	Duplicate	Sample	Duplicate	
AUG-012	Top	795	766	0.225	0.182	16.5
AUG-014	Bottom	4990	5100	2.189	2.615	41.0
AUG-015	Top	1010	1050	2.058	1.889	49.4
	Bottom	1030	1120	1.902	1.715	50.6

Table A-2. Cyanide, Nickel, and Moisture Data for C-109 (Simpson et al. 1993b, Scheele 1995).

Core	Subsegment	Cyanide (wt%, dry)		Nickel (wt%, dry)		Water (wt%)
		Sample	Duplicate	Sample	Duplicate	
47	B	0.305	0.303	---		N/A[a]
	C	0.449	0.423	---		
	D	0.583	0.582	4.6[b]		
48	C	1.10	1.15	---		N/A
	D	0.86	0.87	---		
49	B	0.350	0.357	0.8		N/A
	C	0.814	0.802	3.3		
	D	0.561	0.543	3.2		

Notes:

[a]Samples were dried prior to making measurements. Therefore, no conversion from wet basis to dry basis is necessary.

[b]Nickel measurements were originally performed with nickel crucibles. Measurements were subsequently made on archived samples using non-nickel crucibles, but only a few subsegments were available for reanalysis.

Table A-3. Cyanide, Nickel, and Moisture Data for C-111 (Kelly 1995).

Auger	Subsegment	Cyanide (μg/g, wet)		Nickel (wt%, dry)		Water (wt%)
		Sample	Duplicate	Sample	Duplicate	
Aug-016	B	94	84	2.16	2.89	28.1
	C	155	151	3.85	4.68	41.7
	D	107	104	2.06	2.05	44.2

Table A-4. Cyanide, Nickel, and Moisture Data for C-112 (Simpson et al. 1993a, Scheele 1995).

Core	Subsegment	Cyanide (wt% dry)		Nickel (wt%, dry)		Water (wt%)
		Sample	Duplicate(s)	Sample	Duplicate	
34	1D	0.51	0.54, 0.52	---	---	
				---	---	
	2B	0.43	0.43	3.8	---	N/A[a]
	2C	0.87	0.79	4.9	---	
	2D	0.77	0.74, 0.73	3.2	---	
	1D	0.73	0.71	5.1	---	
	2A	0.91	0.94	---	---	
36	2B	0.75	0.74	---	---	N/A
	2C	0.41	0.39	4.9	---	
	2D	0.57	0.55	0.2	---	

Notes:

[a]Samples were dried prior to making measurements. Therefore, no conversion from wet basis to dry basis is necessary.

A.4 RESULTS

The results of the statistical evaluation are described below. There could be no direct estimation of spatial variation in layers having sample results for only one core or auger subsegment. Therefore, reasonable estimates of variability were developed for these cases using the variabilities calculated for the other ferrocyanide C Farm tanks.

Ferrocyanide Concentrations

Assumptions

For Layer 5 of C-112, the standard deviation from Layer 4, estimated to be the "most similar" layer, is used as a surrogate to generate the t-test and confidence interval.

For all three layers of C-111, a pooled estimate of the standard deviation within layers from the other three tanks is derived and used as a surrogate to generate the t-test and confidence interval.

Where sample size (n) or degrees-of-freedom (n-1) are needed (obtaining the standard error, p-value and confidence interval), 2 is used for n and 1 is used for the degrees-of-freedom.

Results

The results of the t-tests and confidence intervals are given in Table A-5 for ferrocyanide concentrations. From Table A-5, the probabilities that the ferrocyanide concentration is 8 wt%, dry basis are quite low, ranging from <0.001 to 0.03. The resulting conclusion is that it is very unlikely any of these layers contain an average 8 wt% fuel content. The upper 95% confidence level estimates for sodium nickel ferrocyanide concentrations are all below the 8 wt% criterion.

Nickel Concentrations

Assumptions

For Layer 4 of C-108, the standard deviation from Layer 3, considered to be most similar layer, is used as a surrogate to generate the t-test and confidence interval.

For Layers 2 and 3 of C-109, the standard deviation from Layer 1 is used as a surrogate to generate the t-test and confidence intervals.

For all three layers of C-111, a pooled estimate of the standard deviation within layers from the other three tanks was derived and used as a surrogate to generate the t-test and confidence interval.

For Layers 2, 3, 5, and 6 of C-112, the standard deviation from Layer 1 is used as a surrogate to generate the t-test and confidence intervals.

Where sample size (n) or degrees-of-freedom (df = n-1) are needed (obtaining the standard error, t-statistic, p-value and confidence interval), 2 is used for n and 1 will be used for df.

Results

Table A-6 shows the results for nickel concentrations. From Table A-6, the probabilities that the nickel concentration in the layers is less than 0.8 wt% range from 0.065 to 0.49. It is concluded, using a 0.20 criteria, that it is very unlikely that most of these layers contain less than 0.8 wt% nickel concentration. The exceptions to this conclusion would be for the top quarter segment layers in tank C-108 and C-109. Although the top layer sample average in C-108 is 1.15 wt%, there is a reasonable probability that the sample could have come from a layer whose average nickel concentration was less than 0.8 wt%. This is corroborated by the historical records (Brevick 1995) that show additional waste was added to the tanks after the ferrocyanide scavenging campaigns were completed.

Careful examination of the physical appearance and chemical species of the surface samples from tanks C-108 and C-109 indicates something other than ferrocyanide sludge was placed on the surface of the waste. The surface sample from one riser in C-108 (AUG-012) had low nickel concentration (0.18 to 0.22 wt%). However, this surface sample was yellow to brown in color and crumbly in texture (Esch 1995). The other C-108 samples were tan in color and pasty in texture (Esch 1995). A pasty texture is characteristic of the ferrocyanide sludge simulants.

The surface sample from one riser in C-109 (Core 49) also showed lower nickel concentration (~0.8 wt%). However, this surface sample was grey in color and contained high concentrations (>20 wt%) of aluminum (Simpson et al. 1993b). The color, texture, and chemical species indicate that this surface sample is aluminum decladding waste. The other C-109 samples were tan to brown in color and pasty in texture (Sprouse 1993), similar to other ferrocyanide sludge samples.

Table A-5. Average Sodium Nickel Ferrocyanide Concentration, t-Statistic, p-Value, and Upper 95% Confidence Limit.

Tank	Layer	Average $Na_2NiFe(CN)_6$ Conc (dry wt%)	t-stat	p-value	Upper 95% $Na_2NiFe(CN)_6$ Conc (dry wt%)
C-108	Top	1.09	-10.68	0.030	5.17
	Bottom	0.30	-70.58	0.005	0.99
C-109	1	1.35	-32.84	<0.001	1.94
	2	1.60	-15.84	0.002	2.78
	3	0.67	-146.07	0.002	0.98
C-111	1	0.038	-24.81[b]	0.013[b]	2.075[b]
	2	0.053	-24.76[b]	0.013[b]	2.08[b]
	3	0.025	-24.85[b]	0.013[b]	2.05[b]
C-112	1	1.33	-35.31	0.009	2.52
	2	1.25	-15.53	0.020	3.99
	3	1.19	-21.15	0.015	3.22
	4	1.47	-16.07	0.020	4.03
	5	1.45	-16.08[a]	0.020[a]	4.02[a]

Notes:

[a]t-test and confidence limit for Layer 5 of C-112 are based on standard deviation from layer 4 and sample size of 2.

