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WHC-EP-0721

Program Plan for Evaluation of the Ferrocyanide Waste Tank Safety Issue at the Hanford Site

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LIST OF TERMS

CASS	Computer Automated Surveillance System
CPAC	Center for Process Analytical Chemistry
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	Data Quality Objectives
DSC	Differential Scanning Calorimetry
EA	Environmental Assessment
Ecology	Washington State Department of Ecology
EDTA	Ethylenediaminetetraacetic Acid
EIS	Environmental Impact Statement
EPA	Environmental Protection Agency
FAI	Fauske and Associates, Inc.
FONSI	Finding of No Significant Impact
FTIR	Fourier Transform Infrared
FY	Fiscal Year
GAO	General Accounting Office
HEDTA	Hydroxyethylenediaminetriacetic Acid
HLW	High-Level Radioactive Waste
IC	Ion Chromatography
IR	Infrared
ISB	Interim Safety Basis
LANL	Los Alamos National Laboratory
LFL	Lower Flammability Limit
LOW	Liquid Observation Well
MCNP	Monte Carlo Neutron Photon [Model]
MIT	Multifunctional Instrument Tree
NIR	Near-Infrared
PNL	Pacific Northwest Laboratory
QA	Quality Assurance
RTD	Resistance Temperature Detector
SA	Safety Assessment
SAR	Safety Analysis Report
SRS	Savannah River Site
SST	Single-Shell Tank
TAP	Tanks Advisory Panel
TC	Thermocouple
TPA	Tri-Party Agreement
TMACS	Tank Monitor and Control System
USQ	Unreviewed Safety Question
WAC	Washington State Administrative Code
WHC	Westinghouse Hanford Company
WSU	Washington State University

GLOSSARY

Ferrocyanide content: The purpose of ferrocyanide scavenging was to precipitate soluble ^{137}Cs as insoluble sodium cesium nickel ferrocyanide [$NaCsNiFe(CN)_6$]. The scavenger ferrocyanide component [$Na_4Fe(CN)_6$] was added at a concentration of several hundred times that required to precipitate all of the cesium as sodium cesium nickel ferrocyanide. Therefore, the predominant ferrocyanide compound in as-precipitated ferrocyanide scavenged solids is presumed to be disodium nickel ferrocyanide [$Na_2NiFe(CN)_6$]. However, the only validated analytical procedure for the actual waste measures total cyanide (CN). Thus, the reported total cyanide concentration in waste is converted to the equivalent $Na_2NiFe(CN)_6$ value. Of course, the number of g-moles of a nickel ferrocyanide [e.g., $Na_2NiFe(CN)_6$] is numerically equivalent to the number of g-moles of the ferrocyanide anion, $Fe(CN)_6^{4-}$. In this report, the ferrocyanide content has occasionally been abbreviated as FeCN (e.g., in Table 2-1) in order to conserve space.

Water content: The ferrocyanide-bearing solids may be dry; i.e., they may contain only $Na_2NiFe(CN)_6$ without water (other inert solids are also present in actual waste), or contain bound and free water.

Free water content: Free water in ferrocyanide waste is water that can be removed from samples using standard drying methods; for example, by drying the samples at 120 °C (248 °F) for 18 hr, or by using an equivalent analytical procedure. As an example, if a 10.0 g sample of waste lost 5.0 g of weight after drying at 120 °C for 18 hr, the free water content of the waste would be assigned a value of 50 wt%.

Bound water content: Bound water in ferrocyanide waste is water remaining after free water is removed. Bound water has been calculated to amount to 4.6 molecules of H_2O per molecule of disodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] on the basis of tests described in Postma et al. 1994 (Appendix B, Section B.3.2). This water is not driven off until the sample is heated to at least 160 °C (320 °F) or more.

Ferrocyanide concentration on an energy equivalent basis: The energy equivalent concentration of ferrocyanide is calculated by dividing the measured heat of reaction of a sample (in J/g of waste) by the heat of reaction of sodium nickel ferrocyanide (6,000 J/g of waste). Multiplying this value by 100% yields wt% energy equivalent sodium nickel ferrocyanide.

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PROGRAM PLAN FOR EVALUATION OF THE FERROCYANIDE WASTE TANK SAFETY ISSUE AT THE HANFORD SITE

1.0 INTRODUCTION

This document describes the background, priorities, strategy and logic, and task descriptions for the Ferrocyanide Waste Tank Safety Program. The Ferrocyanide Safety Program was established in 1990 to provide resolution of a major safety issue identified for 24 high-level radioactive waste tanks at the Hanford Site.

In March 1990, the Defense Nuclear Facilities Safety Board (DNFSB) provided its Recommendation 90-3 (DNFSB 1990a) to the U.S. Department of Energy (DOE) regarding the safety of storing ferrocyanide-bearing high-level radioactive waste (HLW) in single-shell tanks (SSTs) at the Hanford Site. The tanks of interest may contain significant amounts of ferrocyanide that, under certain concentrations and conditions, might increase in temperature to a value where ferrocyanide reactions could occur to challenge containment or release radioactive aerosols to the environment.

The DOE submitted an implementation plan to the DNFSB in August 1990 addressing the four parts of Recommendation 90-3. The DNFSB reviewed this implementation plan and determined that the plan did not adequately respond to its recommendation. To strengthen its concerns, the DNFSB restated its position in Recommendation 90-7, consisting of six parts (DNFSB 1990b). The DOE accepted Recommendation 90-7 and agreed to accelerate and expand its programs dealing with HLW safety issues at the Hanford Site. Subsequently, the Ferrocyanide Safety Program elements were accelerated and an expanded implementation plan was prepared for DNFSB Recommendation 90-7 (Cash 1991). DNFSB Recommendation 90-7 superseded Recommendation 90-3 because the actions recommended in 90-3 were reiterated in Recommendation 90-7. The implementation plan for Recommendation 90-7 was revised and resubmitted to the DOE in December 1992 (Borsheim et al. 1992).

The original Ferrocyanide Safety Program Plan (Cash and Mellinger 1991) was revised and reissued in July 1992 (Cash and Dukelow 1992). This revision of the document describes the continuing strategy planned for fiscal years (FY) 1994 and beyond for investigating the physical and chemical characteristics of Hanford Site ferrocyanide waste as required to complete the Ferrocyanide Safety Program. This document combines an update of the Ferrocyanide Program Plan and Implementation Plan into one document. The update, including changes in strategy and schedule, reflects new Ferrocyanide Safety Program information obtained as a result of extensive work on modeling, chemical reaction studies, physical properties, and tank waste sampling activities. The document also outlines the actions underway or planned to lessen environmental and safety concerns with interim storage of ferrocyanide waste until such time as the waste can be retrieved and treated for permanent disposal. A more detailed and current status of the Ferrocyanide Program is found in the quarterly reports (e.g., the quarterly issued for the period ending December 31, 1993) (Meacham et al. 1994). Activity Data Sheet 1110 (ADS 1110) in the *Environmental Restoration and Waste Management Five Year Plan* (DOE 1993a) provides the budget at the ADS level and presents the major milestones for the Ferrocyanide Safety Program. In addition, Reep (1993) provides more specific cost and schedule detail for the Ferrocyanide Safety Program. To assist the reader, the schedules are provided in Section 6.0 of this document.

2.0 BACKGROUND

Radioactive waste from defense operations has accumulated at the Hanford Site in underground waste tanks since the mid-1940s. During the 1950s, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short time period and to minimize the need for constructing additional storage tanks, Hanford Site scientists developed a process to scavenge ^{137}Cs from waste liquids. In implementing this process, approximately 140 metric tons (154 tons) of ferrocyanide were added to waste that was later routed to some Hanford Site SSTs. In 1991, based on available information, 24 tanks were assigned to the Ferrocyanide Watch List based on the criterion that they originally received inventories of at least 1,000 g-moles as the $Fe(CN)_6^{4-}$ anion.

Ferrocyanide, in the presence of oxidizing material such as sodium nitrate and/or nitrite, can be made to propagate and sometimes explode in the laboratory by heating it to high temperatures or by an electrical spark of sufficient energy. Under laboratory conditions deliberately created to enhance the potential for reactions, significant exothermic reactions can start as low as 220 °C (428 °F), but the lowest explosion temperature observed is approximately 285 °C (545 °F). The explosive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo endothermic and exothermic reactions have not been thoroughly studied. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate and nitrite, an intimate mixture of ferrocyanides and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

Efforts have been underway since the mid-1980s to evaluate the potential for ferrocyanide reactions in Hanford Site SSTs (Burger 1989; Burger and Scheele 1988). The potential consequences of a postulated ferrocyanide burn or explosion were not evaluated in the safety analyses or safety analysis reports (SARs) applicable to the Hanford Site SSTs. The SARs historically have considered an explosion from fuel/nitrate reactions as an incredible event and the consequences of incredible events are not required to be analyzed (WHC 1993b).

Although not considered a part of the safety analysis for the storage of waste in the SSTs, the 1987 Environmental Impact Statement (EIS), *Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington* (HDW-EIS) (DOE 1987) did include an environmental impact analysis of potential explosions involving ferrocyanide-nitrate mixtures. The EIS contained the postulation that an explosion could occur during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS authors concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a radiation dose of approximately 200 mrem. A General Accounting Office (GAO) study (Peach 1990) postulates a greater worst-case accident, with independently calculated doses of one to two orders of magnitude greater than in the DOE EIS (DOE 1987).