[b]t-tests and confidence limits for all layers of C-111 are based on pooled layer standard deviations from the other three tanks and sample size of 2.

Table A-6. Average Nickel Concentration, t-Statistic, p-Value, and Lower 80% Confidence Limit.

Tank	Layer	Average nickel conc. (dry wt%)	t-stat	p-value	Lower 80% nickel conc. (dry wt%)
C-108	1	2.41	-1.54	0.18	0.971
	2	1.80	-2.22	0.14	1.179
	3	1.14	-0.37	0.39	-0.150
	4	1.86	-1.13[a]	0.23[a]	0.57[a]
C-109	1	3.90	-4.43	0.07	2.94
	2	3.30	-3.57[b]	0.09[b]	2.38[b]
	3	0.82	-0.03[b]	0.49[b]	-0.14[b]
C-111	1	2.05	-1.48[c]	0.19[c]	0.89[c]
	2	4.26	-4.09[c]	0.08[c]	3.10[c]
	3	2.52	-2.04[c]	0.15[c]	1.36[c]
C-112	1	1.98	-1.32	0.16	1.03
	2	4.90	-4.59[d]	0.07[d]	3.67[d]
	3	3.80	-3.36[d]	0.09[d]	2.57[d]
	5	5.10	-4.82[d]	0.07[d]	3.87[d]
	6	4.90	-4.59[d]	0.07[d]	3.67[d]

Notes:

[a]t-test and confidence limit for Layer 4 of C-108 based on the standard deviation from Layer 3 and sample size of 2

[b]t-tests and confidence limits for Layers 2 and 3 of C-109 are based on the standard deviation from Layer 1 and sample size of 2

[c]t-tests and confidence limits for all layers of C-111 based on a pooled layer standard deviation from the other three tanks and sample size of 2.

[d]t-tests and confidence limits for Layers 2, 3, 5, and 6 of C-112 based on the standard deviation from Layer 1 and sample size of 2

A.5 REFERENCES

Babad, H., J. E. Meacham, B. C. Simpson, and R. J. Cash, 1993, *The Role of Aging in Resolving the Ferrocyanide Safety Issue,* WHC-EP-0599, Westinghouse Hanford Company, Richland, Washington.

Esch, R. A., 1995, *45 Day Safety Screen Results for Tank 241-C-108, Augers 94-012, 94-014, and 94-015*, WHC-SD-WM-DP-082, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Kelly, S. E., 1995, *Tank Characterization Report for Single Shell Tank 241-C-111*, WHC-SD-WM-ER-475, Rev. 0-B, Westinghouse Hanford Company, Richland, Washington.

Lilga, M. A., M. R. Lumetta, and G. F. Schiefelbein, 1993, *Ferrocyanide Safety Project, Task 3: Aging Studies - FY 1993 Annual Report*, PNL-8888, Pacific Northwest Laboratory, Richland, Washington.

Lilga, M. A., E. V. Alderson, M. R. Lumetta, and G. F. Schiefelbein, 1994, *Ferrocyanide Safety Project, Task 3: Ferrocyanide Aging Studies - FY 1994 Annual Report*, PNL-10126, Pacific Northwest Laboratory, Richland, Washington.

Lilga, M. A., E. V. Alderson, R. T. Hallen, M. O. Hogan, T. L. Hubler, G. L. Jones, D. J. Kowalski, M. R. Lumetta, G. F. Schiefelbein, and M. R. Telander, 1995, *Ferrocyanide Safety Project: Ferrocyanide Aging Studies - FY 1995 Annual Report*, PNL-10713, Pacific Northwest Laboratory, Richland, Washington.

Meacham, J. E., R. J. Cash, B. A. Pulsipher, and G. Chen, 1995, *Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives Process*, WHC-SD-WM-DQO-007, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Sasaki, L. M., 1995, *Tank Characterization Report for Single Shell Tank 241-C-108*, WHC-SD-WM-ER-503, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Scheele, R. D., 1995, *Ferrocyanide Safety Project: Comparison of Actual and Simulated Ferrocyanide Waste Properties*, PNL-10175, Supplement 1, Pacific Northwest Laboratory, Richland, Washington.

Simpson, B. C. , G. L. Borsheim, and L. Jensen, 1993a, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0688, Westinghouse Hanford Company, Richland,

Sprouse, B. S., 1993, *Single-Shell Tank Waste Characterization Project - Cores 47, 48, and 49 Data Report - Tank 241-C-109 Narrative*, WHC-SD-WM-DP-036, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank.

APPENDIX B

EVALUATION OF SODIUM NICKEL FERROCYANIDE AND NICKEL SAMPLE DATA FOR C FARM WASTE TANKS

This page intentionally left blank.

B.0 EVALUATION OF SODIUM NICKEL FERROCYANIDE AND NICKEL SAMPLE DATA FOR C FARM WASTE TANKS

B.1 INTRODUCTION AND OBJECTIVES

The sample data from four C Farm tanks (241-C-108, C-109, C-111, and C-112) are evaluated to address two questions identified in the ferrocyanide data quality objectives (DQO) document (Meacham et al. 1995). The two questions are: (1) Does the waste in the tank contain a sodium nickel ferrocyanide (fuel) concentration less than 8 wt% $Na_2NiFe(CN)_6$?; and (2) Does the waste in the tank have a nickel concentration above 0.8 wt%? These two questions are addressed by considering that the material concentrations in each tank can be represented by a model statistical distribution.

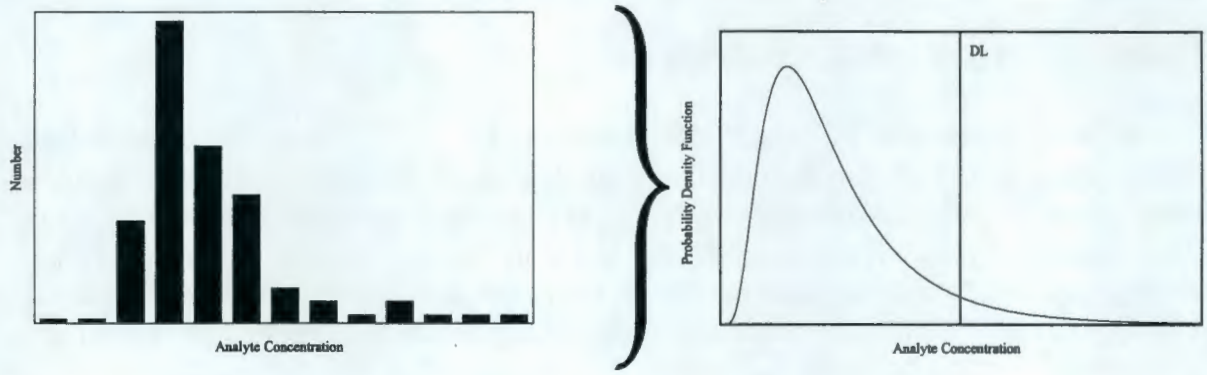
The objectives of the following evaluation are: (1) to develop a model statistical distribution for sodium nickel ferrocyanide and nickel from the tank sample data; (2) to calculate, from the statistical distribution, the probability of exceeding the decision limit of 8 wt% $Na_2NiFe(CN)_6$ and 0.8 wt% nickel; and therefore (3) to demonstrate that based on the DQO decision logic, the four C Farm ferrocyanide tanks are categorized as SAFE.

B.2 RELATING SAMPLE DATA TO WASTE TANK DISTRIBUTION

Figure B-1 illustrates the concept of using sample data from a tank to represent a specific material by a model probability density function. For visual purposes, the sample data are displayed in the form of a histogram for the specific analyte concentration on the left side of Figure B-1. However, neither the histogram nor the histogram bins are an important factor in the analysis. Rather, the techniques identified below are used to model the sample data by a probability density function as illustrated on the right side of Figure B-1. The probability of exceeding a defined decision limit (DL) is then the area under the probability distribution function beyond the decision limit.

The process assumes a model probability density function, and the appropriate parameters are estimated based on available sample data. Probability plots are constructed in order to determine whether or not the proposed model is reasonable. If the probability plot suggests the model is reasonable, then model parameters are determined by the maximum likelihood method. A goodness-of-fit test is then completed. Maximizing the likelihood function provides the best values for the model parameters.

Figure B-1. Schematic of Sample Data Related to an Analyte Concentration Distribution via a Model Probability Density Function.



The "best" estimates of the parameters of a probability distribution (e.g., maximum likelihood estimates) contain all of the information in the sample data. Hence, the particular probability distribution that is selected from an infinite family of distributions, based on the maximum likelihood estimates of the parameters, provides the best estimate of the true underlying distribution of the population from which the sample was drawn.

B.3 MODEL PROBABILITY DENSITY FUNCTION

The model used is the Weibull probability density function (Evans et al. 1989) given by;

$$f(x;\ \eta,\ \beta,\ \gamma) = \frac{\beta}{\eta}\left(\frac{x-\gamma}{\eta}\right)^{\beta-1} e^{-\left(\frac{x-\gamma}{\eta}\right)^{\beta}} \quad . \qquad \text{[B-1]}$$

The Weibull probability density function was used for two reasons. First, it is extremely flexible. A Weibull probability density function can represent many other normally used probability density functions by changing the shape parameter β. For example, when the Weibull shape parameter is less than one ($\beta < 1$), the distribution is exponentially decreasing. For β between 1 and 3, the distribution is skewed to the right; for β in the interval 3 to 4, the distribution is nearly normal (i.e., symmetric), and for β above about 5, the distribution is skewed to the left. Thus, a Weibull probability density function can represent, for example, an exponentially decreasing probability density function, a lognormal probability density function, a normal probability density function, or other commonly used probability density functions.

Second, the cumulative distribution function is available in closed form. This greatly facilitates the calculation of the probability of exceeding a specified limit.

B.4 SAMPLE ANALYSIS

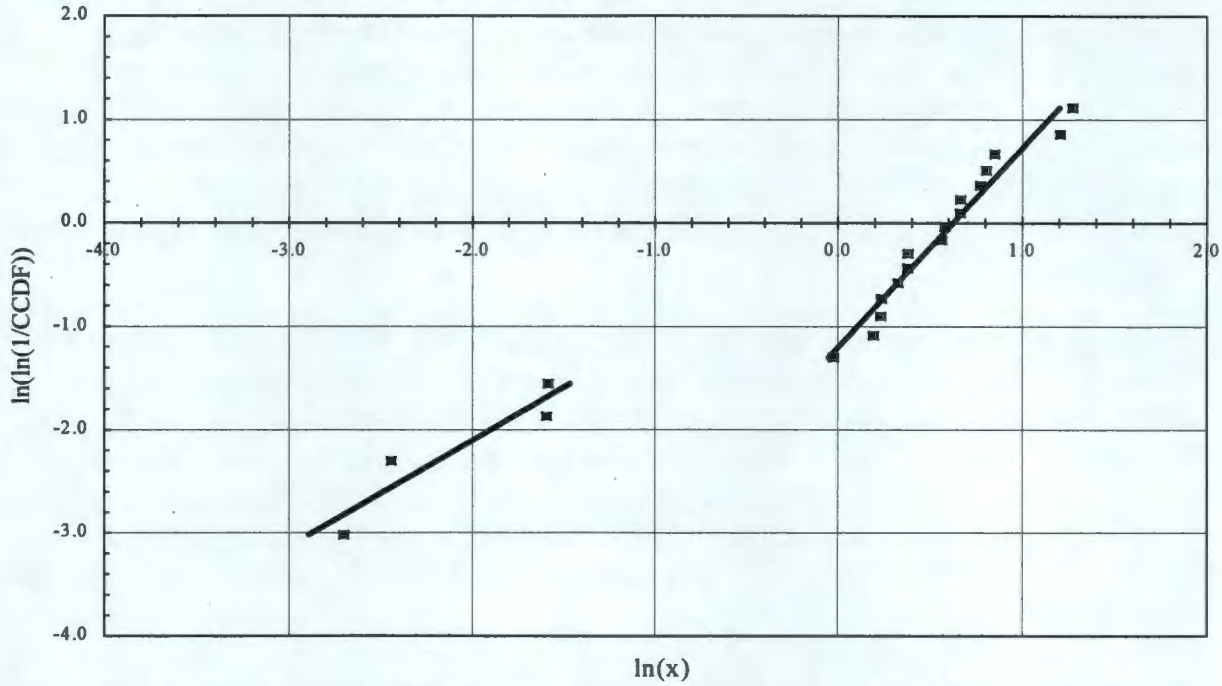
The waste contained in the C Farm tanks (C-108, C-109, C-111, and C-112) consists of non-complexed waste with the volume of sludge waste from 235 to 394 m^3 (62 to 104 kgal) (Hanlon 1996). The corresponding thickness of sludge waste in these tanks ranges from 53 to 114 cm (21 to 45 in.) (Hanlon 1996). For this analysis it was assumed that the material concentration for each analyte could be represented by a probability density function. The tank sample data for sodium nickel ferrocyanide and nickel for each of the C Farm tanks (Kelly 1995, Sasaki 1995, Scheele 1995, Simpson 1993a, and Simpson 1993b) were used in the evaluation.

Probability plots were constructed for the C Farm tanks (C-108, C-109, C-111, and C-112) and each probability plot suggested that a Weibull probability density function model was reasonable, except for the nickel concentration in tank C-108. The sample data for the nickel concentration in tank C-108 is bi-modal, as can be seen in the probability plot presented in Figure B-2, in that one straight line does not represent all the data. In the case of the Weibull probability density function, the probability plot consists of a graph of the log-log of the reciprocal of the complementary cumulative distribution function as a function of the logarithm of the sample data.