Coupling the ferrocyanide concerns with concerns about high organic concentrations and potential hydrogen accumulations in other Hanford Site HLW tanks, the DOE established the High-Level Radioactive Waste Tanks Task Force and Tanks Advisory Panel (TAP) in August 1990. These two groups were formed to ensure that all safety concerns with HLW tanks at DOE sites are identified and addressed in a systematic and timely manner. The initial focus of the task force and TAP was on the Hanford Site Flammable Gas and Ferrocyanide Safety Issues. In September 1990, a special Hanford Site ferrocyanide task team was commissioned by the Westinghouse Hanford Company (WHC) to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident.

The root cause of the ferrocyanide problem results from a combination of factors, beginning with the safety studies performed as precursors to using the ferrocyanide scavenging flowsheets. These studies did not include ultimate disposal of the ferrocyanide solids, and were not performed to the conservative standards used today, because the studies did not discuss the risk of adding ferrocyanide to waste tanks. In addition, no rigorous inventory was kept of the ferrocyanide or other chemicals added to the tanks. Subsequent safety studies either were not performed, or were performed to less conservative standards, to demonstrate that other chemicals would not increase the level of risk. Monitoring systems for designated SSTs, such as temperature measurement instrumentation, were allowed to be disconnected and to fall into disrepair because the potential hazard was not highlighted.

Although the HDW-EIS (DOE 1987) recognized the potential for a postulated explosion, the GAO disagreed with the assumptions of that document. Work performed by Pacific Northwest Laboratory (PNL) in 1984-85 identified a potential safety problem, but no funding was provided until 1989 to study this safety issue. An additional issue was subsequently communicated about the assumed radioactive material source term (release fraction) resulting from a postulated explosion (Peach 1990).

In October 1990 (Deaton 1990), the Ferrocyanide Safety Issue was declared an Unreviewed Safety Question (USQ)* because the safety envelope for these tanks was no longer bounded by the existing safety analysis report (RHO 1986). In 1991, using process knowledge, process records, transfer records, and log books, 24 tanks were identified at the Hanford Site as potentially containing 1,000 g-moles (465 lb) or more of ferrocyanide [as the

*An Unreviewed Safety Question, as defined by DOE Orders 5480.5 (DOE 1986) and 5480.21 (DOE 1991a), is determined as follows. "A proposed change, test or experiment shall be deemed to involve an USQ if the following apply:

a. The probability of occurrence or the consequences of an accident or malfunction of equipment important to safety, evaluated previously by safety analysis will be significantly increased, or

b. A possibility for an accident or malfunction of a different type than any evaluated previously by safety analysis will be created which could result in significant safety consequences."

$Fe(CN)_6^{4-}$ anion]. These tanks were placed on a Ferrocyanide Watch List (Public Law 101-510) because of the USQ. Work in and around any of the ferrocyanide tanks requires detailed planning, including preparing the supporting safety and environmental documentation and approval by DOE top management. These restrictions are imposed to ensure that appropriate precautions are taken to minimize the potential safety and environmental impacts associated with the USQ hazard. The need to evaluate the hazards and ensure that appropriate controls are implemented has, to date, increased the time required to complete work or install equipment in the tanks. Re-examination of the historical records (Borsheim and Simpson 1991) indicated that 6 of the 24 tanks do not contain the requisite 1,000 g-moles of ferrocyanide and should not have been included on the Watch List. Four of the 6 tanks were removed from the Watch List in July 1993 (Anttonen 1993) and removal of the other two tanks is pending (Borsheim et al. 1993).

The ferrocyanide USQ was closed on March 1, 1994 by order of the DOE Assistant Secretary for Environmental Restoration and Waste Management. Closure of the Ferrocyanide USQ was based upon safety criteria proposed by WHC and concurred on by outside reviewers and reviewers within DOE. This is the first USQ closure in the current Waste Tank Safety Program since the Watch List was created in 1991. The remainder of this document addresses the elements in the program to resolve the Ferrocyanide Safety Issue.

The current list of 20 ferrocyanide tanks is shown in Table 2-1. Five of the ferrocyanide tanks (241-BY-104, 241-BY-105, 241-BY-106, 241-BY-108, and 241-BY-110) have temperature readings above 38 °C (100 °F), but below 55 °C (131 °F). Each of these five tanks was estimated to contain an original inventory of ferrocyanide ranging from 36,000 g-moles (16,750 lb) to 83,000 g-moles (38,600 lb), and have been assigned a high priority for installation of expanded tank monitoring capabilities. Temperatures in the remaining 15 tanks are below 38 °C (100 °F), and many contain an original inventory of less than 10,000 g-moles (4,650 lb) of ferrocyanide. The four 241-C farm tanks (241-C-108, 241-C-109, 241-C-111, and 241-C-112) were estimated to have originally received a somewhat smaller ferrocyanide inventory, 25,000 g-moles (11,600 lb) to 33,000 g-moles (15,300 lb), but are postulated to have the highest ferrocyanide concentrations because they contain waste from a scavenging flowsheet different from the 241-BY tanks. These C Farm tanks are a high priority for core sampling and two of the tanks (241-C-109 and -112) have been core sampled. (Sample results are discussed in Section 5.4).

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Tank	Waste Processing Source	FeCN* Content (1,000 g-moles)	^{137}Cs (Ci) Decayed To January 1991			^{90}Sr (Ci) Decayed To January 1991		Stabiliz	
		(1)	Total (2)	Total (3)	FeCN sludge content only (1)	(3)	FeCN sludge content only (1)	Interim stabilized	Sal pun
BX-102	U Plant	<1		2.6 E+05	--	1.7 E+05	--	Y	
BX-106	U Plant	<1		6.1 E+06	--	1.7 E+06	--	N	
BY-103	U Plant	66	1.4 E+05	2.6 E+04	1.6 E+05	6.9 E+05	2.3 E+05	N	
BY-104	U Plant	83	2.1 E+05	5.2 E+05	2.0 E+05	2.6 E+05	3.0 E+05	Y	Y
BY-105	U Plant	36	1.8 E+05	4.4 E+05	8.8 E+04	2.6 E+05	1.3 E+05	N	
BY-106	U Plant	70	4.5 E+05	5.2 E+05	2.2 E+05	3.5 E+05	3.3 E+05	N	
BY-107	U Plant	42	1.7 E+05	1.7 E+05	1.3 E+05	1.7 E+05	2.2 E+05	Y	Y
BY-108	U Plant	58		2.6 E+05	2.1 E+05	5.2 E+04	2.6 E+05	Y	Y
BY-110	U Plant	71	2.3 E+05	5.2 E+05	1.9 E+05	3.5 E+05	3.2 E+05	Y	Y
BY-111	U Plant	6	1.0 E+05	5.2 E+05	1.1 E+04	3.5 E+05	1.9 E+04	Y	Y
BY-112	U Plant	2	7.5 E+04	7.8 E+04	5.1 E+03	7.8 E+04	8.1 E+03	Y	Y
C-108	In Farm	25		4.0 E+00	6.5 E+04	2.6 E+04	5.9 E+02	Y	
C-109	In Farm	6.8[8]		5.2 E+03	1.1 E+05	7.0 E+01	3.8 E+03	Y	
C-111	In Farm	33		4.3 E+03	1.4 E+04	8.6 E+04	8.1 E+02	Y	
C-112	In Farm	11.5[9]		3.5 E+03	1.3 E+05	4.3 E+04	1.4 E+03	Y	
T-107	U Plant	5		--	7.8 E+03	3.5 E+04	1.3 E+04	N	
TX-118	U and T Plants	<3	5.3 E+04	9.0 E+05	--	1.0 E+06	--	Y	Y
TY-101	T Plant	23		7.0 E+03	4.2 E+04	1.7 E+04	3.7 E+04	Y	Y
TY-103	T Plant	28	3.7 E+04	1.7 E+05	5.2 E+04	8.7 E+04	4.5 E+04	Y	Y
TY-104	T Plant	12		1.7 E+03	2.1 E+04	7.0 E+03	1.9 E+04	Y	

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4. Hanlon, B. M., *Tank Farm Surveillance and Waste Tank Summary Report for November 1993*, WHC-EP-0182-68, Westinghouse Hanford
5. Anderson, J. D., *A History of the 200 Area Tank Farms*, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington, 1990.
6. Readings from newly installed instrument trees; Tank 241-BY-105 already had two trees.
7. Reading from TC element in LOW.
8. Simpson, B. C., et al., *Tank Characterization Report: Tank 241-C-109*, WHC-EP-0668, Westinghouse Hanford Company, Richland, Wasl
9. Simpson, B. C., et al., *Tank Characterization Data Report: Tank 241-C-112*, WHC-EP-0640, Rev. 1, Westinghouse Hanford Company, I
10. Readings not yet taken on the new instrument tree.

DT = Dip tubes FIC = Food Instruments Corporation (Auto tape) MT = Manual tape NM = Not mea
*FeCN = $Fe(CN)_6^{4}$ LOW = Liquid observation well (thermocouple) N = No P = Partially

Table 2-1. Ferrocyanide Tank Data Summary.