It should be noted that a waste stratification model exists for these four C Farm tanks, and a higher nickel concentration would exist in the waste layer that originally contained sodium nickel ferrocyanide. The nickel sample data for tank C-108 clearly demonstrated the waste stratification by a bi-modal probability density function. However, the other data could be adequately represented by a model where the entire waste volume was assumed to be represented by a single probability density function. The nickel concentration for tank C-109 could also be bi-modal, but the number of sample data are too few to make a clear distinction. As noted, all of the other sample data could be adequately represented by a single probability density function.

The results for sodium nickel ferrocyanide for tank C-108 are presented in Figure B-3. The left-hand axis is for the histogram of the sample data. Remember that neither the histogram nor the histogram bins are important factors in the analysis. The histogram is shown in Figure B-3 to illustrate the sample data. The right-hand axis in Figure B-3 is for the probability density function with the Weibull parameters shown in the legend. The Weibull parameters shown in the legend are those determined from maximizing the likelihood function. The decision limit of 8 wt% $Na_2NiFe(CN)_6$ is shown by the short straight line at 8 wt%, and, for this data set, the probability of exceeding the decision limit is very small.

Figure B-2. Probability Plot for the Nickel Sample Data From Waste Tank 241-C-109, With a Bi-Modal Probability Density Function.



The combined (i.e., bi-modal) distribution of the nickel concentration in tank C-108 is presented in Figure B-4. The combined bi-modal distribution is a mixture of two Weibull probability density functions weighted by the number of sample data points per distribution. Again, the left-hand axis is for the histogram of the sample data. The right-hand axis is for the probability density function, with the Weibull parameters shown in the legend. The Weibull parameters are those determined from maximizing the likelihood functions for both sets of sample data. The decision limit of 0.8 wt% Ni is shown by the straight line at 0.8 wt%. For this data set, the probability of the nickel concentration being larger than 0.8 wt% is 0.75 for the combined probability density function. Conversely, the probability that the nickel concentration is less than 0.8 wt% is 0.25. The nickel probability is not higher because all nickel determinations for the subsegments were used for the distribution model and other waste in the tanks (before and after ferrocyanide additions) was essentially devoid of nickel. This averaging over all the waste skews the nickel concentrations to the left in Figure B-4. This happens for the nickel concentrations shown for the other tanks as well (Figures B-6, B-8, and B-10).

Results are shown in Figures B-5 and B-6 for tank C-109. Figures B-7 and B-8 give the results for tank C-111, and Figures B-9 and B-10 provide the results for tank C-112, respectively. Table B-1 provides a summary of the results, including the goodness-of-fit test results. The modified Anderson-Darling statistic (Evans et al. 1989) was used for the goodness-of-fit test.

Figure B-3. Sodium Nickel Ferrocyanide Analysis Results For Tank C-108, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 8 wt% Decision Limit.

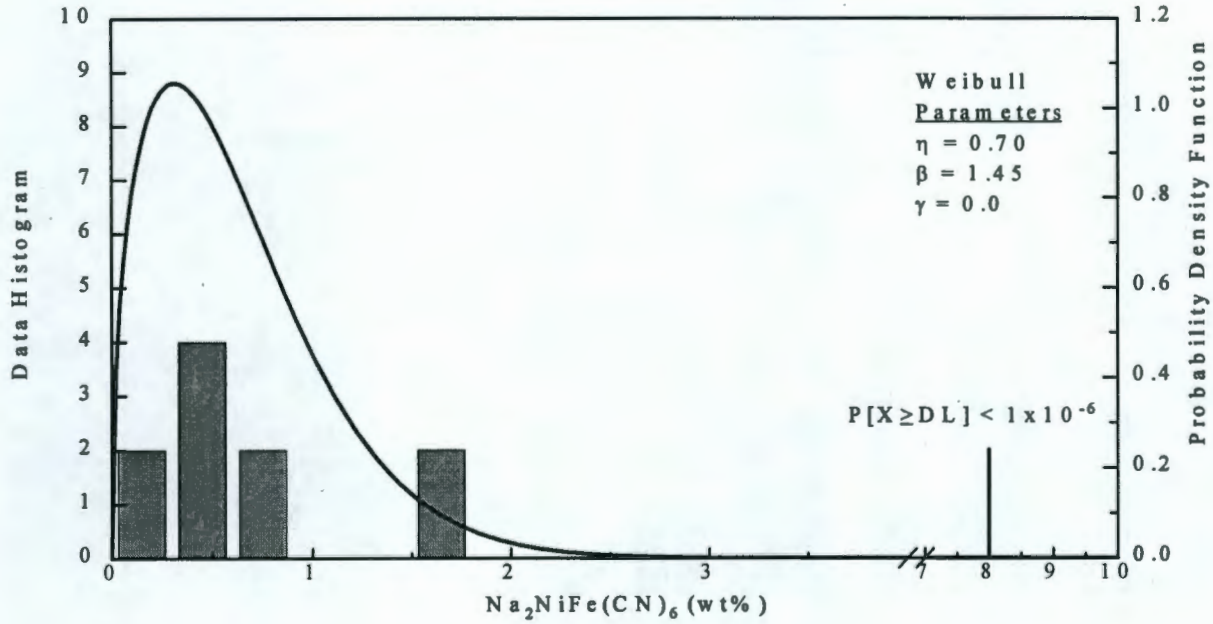


Figure B-4. Nickel Analysis Results For Tank C-108, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 0.8 wt% Decision Limit.

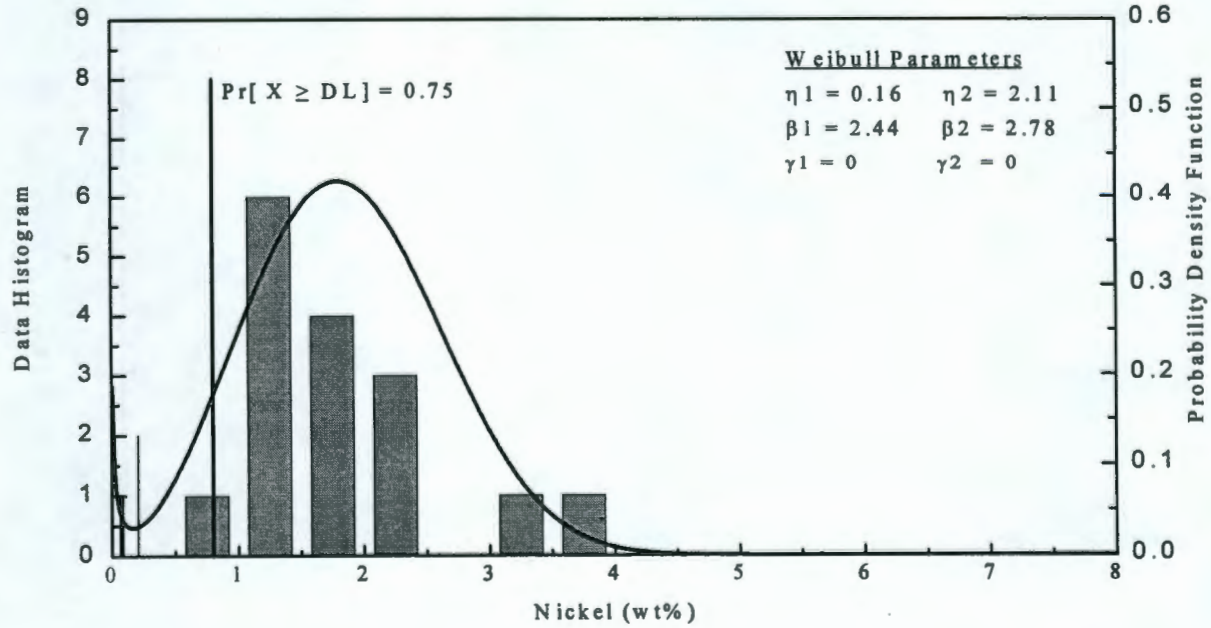


Figure B-5. Sodium Nickel Ferrocyanide Analysis Results For Tank C-109, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 8 wt% Decision Limit.

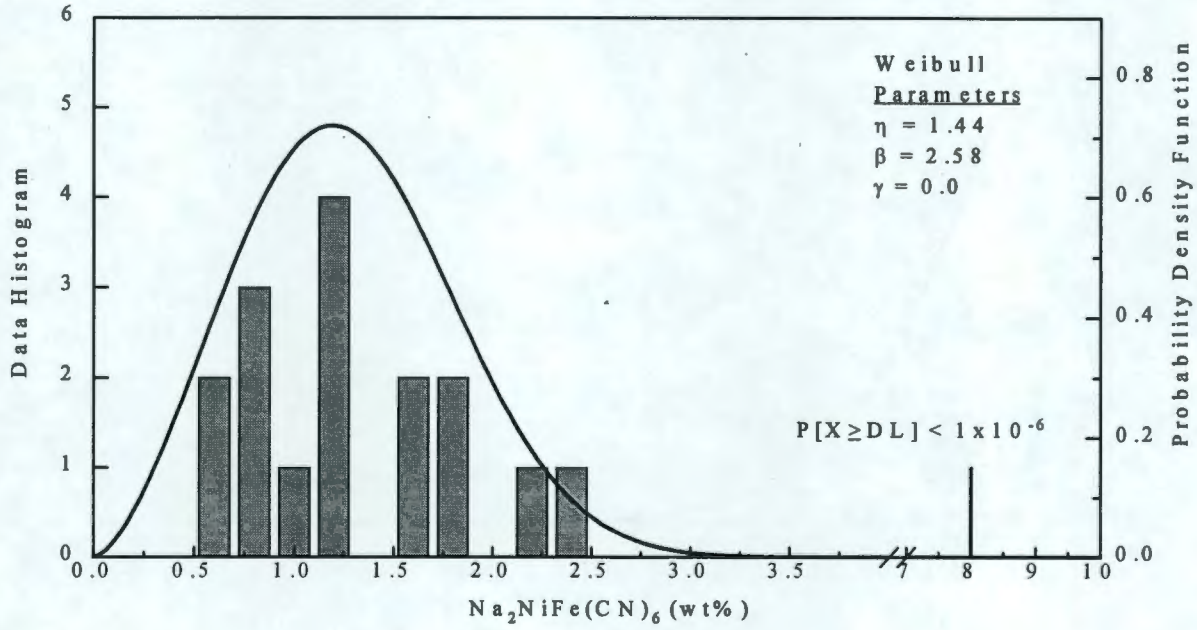


Figure B-6. Nickel Analysis Results For Tank C-109, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 0.8 wt% Decision Limit.

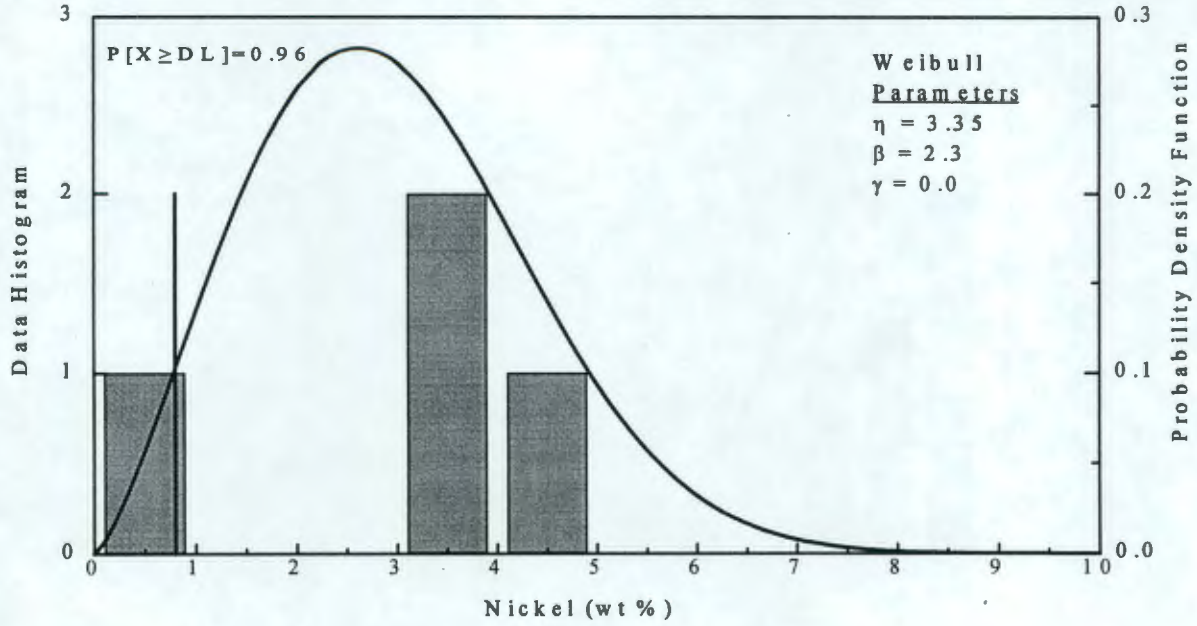


Figure B-7. Sodium Nickel Ferrocyanide Analysis Results For Tank C-111, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 8 wt% Decision Limit.