...tion Status		Solids Volume/Height (kgal/ft)			Supernate Above Solids	Liquid Levels (ft)		Maximum Temperature As Of February 1994
...well jet ...ped (end ...date)	Contains LOW	Total	FeCN sludge		(4)	DT/MT ZC/FIC	LOW (neutron/ gamma)	°C (°F)
		(4)	(5)	(1)				
N	N	96/3.5	NM	0	N	2.5	--	17 (63)
N	N	31/1.6	NM	0	Y	1.0	--	18 (64) 18 (64)[6]
P	Y	400/12.7	NM	212/7.0	N	10.0	11.9/11.3	27 (81)
(11/84)	Y	406/12.9	244/8.0	260/8.5	N	4.0	7.0/6.7	54 (128) 46 (114)[6]
N	Y	503/15.9	213/7.1	96/3.5	N	--	13.6/14.8	45 (113) 49 (120)
N	Y	642/20.1	111/4.0	228/7.5	N	--	18.5/18.6	54 (129)
(7/79)	Y	266/8.7	172/5.8	158/5.4	N	--	5.1/5.6	34 (93)
(12/84)	N	228/7.5	201/6.7	208/6.9	N	4.8	--	43 (110)
(12/84)	Y	398/12.7	211/7.0	225/7.4	N	5.0	6.2/5.9	48 (118) 43 (109)[6]
(11/84)	Y	459/14.5	26/1.4	14/1.1	N	2.3	6.8/4.0	31 (87)[7] 29 (84)[6]
(5/84)	Y	291/9.4	NM	7/0.7	N	1.6	2.8/3.1	28 (83)[7] 32 (90)[6]
N	N	66/2.6	79/3.0	77/3.0	N	1.6	--	23 (74) 24 (76)[6]
N	N	62/2.5	90/3.3	109/3.9	Y	1.6	--	26 (78) 24 (76)[6]
N	N	57/2.3	95/3.5	98/3.6	N	1.3	--	22 (72)
N	N	104/3.8	46/2.0	84/3.2	N	--	--	27 (80) 24 (76)[6]
N	N	171/5.8	201/6.7	212/7.0	Y	5.1	--	18 (65)
(2/83)	Y	347/11.1	6/0.6	--	N	3.3	4.4/4.8	25 (77) -- (--)[10]
(2/83)	N	118/4.2	183/6.2	151/5.2	N	1.4	--	18 (65)
(12/82)	Y	162/5.5	188/6.3	179/6.0	N	4.7	4.9/4.1	21 (69)
N	N	43/1.9	74/2.9	75/2.9	Y	2.0	--	18 (65)

...ouse Hanford Company, Richland, Washington, 1991.
...*ste Tanks*, WHC-SA-1196-A, Westinghouse Hanford Company, Richland, Washington, 1991.
...ll Hanford Operations, Richland, Washington, 1984.
...ompany, Richland, Washington, 1994.

...ngton, 1993a.
...chland, Washington, 1993b.

...ured Y = Yes
ZC = Zip cord

3.0 THE FERROCYANIDE SAFETY PROGRAM

3.1 OBJECTIVES

The Ferrocyanide Safety Program objectives are to obtain a thorough understanding of the ferrocyanide tank waste and the reactive behavior of the waste constituents so that: (1) safety criteria and tank conditions can be defined that ensure interim safe storage of the waste with minimal risk of an accident; (2) the Ferrocyanide USQ can be closed in an expedient manner; and (3) sufficient information can be gathered to resolve the safety issue and remove all ferrocyanide tanks from the Watch List. If the third objective cannot be met, then one or more strategies must be selected to implement mitigation or remediation of the waste.

3.2 PRIORITIES

All activities of the waste tank safety program are prioritized according to the methods discussed in Section 6.1 of the *Waste Tank Safety Program Overview Plan, N2 End Function* (Gasper and Reep 1992). All work being conducted for the Ferrocyanide Safety Program in FY 1994 and beyond is classified as Priority 1 work until the individual tanks are removed from the Watch List or the Ferrocyanide Safety Issue is resolved. Priority 1 work definitions are summarized below.

Priority 1 work includes activities necessary to prevent near-term adverse impacts to workers, the public, or the environment. Examples include: (1) containment to prevent the spread of contamination; (2) actions to prevent or minimize releases to the environment; and (3) ongoing waste management activities to maintain safe conditions. Priority 1 work also includes ongoing activities that, if terminated, could result in significant program and/or resource impacts, such as significantly increased risk to the environment (or to workers) or significantly increased costs.

Priority 1 Subcategories are as follows:

Priority Subcategory 1A: Provide Safe Operation.

- Address an imminent human health and safety problem, or an imminent release that could cause a widespread environmental impact.
- Reduce the probability of major damage to equipment/facilities to avoid impacts to human health and/or the environment.
- Maintain safe conditions.

Prioritization within Subcategory 1A was developed by DOE-RL and WHC because of the large amount of Subcategory 1A work. Divisions to Subcategory 1A are as follows:

- 1A.a Safe Operations (base case)
- 1A.b USQ Work
- 1A.c Safety Mitigation Work
- 1A.d Improvements (new) to Safe Operations
- 1A.e Safety Remediation
- 1A.f Improvements (longer term) to Safe Operations.

Priority Subcategory 1B: Prevent Potential Releases to the Environment.

- Provide monitoring and surveillance of waste problem.
- Contain, treat, or remove materials that could potentially cause near-term impact.

Priority Subcategory 1C: Maintain Ongoing Activities.

- Complete activities being conducted to minimize near-term health, safety, or environmental impacts, for which substantial funding has been expended.
- Maintain ongoing activities that, if terminated, could result in significant Environmental Restoration and Waste Management program impacts and/or resource impacts.

Major Ferrocyanide Safety Program activities for FY 1994 and beyond have been prioritized using the guidelines above. These categories are listed (as follows) to provide effective use of resources.

1. Enhance monitoring of ferrocyanide tank conditions.
2. Complete interim stabilization of the ferrocyanide tanks (to meet Tri-Party Agreement pumping milestone).
3. Continue characterization of ferrocyanide tank waste.
4. Continue ferrocyanide waste simulant chemical reaction studies.

5. Develop a DOE-approved strategy for closure of the Ferrocyanide USQ and resolving the safety issue.

6. Determine effects of changing ferrocyanide tank conditions resulting from pumping/removal of supernate and/or drainable interstitial liquid from tanks.

7. Evaluate ferrocyanide tanks to determine if waste can be safely stored or if mitigation/remediation is required.

These priorities are used to establish the baseline budgets for FY 1994 and beyond. Activities being conducted within the baseline budget are described in Section 5.0.

3.3 DRIVERS

Several requirements, or drivers, for conducting activities in the Ferrocyanide Safety Program have been identified and are briefly summarized below. These requirements (laws, codes, regulations, orders) provide the basis for establishing program priorities and the technical criteria for completing program activities.

3.3.1 Safety Measures Law

Waste tank safety is a primary safety concern within the DOE complex. Concern for waste tank safety at the Hanford Site was sufficient to compel the U.S. Congress to pass Public Law 101-510, Section 3137, *Safety Measures for Waste Tanks at Hanford Nuclear Reservation* (the Safety Measures Law). This law requires the following actions.

- Identify tanks that "may have a serious potential for release of high-level waste due to uncontrolled increases in temperature or pressure."

- Ensure that "continuous monitoring to detect a release or excessive temperature or pressure" is being carried out.

- Develop "action plans to respond to excessive temperature or pressure or a release from any tank identified."

- Restrict additions of high-level nuclear waste to the identified tanks unless no safer alternative exists, or the serious potential for a release of high-level nuclear waste is no longer a threat.

- Report "on actions taken to promote tank safety, including actions specifically taken pursuant to this section of the law, and the ... timetable for resolving the outstanding issues on how to handle the waste in such tanks."

The Waste Tank Safety Programs are the key element in responding to this law. (See also Reep 1993).

3.3.2 Atomic Energy Act of 1954

The following DOE orders are major drivers. The orders involve the management of waste containing radioactivity for the DOE under the *Atomic Energy Act of 1954*, as amended by Public Law 83-703.

- DOE Order 5820.2A, *Radioactive Waste Management* (DOE 1988)
- DOE Order 5480.1B, *Environmental, Safety, and Health Program for Department of Energy Operations* (DOE 1993b)
- DOE Order 5480.5, *Safety of Nuclear Facilities* (DOE 1986)
- DOE Order 5480.23, *Nuclear Safety Analysis Reports* (DOE 1992)
- DOE Order 6430.1A, *General Design Criteria* (DOE 1989)
- DOE Order 5480.21, *Unreviewed Safety Questions* (DOE 1991a).

3.3.3 Code of Federal Regulations

The following Federal regulations are drivers for Waste Tank Safety Programs:

- 10 CFR 962, "Radioactive Waste: Byproduct Material"
- 10 CFR 1021, "Department of Energy NEPA Implementing Procedures"
- 40 CFR 191, "Environmental Radiation Protection Standards for Management and Disposal of Spent Nuclear Fuel, High-Level and Transuranic Radioactive Wastes"
- 40 CFR 261, "Identification and Listing of Hazardous Waste"
- 40 CFR 262, "Standards Applicable to Generators of Hazardous Waste"
- 40 CFR 1500-1508, "Regulations for Implementing the Procedural Provisions of the National Environmental Policy Act."

3.3.4 Unreviewed Safety Question

The safety issue of potentially explosive ferrocyanide mixtures has been identified as a USQ (Deaton 1990) because it "represents conditions outside the identified safety envelope" as specified in DOE Order 5480.21 (DOE 1991a) and WHC-CM-1-3, *Management Requirements and Procedures,* Section 5.12, "Identification and Resolution of Unreviewed Safety Questions" (WHC 1992).

3.3.5 Washington State Administrative Code

Waste Tank Safety Programs activities must comply with the State of Washington Administrative Codes (WAC) with respect to managing dangerous waste. The specific regulation is WAC 173-303, *Dangerous Waste Regulations*, Section 110, "Sampling and Testing Methods."

3.3.6 Defense Nuclear Facilities Safety Board

The DNFSB was created to provide advice and formal recommendations to the President of the United States and to the Secretary of Energy regarding public health and safety issues at DOE nuclear facilities. The DNFSB reviews operations, practices, and occurrences at DOE nuclear facilities and makes appropriate health and safety recommendations. If any aspect of operations, practices, or occurrences reviewed by the DNFSB is determined to present an imminent or severe threat to public health or safety, the DNFSB transmits its recommendations directly to the President.

3.3.7 Tri-Party Agreement

The *Hanford Federal Facility Agreement and Consent Order* [Tri-Party Agreement (TPA)] (Ecology et al. 1990) contains provisions governing the treatment, storage, and disposal of hazardous waste, including remedial and corrective action activities. During 1993 new negotiations were conducted by DOE, U.S. Environmental Protection Agency (EPA), and Washington State Department of Ecology (Ecology). New milestones were negotiated and a reduced set of specifications for waste analyses and characterization was adopted (Ecology et al. 1994).

3.4 QUALITY ASSURANCE

Quality Assurance (QA) is an integral part of any successful program. It provides for independent oversight at the planning, implementation, and completion stages to ensure appropriate management so that stated objectives and goals are achieved. The QA process allows for: (1) statistical evaluation of technical analysis for sufficiency and accuracy; (2) methodology review and evaluation; and (3) records management and validation of data (including traceability).

At the Hanford Site, DOE has the primary responsibility to ensure that performed activities are handled in an efficient and cost-effective manner. To control the quality of these activities, DOE has imposed DOE Order 5700.6C (DOE 1991b). These orders require the selective and judicious application of requirements from the national consensus standard *ASME NQA-1, Quality Assurance Requirements for Nuclear Facilities*.

For environmental programs at the Hanford Site, quality program requirements are imposed by the Tri-Party Agreement (Ecology et al. 1990, 1994). The Tri-Party Agreement, and amendments thereto, specify that all parties shall use procedures for QA and Quality Control in accordance with EPA methods. Two EPA documents that define guidance to this methodology are QAMS OO5/80, *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* (EPA 1983), and EPA/540/G-87/003, *Data Quality Objectives for Remedial Response Activities* (EPA 1987). During 1993 new negotiations were conducted by DOE, EPA, and Ecology. New milestones were negotiated and a reduced set of specifications for waste analyses and characterization was adopted. However, the QA requirements were not changed.

WHC directs compliance with DOE quality requirements in WHC-CM-4-2, *Quality Assurance* (WHC 1993a), which imposes the criteria of ASME NQA-1 on all quality-affecting activities performed by WHC personnel. The EPA quality requirements are specified in the existing quality programs to ensure overall compliance with the Tri-Party Agreement.

4.0 FERROCYANIDE PROGRAM STRATEGY, LOGIC, AND DOCUMENTATION

The ultimate objective of the Ferrocyanide Safety Program is to resolve the safety issue by determining if storage of ferrocyanide waste in Hanford Site SSTs is safe until the waste can be exhumed and treated for final disposal in the Hanford Waste Vitrification Plant. This section identifies why, when, and how activities leading to resolution of the Ferrocyanide Safety Issue are to be accomplished. Decision points in the logic diagrams will be used to determine the activities that will actually be conducted to address high priority issues and to use resources in an effective manner.

4.1 CLOSURE OF THE FERROCYANIDE UNREVIEWED SAFETY QUESTION AND RESOLUTION OF THE SAFETY ISSUE

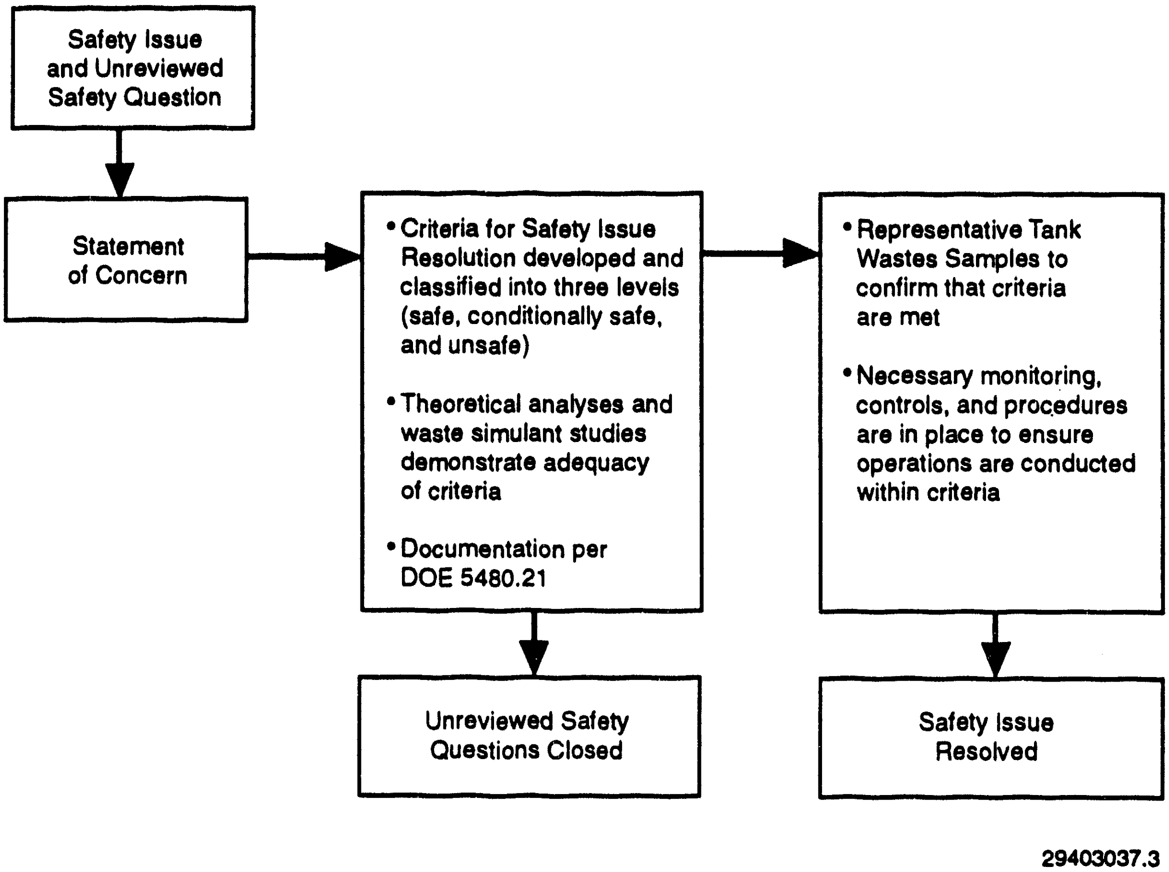
A strategy for closing the USQ and resolving the safety issue surrounding the ferrocyanide waste was developed by DOE and WHC and presented to DNFSB in August 1993 (Grumbly 1993). A summary of the strategy is presented in Figure 4-1. The strategy contains two key steps: (1) development of criteria for 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 of the tank contents.

As part of the accelerated Safety Initiatives (O'Leary 1993), closure of the Ferrocyanide USQ was moved forward from September 1994 to January 1994. This, coupled with the new strategy for USQ closure, resulted in the improved schedule for USQ closure. The USQ was closed formally by DOE on the basis of documented criteria (Sheridan 1994). Resolving the Ferrocyanide Safety Issue, however, will be a follow-on effort that requires the sampling of the ferrocyanide tank waste to quantify the potential for hazardous reactions.

The new strategy uncoupled USQ closure from resolving the safety issue. Figure 4-1 shows USQ closure as a milestone on the path to resolving the safety issue. The USQ was closed using the criteria document that identifies safety categories, criteria for each category, and the technical basis for the criteria (Postma 1994).

To close the USQ, the tanks were categorized using these criteria into one of three safety levels: SAFE, CONDITIONALLY SAFE, or UNSAFE. The safety issue can be resolved after the tanks are characterized and necessary monitoring and controls are in place, if required, to ensure operations are conducted within the SAFE or CONDITIONALLY SAFE levels. While closure of the USQ was a near-term objective, resolving the safety issue will require a longer time frame, because it requires obtaining samples and characterization data on the tank waste.

Figure 4-1. Strategy for Closing the Ferrocyanide USQ and Resolving the Safety Issue.



The logic leading to resolution of the Ferrocyanide Safety Issue was developed from a concept paper prepared by Science Applications International Corporation (SAIC 1991) and is presented in Figure 4-2. Discussion of the tasks identified in the logic diagrams follows the figures. These logic diagrams show the flow of work and the major task relationships for the zero option (demonstrating that continued storage of waste containing ferrocyanide is safe) and alternative options of mitigation and/or remediation if the zero option does not lead to resolving the safety issue. The present corrective action path is to confirm that in situ safe storage of the waste is already in effect or is possible by establishing the types of controls and surveillances that might be necessary. Controls and surveillances for temperature and moisture may be required to ensure some tanks are CONDITIONALLY SAFE.

Task 1.0 - Define and Evaluate the Ferrocyanide Safety Problem

To develop the safety envelope, the hazards associated with ferrocyanide waste stored in Hanford Site SSTs are being evaluated.