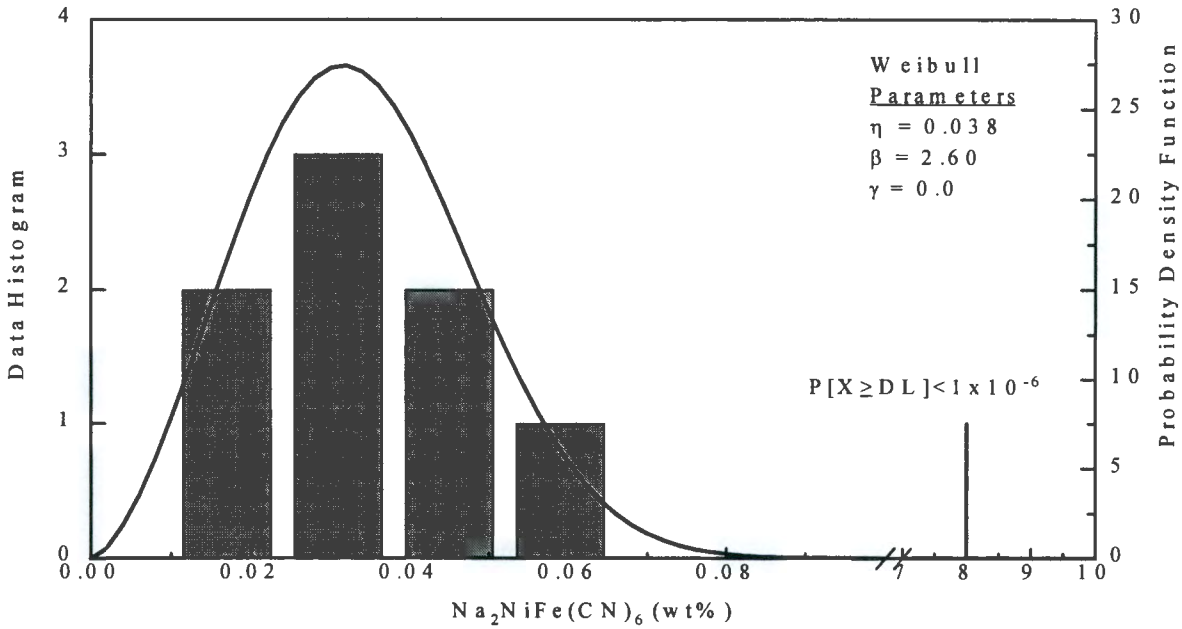


Figure B-8. Nickel Analysis Results For Tank C-111, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 0.8 wt% Decision Limit.

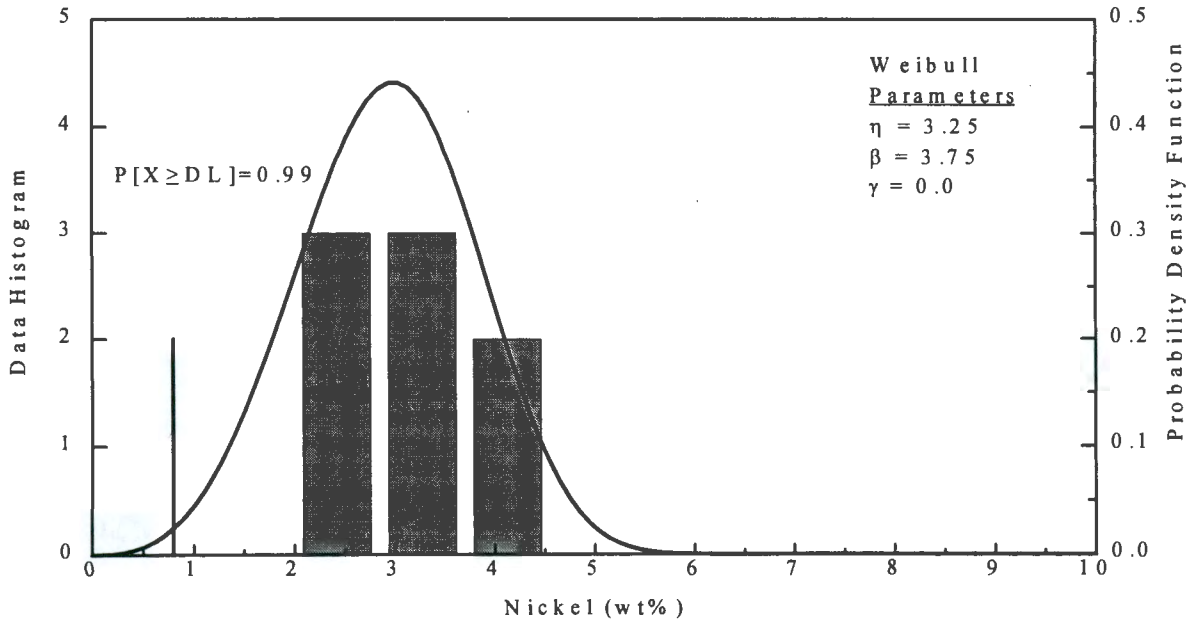


Figure B-9. Sodium Nickel Ferrocyanide Analysis Results For Tank C-112, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 8 wt% Decision Limit.

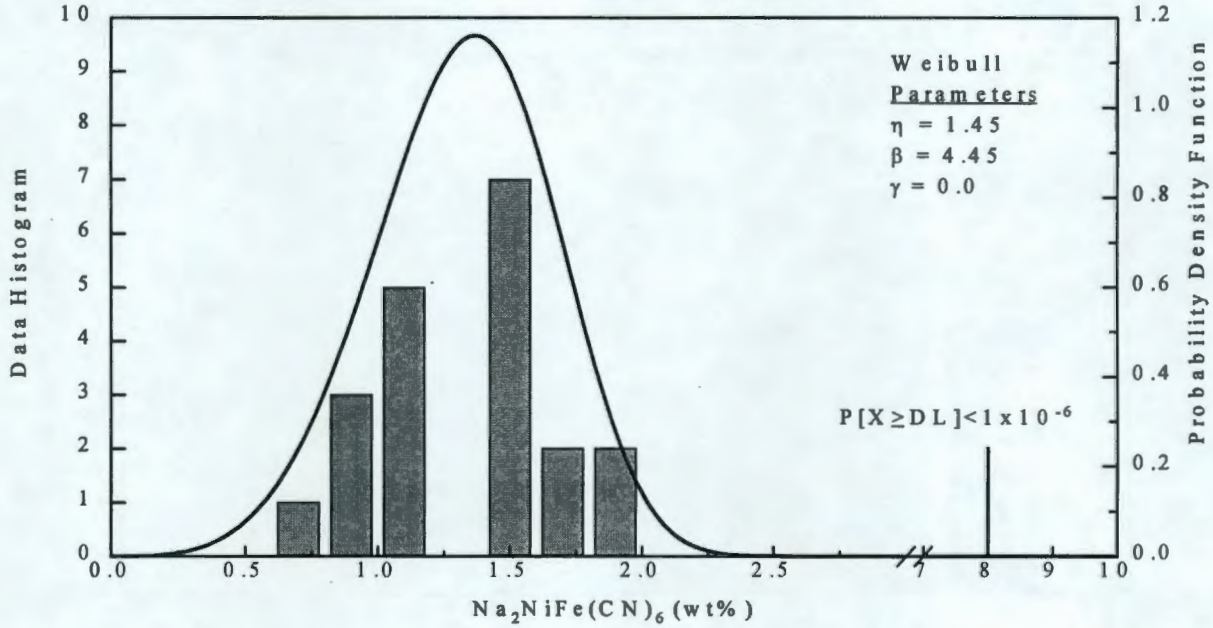


Figure B-10. Nickel Analysis Results For Tank C-112, Showing the Data Histogram, Probability Density Function, and Probability of Exceeding the 0.8 wt% Decision Limit.

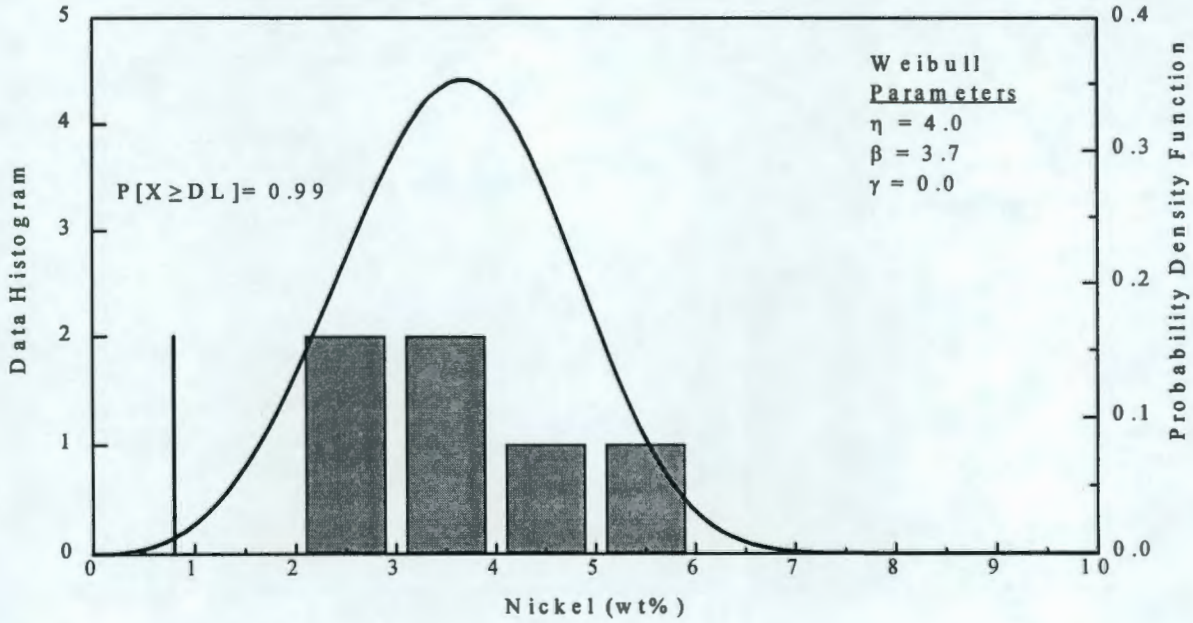


Table B-1. Sodium Nickel Ferrocyanide Summary Information for Four C Farm Tanks.

Tank	Weibull parameters		Probability of exceeding a concentration of 8 wt% $Na_2NiFe(CN)_6$	$Na_2NiFe(CN)_6$ concentration at a 0.05 probability of exceedance wt%	Modified Anderson-Darling statistic*	
	η	β			A^2	Critical value
C-108	0.70	1.45	$< 1 \times 10^{-6}$	1.50	0.638	0.701
C-109	1.44	2.58	$< 1 \times 10^{-6}$	2.20	0.442	0.664
C-111	0.04	2.60	$< 1 \times 10^{-6}$	0.058	0.274	0.663
C-112	1.45	4.45	$< 1 \times 10^{-6}$	1.85	0.591	0.636

* Note that the Anderson-Darling statistic, A^2, is lower than the critical value (0.05 level of significance) for all four tanks; thus, the models cannot be rejected.

The analysis demonstrates that the probability of exceeding a $Na_2NiFe(CN)_6$ concentration in the tank waste larger than 8 wt% for all four C Farm tanks is extremely small (fourth column in Table B-1, less than 1×10^{-6}). Conversely, there is a large probability (approaching 1) that the $Na_2NiFe(CN)_6$ concentration in the tank waste is less than 8 wt%. For comparison to the ferrocyanide DQO (Meacham et al. 1995), the fifth column in Table B-1 provides the $Na_2NiFe(CN)_6$ concentration at an exceedance probability of 0.05. That is, the probability of

Table B-2. Nickel Summary Information for Four C Farm tanks

Tank	Weibull parameters		Probability of exceeding a concentration of 0.8 wt% Ni	Ni concentration at a 0.8 probability of exceedance wt%	Modified Anderson-Darling statistic*	
	η	β			A^2	Critical value
C-108	0.16 2.11	2.44 2.78	0.75 combined 0.93 upper data set	0.3 combined 1.25 upper data set	0.569 0.607	0.668 0.659
C-109	3.35	2.3	0.96	1.75	0.535	0.672
C-111	3.25	3.75	0.99	2.18	0.553	0.642
C-112	4.00	3.70	0.99	2.67	0.376	0.642

* Note that the Anderson-Darling statistic, A^2, is lower than the critical value (0.05 level of significance) for all four tanks; thus, the models cannot be rejected.

the $Na_2NiFe(CN)_6$ concentration being larger than the value listed in the fifth column for each tank is 0.05. This information can be generally compared to the upper 95% $Na_2NiFe(CN)_6$ concentration values in Table A-5 of Appendix A.

The analysis demonstrates that the probability of exceeding a nickel concentration in the tank waste larger than 0.8 wt% for all four C Farm tanks ranges from 0.75 to 0.99 (fourth column in Table B-2). For comparison to the ferrocyanide DQO, the fifth column in Table B-2 provides the nickel concentration at an exceedance probability of 0.8. That is, the probability of the nickel concentration being larger than the value listed in the fifth column for each tank is 0.8. The information presented here can be generally compared to the lower 80% nickel concentration values in Table A-6 of Appendix A.

B.5 UNCERTAINTY ANALYSIS

The goodness-of-fit statistic used was the modified Anderson-Darling statistic (Evans et al. 1989). In all cases the value of the modified Anderson-Darling statistic, A^2, was lower than the critical value at the 0.05 level of significance. Hence, the models cannot be rejected (Table B-1 and B-2). It should be noted that if a single probability density function were used to fit the bi-modal sample data for tank C-108, the A^2 statistic would be larger than the critical value, and the model would be rejected. Thus, the probability plot and goodness-of-fit test are essential in developing the best model to represent the sample data.

The uncertainty in the Weibull probability density function parameters and/or confidence bands on the cumulative distribution function have been determined for each model using the maximum likelihood estimates of the parameters and the sample data. The results of these analyses do not alter the conclusions regarding the probability that the $Na_2NiFe(CN)_6$ concentration is less than 8 wt% for these four C Farm tanks.