Task 1.1 - Establish Preliminary Hypothesis

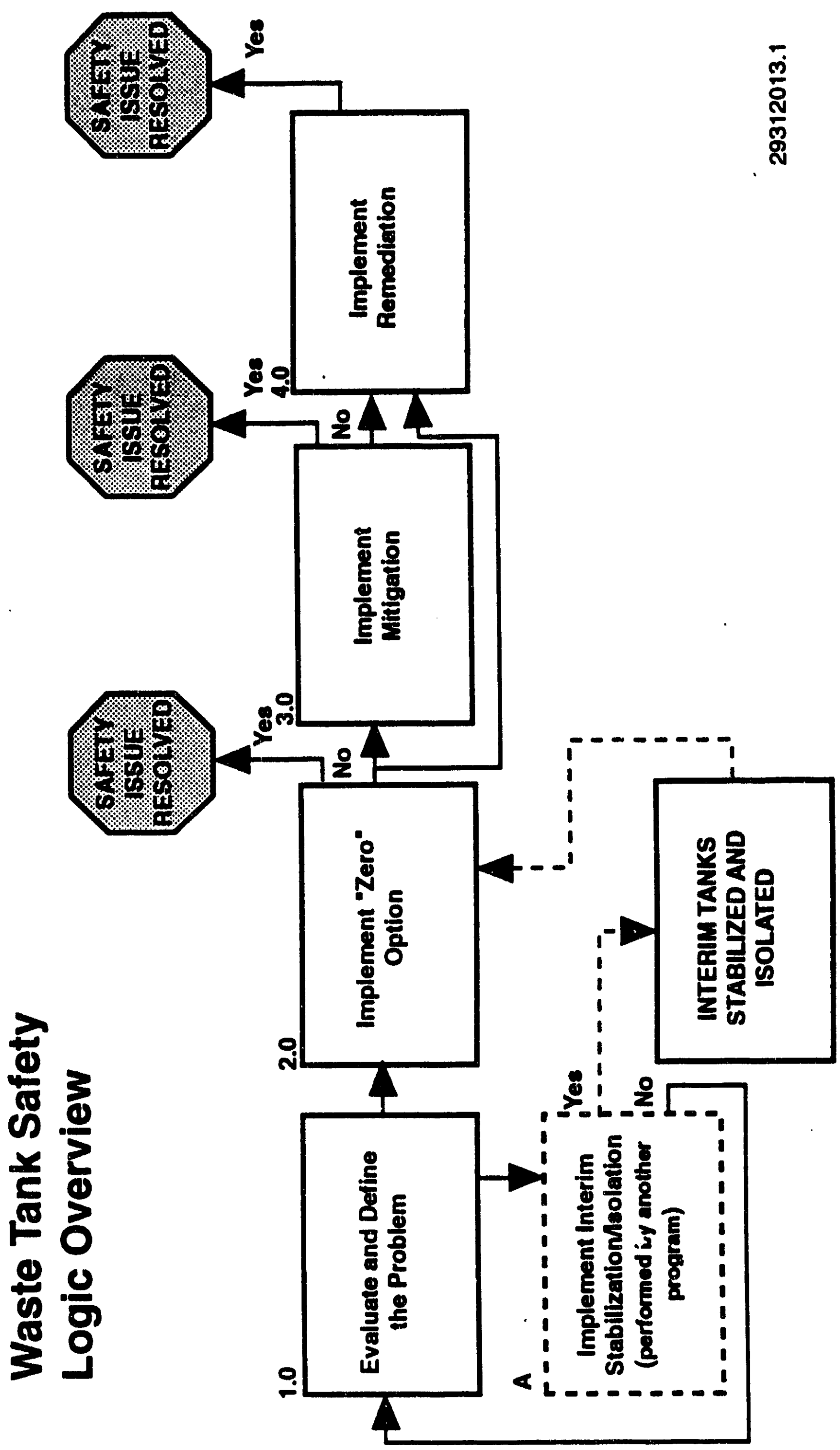
Preliminary hypotheses of hazardous mechanisms associated with ferrocyanide waste stored in Hanford Site SSTs have been established. A candidate model was developed that replicates the conditions expected in the tank, consistent with the tank contents as estimated from simulant flowsheet data, tank monitoring, and actual waste sample analyses.

Develop Model. Evaluation of the Ferrocyanide Safety Issue is being pursued through five paths: (1) historical information, (2) waste monitoring, (3) waste modeling, (4) simulant waste studies, and (5) analyses of actual waste samples. No combination of these paths, short of all paths, is adequate to address all of the safety concerns associated with the Ferrocyanide Safety Issue. Results from each of these five paths must be used in the decision logic to resolve the safety issue.

Information needed to determine actions necessary to address any unsafe condition in ferrocyanide waste tanks that may be identified include: (1) categorizing tanks that contain greater than 1,000 g-moles (465 lb) of ferrocyanide according to the flowsheet used; (2) establishing a reaction onset temperature for the ferrocyanide waste in each of these tanks; (3) establishing the moisture content for which the ferrocyanide waste in each designated ferrocyanide tank cannot react and propagate; and (4) identifying the ferrocyanide concentration in each ferrocyanide tank below which the waste cannot react and propagate.

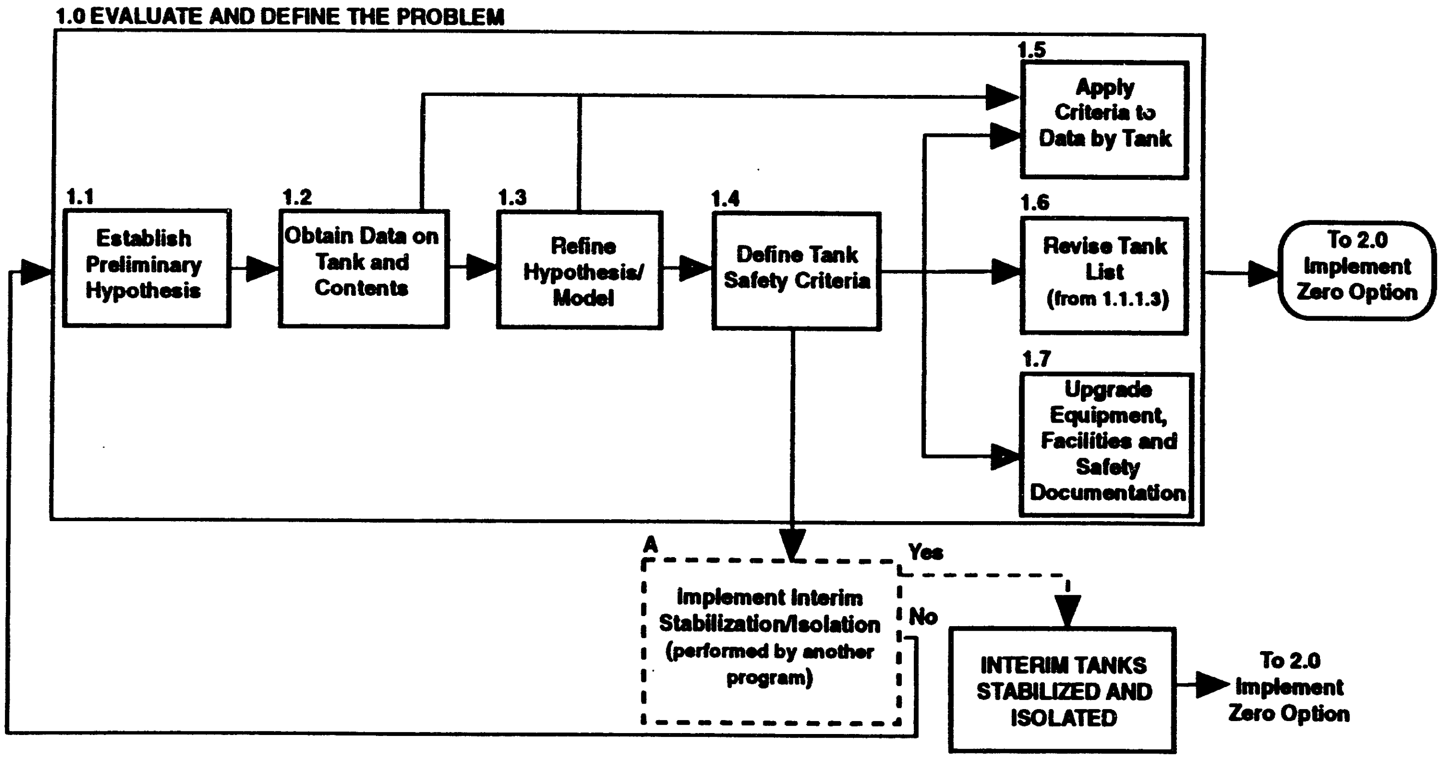
As necessary, the Hanford Site Emergency Plan response actions have been and will continue to be upgraded to include actions to be taken if abnormal conditions are detected and must be corrected (Cash and Thurman 1991b, WHC 1991). The planned response is reviewed and revised as required to accommodate an improved understanding of possible events.

Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 1 of 8)



Logic for Waste Tank Safety Issue Resolution in Network Format

(By Tank or Groups of Tanks)



29312013.2

Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 2 of 8)

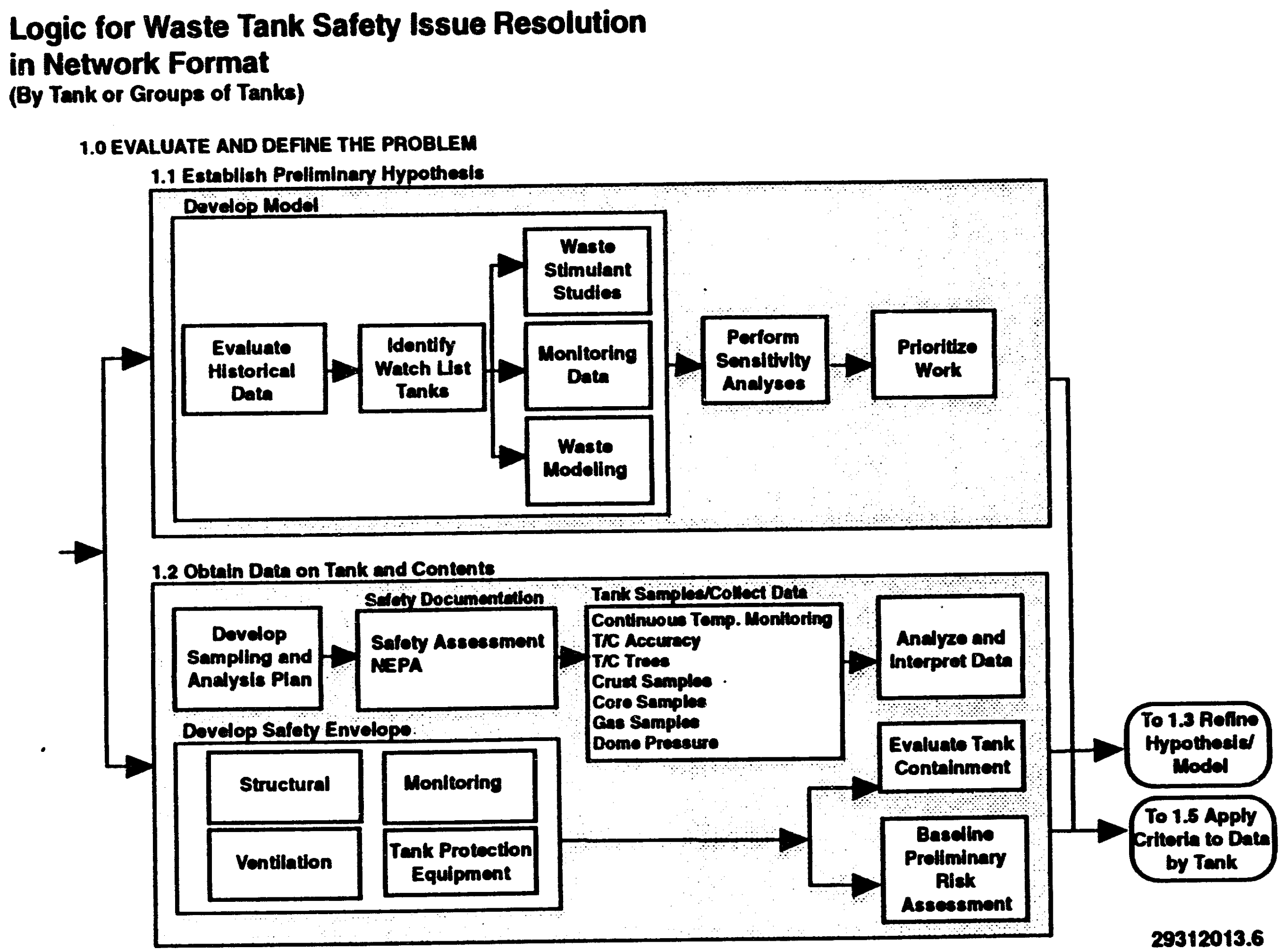


Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 3 of 8)

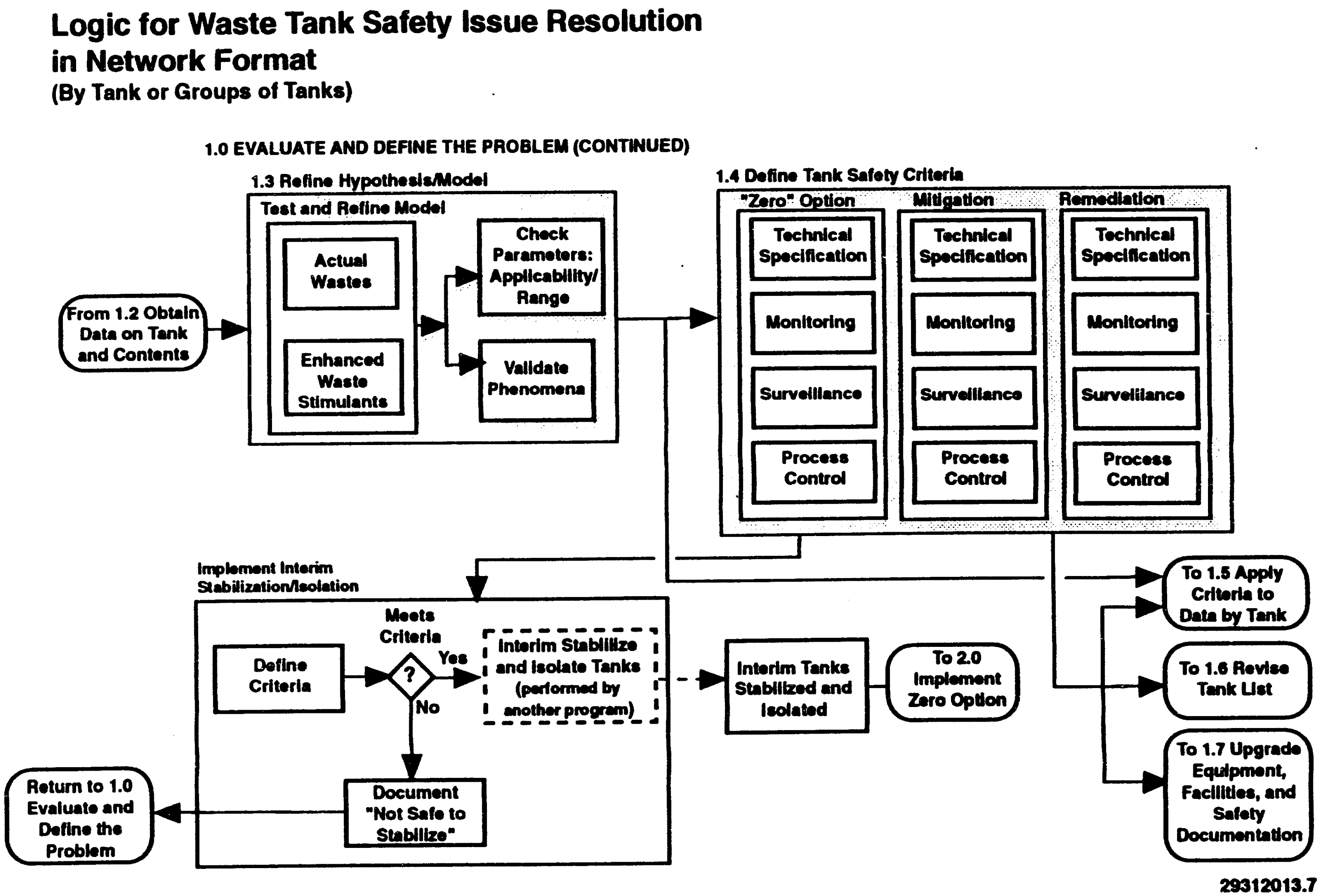


Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 4 of 8)

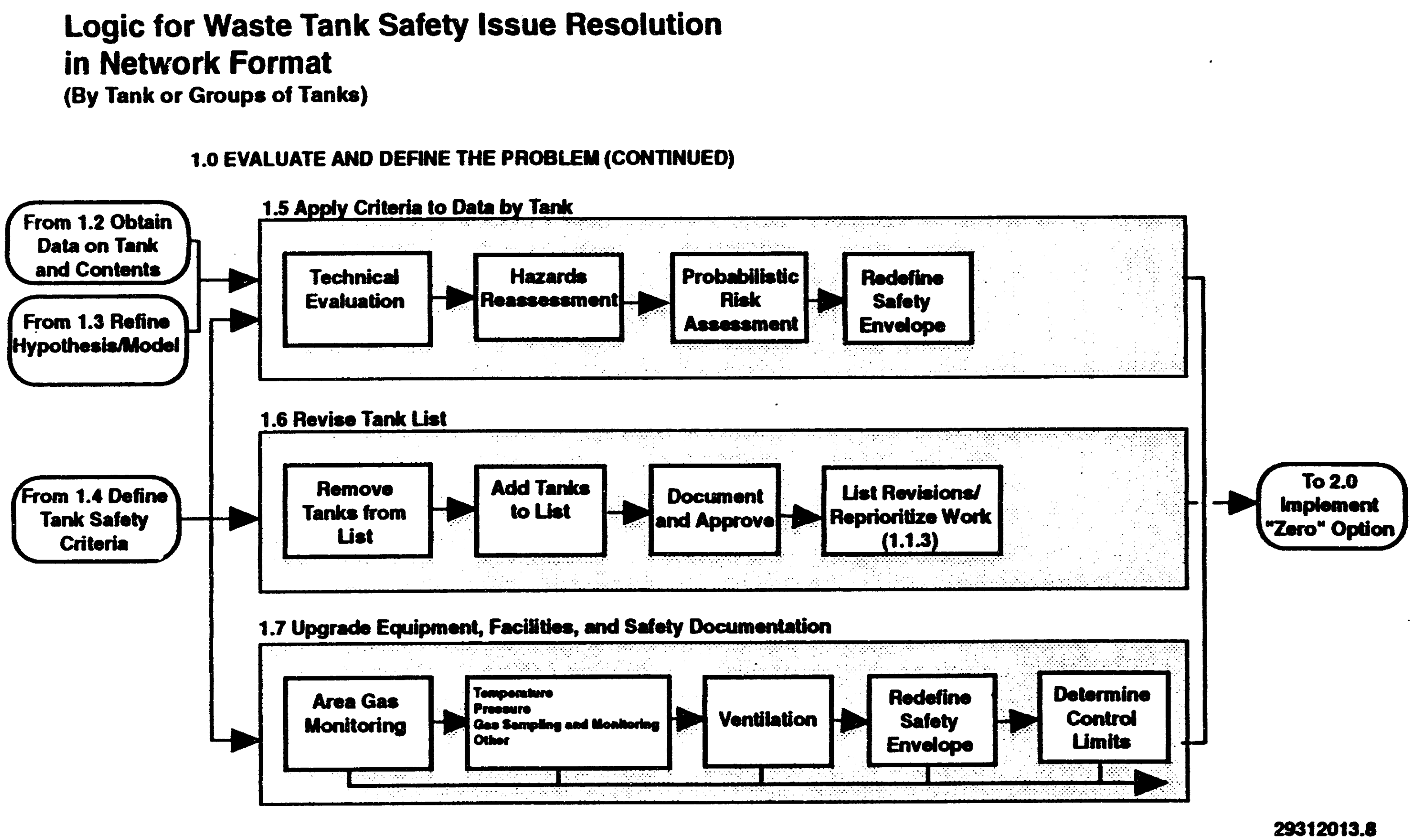


Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 5 of 8)