B.6 CONCLUSIONS

The evaluation developed a statistical distribution model for each of the four C Farm tanks (C-108, C-109, C-111, and C-112) for sodium nickel ferrocyanide and nickel based on the tank sample data. The statistical distribution was used to calculate the probability of exceeding a $Na_2NiFe(CN)_6$ concentration of 8 wt% and a nickel concentration of 0.8 wt%. The analysis demonstrated that for all four C Farm tanks there is a large probability (approaching 1) that the $Na_2NiFe(CN)_6$ concentration in the tank waste is less than 8 wt%. There is a reasonable probability (above 0.96 for tanks C-109, C-111, and C-112, and 0.75 for tank C-109) that the tank waste has a nickel concentration above 0.8 wt%. The analysis, therefore, supports the conclusion that the four C Farm tanks are properly placed in the SAFE category.

B.7 REFERENCES

Evans, J. W., R. A. Johnson, and D. W. Green, 1989, *Two- and Three Parameter Weibull Goodness of Fit Tests,* Research Paper FPL-RP-493, U.S. Department of Agriculture, Forest Service, Forest Product Laboratory, Madison, Wisconsin.

Hanlon, B. M., 1996, *Waste Tank Summary Report for Month Ending October 31, 1995*, WHC-EP-0182-91, Westinghouse Hanford Company, Richland, Washington.

Kelly, S. E., 1995, *Tank Characterization Report for Single-Shell Tank 241-C-111*, WHC-SD-WM-ER-475, Rev. 0-B, Westinghouse Hanford Company, Richland, Washington.

Meacham, J. E., R. J. Cash, B. A. Pulsipher, and G. Chen, 1995, *Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives Process*, WHC-SD-WM-DQO-007, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Sasaki, L. M., 1995, *Tank Characterization Report for Single Shell Tank 241-C-108*, WHC-SD-WM-ER-503, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Scheele, R. D., 1995, *Ferrocyanide Safety Project: Comparison of Actual and Simulated Ferrocyanide Waste Properties*, PNL-10175, Pacific Northwest Laboratory, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993 a, *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Simpson, B. C., G. L. Borsheim, and L. Jensen, 1993b, *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Washington.

This page intentionally left blank.

DISTRIBUTION

Number of copies

OFFSITE

8	U.S. Department of Energy EM-36, Trevion II 12800 Middlebrook Road Germantown, MD 20874 James V. Antizzo, EM-36 Charles O'Dell, EM-36 (5) U.S. Department of Energy Forrestal Building 1000 Independence Avenue SW Washington, DC 20585 Shirley Campbell, EH-71 John Kaysak, EM-25
1	Charles S. Abrams 1987 Virginia Idaho Falls, ID 83404
1	David O. Campbell 102 Windham Road Oak Ridge, TN 37830
1	Fred N. Carlson 6965 North 5th West Idaho Falls, ID 83401
1	Billy C. Hudson 202 Northridge Court Lindsborg, KA 67456
1	Thomas S. Kress 102-B Newridge Road Oak Ridge, TN 37839

DISTRIBUTION (Continued)

Number of copies

OFFSITE

1	Thomas E. Larson 2711 Walnut Street Los Alamos, NM 87544
1	Air Products & Chemicals, Inc. 7201 Hamilton Blvd Allentown, PA 18195-1501 George E. Schmauch
1	Brookhaven National Laboratory Upton, NY 11973 Kamal K. Bandyopadhyay
2	Fauske and Associates, Inc. 16W070 W. 83rd St. Burr Ridge, IL 60521 Michael Epstein Hans K. Fauske
1	G & P Consulting, Inc. 3640 Ballard Road Dallas, OR 97338 Arlin K. Postma
1	Harvard University 295 Upland Avenue Newton Highlands, MA 02161 Melvin W. First

DISTRIBUTION (Continued)

Number of copies

OFFSITE

1	Los Alamos National Laboratory P.O. Box 1663 Los Alamos, NM 87545 Steve F. Agnew
1	MIT/Department of Nuclear Engineering 77 Massachusetts Ave. Room 24-102 Cambridge, MA 02139 Mujid S. Kazimi
1	Nuclear Consulting Services, Inc. P.O. Box 29151 Columbus, OH 43229-0151 J. Louis Kovach
	Oak Ridge National Laboratory
1	Emory D. Collins P.O. Box 2008 7930, MS-6385 Oak Ridge, TN 37831-6385
1	Charles W. Forsberg P.O. Box 2008 MS-6495 Oak Ridge, TN 37831-6495
1	Rice University 5211 Paisley Houston, TX 77096 Andrew S. Veletsos

DISTRIBUTION (Continued)

Number of copies

OFFSITE

2	Sandia National Laboratories P.O. Box 5800 Albuquerque, NM 87185	
	Dana A. Powers, MS-0744 Scott E. Slezak, MS-0741	
3	Science Applications International Corporation 20300 Century Blvd, Suite 200-B Germantown, MD 20874	
	Ray S. Daniels (3)	
	State of Washington - Department of Ecology	
1	Robert C. King P. O. Box 47600 Olympia, WA 98504-7600	
1	Alex B. Stone 1315 W. 4th Avenue Kennewick, WA 99336	
1	Waste Policy Institute 555 Quince Orchard Road, Suite 600 Gaitherburg, MD 20878-1437	
	Donald T. Oakley	

ONSITE

10	U.S. Department of Energy, Richland Operations Office	
	R. G. Harwood	S7-54
	W. F. Hendrickson (2)	S7-54
	M. F. Jarvis	S7-54

DISTRIBUTION (Continued)

	A. G. Krasopoulos	A4-81
	J. K. McClusky	S7-53
	J. C. Peschong	S7-53
	Public Reading Room	H2-53
	RL Docket File (2)	B1-17
5	Pacific Northwest Laboratory	
	J. W. Brothers	K5-22
	R. T. Hallen	P8-38
	M. A. Lilga	P8-38
	C. S. Simmons	K9-33
	Hanford Technical Library	P8-55
37	Westinghouse Hanford Company	
	H. Babad	S7-30
	J. B. Billetdeaux	S7-16
	W. S. Callaway	S3-90
	R. J. Cash (5)	S7-14
	M. D. Crippen	L5-31
	R. D. Crowe	H0-38
	M. L. Dexter	R1-51
	D. R. Dickinson	L5-31
	G. T. Dukelow	S7-14
	J. M. Grigsby	A3-37
	M. N. Islam	R3-08
	D. W. Jeppson	L5-31
	N. W. Kirch	R2-11
	C. A. Kuhlman	B3-30
	L. L. Lockrem	S3-90
	J. M. McLaren	H0-34
	J. E. Meacham (2)	S7-14
	N. J. Milliken	H4-65
	S. R. Moreno	B3-06
	T. V. Rebagay	T6-30
	F. R. Reich	L5-55
	E. F. Riedel	S3-90
	B. C. Simpson	R2-12
	W. T. Watson	H0-38
	W. D. Winkelman	L5-55

DISTRIBUTION (Continued)

W. D. Wittekind	H0-38
Central Files	A3-88
Correspondence Processing	A3-01
EDMC	H6-08
OSTI (2)	A3-36