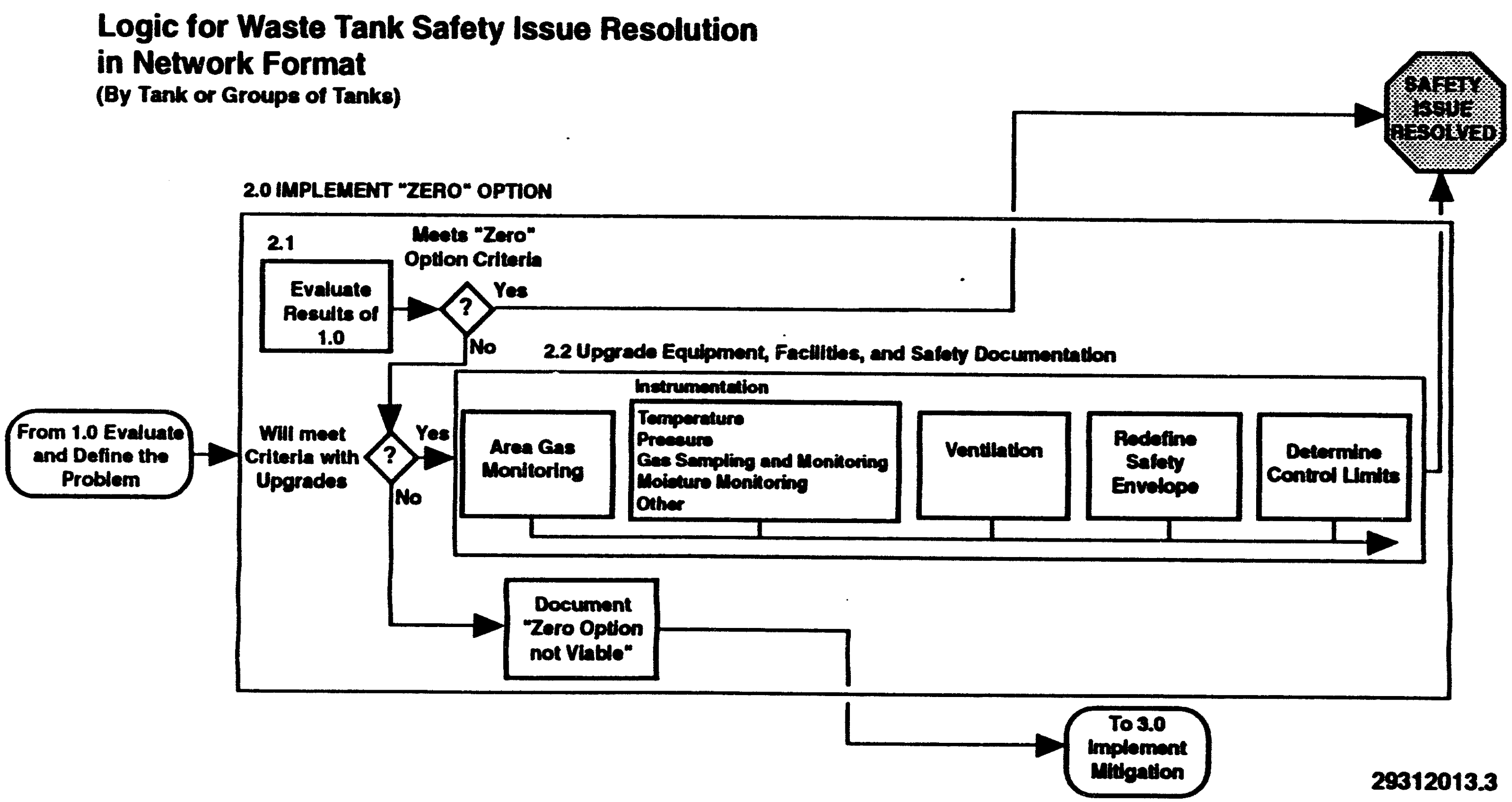


Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 6 of 8)

Logic for Waste Tank Safety Issue Resolution in Network Format
(By Tank or Groups of Tanks)

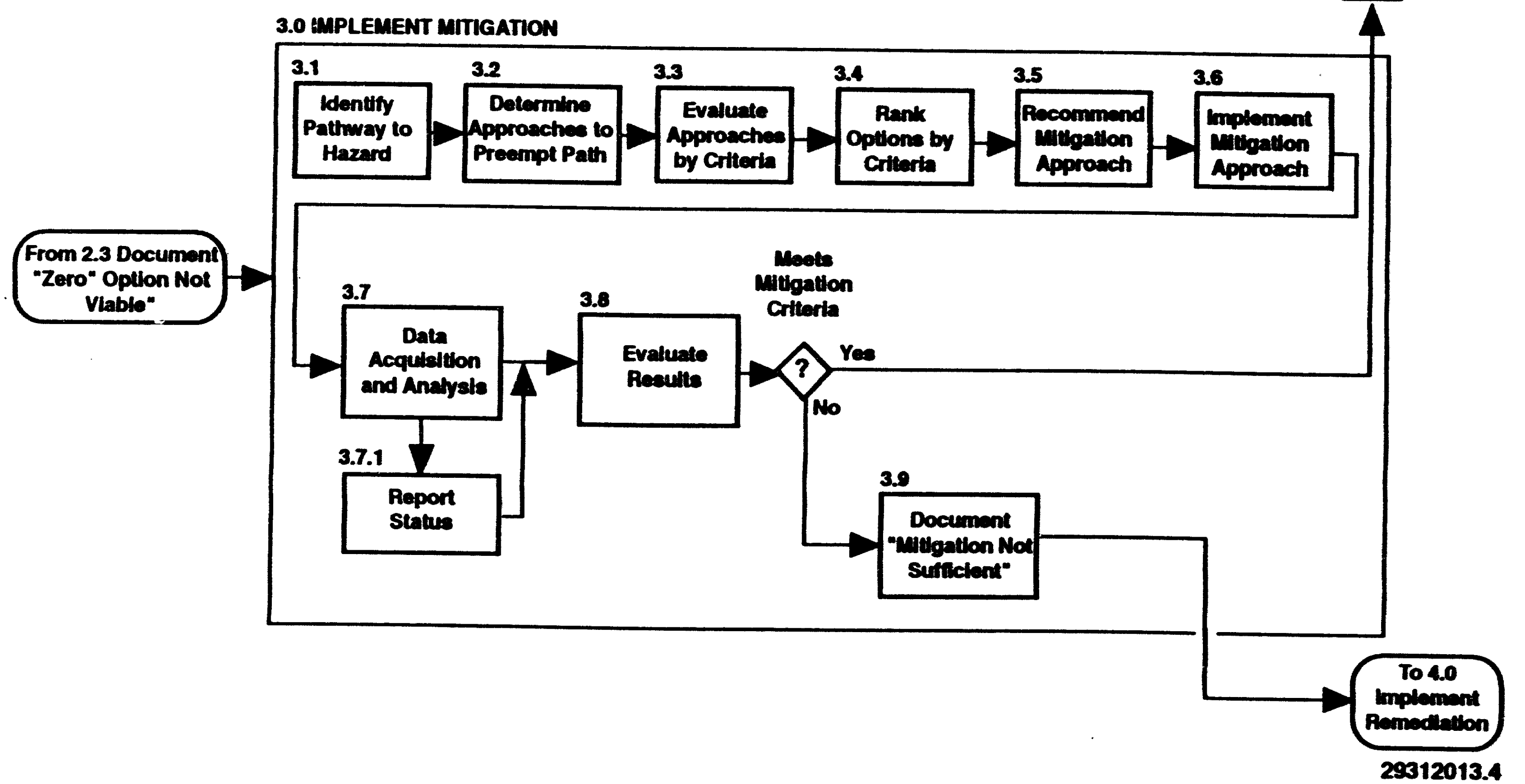
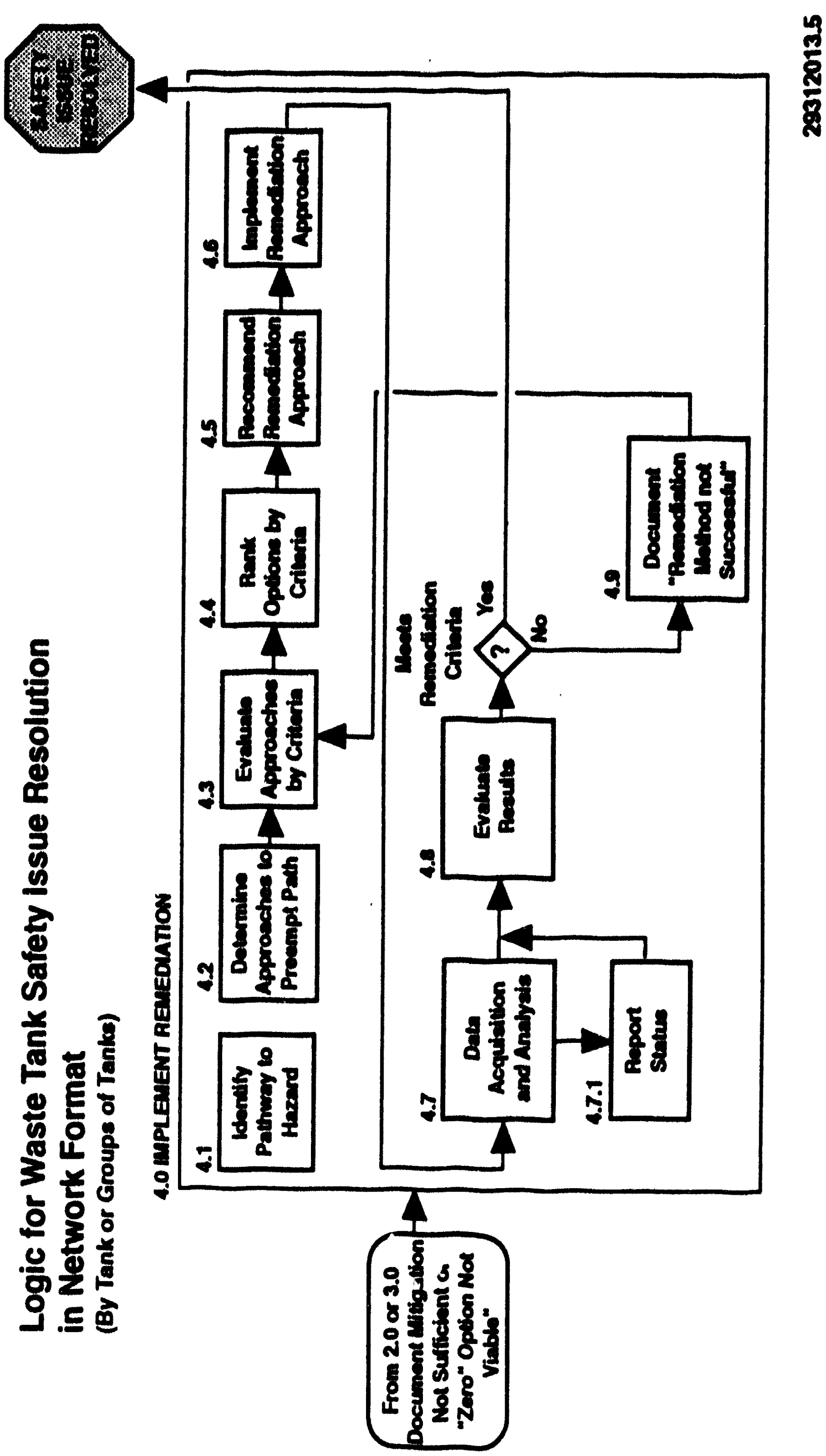


Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 7 of 8)

Figure 4-2. Logic Leading to Resolving the Safety Issue. (Sheet 8 of 8)



The endpoint of this task is to provide a model of the waste incorporating the following parameters for each ferrocyanide tank:

- Fuel concentration
- Moisture concentration
- Temperature
- Energetics (heat of reaction)
- Propagation characteristics
- Concentration of heat-producing isotopes (cesium and strontium) and total tank heat load
- Thermal conductivity and heat capacity values
- Determining possible catalysts, initiators, and additional fuel sources.

This effort would include defining the probability and, if credible, the size of potential dry and/or hot spots that may allow localized ferrocyanide reactions to cause safety concerns. This task is being conducted in parallel with Task 1.2, and the model development will include available data input from both Tasks 1.1 (Preliminary Hypothesis) and 1.2 (Tank Waste Sample Analyses).

Evaluate Historical Data. Historical process data have been evaluated to provide an assessment of the ferrocyanide inventories that were originally placed in each tank, and any transfers of sludge that may have occurred since then. The evaluation included examination of process flowsheets and information from the Track Radioactive Components Program (Jungfleisch 1984) and the detailed logbook kept during the 1950s scavenging campaigns (GE 1958). Recent efforts at Los Alamos National Laboratory (LANL) have also examined Hanford Site documentation to determine sludge levels in the ferrocyanide tanks (Agnew 1993). Twenty-four tanks were listed as containing greater than 1,000 g-moles (465 lb) of ferrocyanide. However, re-examination of the historical records indicated that six of these tanks were erroneously placed on the Watch List and do not contain the requisite 1,000 g-moles (Borsheim and Simpson 1991, Borsheim et al. 1993). Four of the six tanks were removed from the Watch List in July 1993 (Anttonen 1993) and two additional tanks are pending (Alumkal 1993, Borsheim et al. 1993).

Identify Watch List Tanks. The current list of ferrocyanide tanks was developed from the review of historic records and will be reappraised as additional information is obtained and as actual tank waste samples are analyzed (see Section 4.3).

Waste Simulant Studies. Laboratory studies are being conducted on flowsheet-produced ferrocyanide waste simulants. These studies are being used to provide information on: (1) ferrocyanide species present in tank waste; (2) heats of reaction (energetics) for each flowsheet simulant and actual waste samples; (3) temperatures for initiating reactions; (4) effects of water content on ferrocyanide reactions; (5) effects of possible catalysts, initiators, and diluents on ferrocyanide reactions; (6) thermal hydraulic properties; (7) kinetics of ferrocyanide waste reactions; and (8) heat load modeling.

Five waste simulants (without radioactive species) have been or are being used to represent the various ferrocyanide sludges produced at the Hanford Site. These simulants were prepared to represent the highest ferrocyanide concentrations used in the 1950s (In Farm 1 and U Plant 2), and typical ferrocyanide sludge (U Plant 1, In Farm 2, and T Plant), to effectively relate to all safety considerations. Results from these studies are providing waste characterization and reactivity data about each of the five sludge types in the tanks. Parameters, such as the effect of moisture on propagation rates and onset temperatures, waste density, particle size, and solid diluents present in the waste, are being determined. Thermal conductivity and heat capacity values of ferrocyanide waste and any overburden waste will be measured. Analytical methods will be developed to routinely determine concentrations of ferrocyanide species in the tank sludges. Dissolution and dispersion of ferrocyanide in high pH solutions under radiolysis (aging) are also being examined. Reaction products from hydrolysis and radiolysis, and rates of reactions are being determined. The cesium uptake capacity for flowsheet sludges will be evaluated as a possible mechanism for heat concentration in the waste. Data from these studies, actual tank waste sample analyses, historical accounting of each tank's contents, tank waste monitoring, and modeling efforts have been used to establish safety criteria for ferrocyanide concentration, waste moisture contents, and waste temperatures.

Monitoring Data. Data collected from the tanks include temperature profiles, gamma scan profiles (identifying cesium and europium concentrations), and neutron scans to develop information on moisture content and interstitial liquid levels. The monitoring of tank temperature distributions and temperature changes is necessary to support model development and to confirm model-predicted waste behavior. This will include the use of instrument trees which deploy thermocouples (TCs) or resistance temperature detectors (RTDs) to measure temperatures within the tanks, and possibly infrared temperature mapping of tank waste surfaces. Existing TC elements have been repaired, and new instrument trees are being installed and connected to the Tank Monitor and Control System (TMACS), which is a computer-controlled, continuous monitoring system. These activities are providing information on present storage temperatures and input for thermal models.

The end point of this activity includes one-time, periodic, or continuous monitoring of sludge temperature, waste moisture content, cesium concentration, and tank vapor space for designated gases. Installation and operation of instrument trees with replaceable TC elements or RTDs in each ferrocyanide tank is being provided; 10 new instrument trees have been installed as of July 1993, and new instrument trees will be installed starting in mid-FY 1994. Continued operation of older TC trees will be maintained until failures occur. A moisture monitoring system is being developed and, if required, will be deployed to verify that the water content of the waste is maintained at an acceptable concentration for safety assurance where needed. Gas monitoring of the tank vapor space for reaction product or flammable gases will be conducted as appropriate.

Modeling. Waste modeling is being conducted to evaluate: (1) ferrocyanide and water concentrations throughout the tanks; (2) heat transfer in the waste; and (3) thermal conditions. This information is needed to address the potential hazards in each tank.

Perform Sensitivity Modeling. Sensitivity analyses are conducted to determine parametric effects of modeling variables which affect heat transfer from localized dry or hot spots and from the tanks as a whole, and variations in flowsheet compositions on reaction mechanisms, reaction rates, heat release, and gas release of the ferrocyanide waste. These also include estimates of variations in concentrations of chemicals in the tanks from the analysis of tank samples.

Prioritize Work. The studies are prioritized to focus on significant parameters that affect safety and environmental consequences. Resources will be directed toward high priority issues as determined by input from the DNFSB, TAP and TAP subpanels, Waste Management External Advisory Committee, WHC evaluations and recommendations, and direction from DOE.

Task 1.2 - Obtain Data on Tank Contents

A major step in resolving the Ferrocyanide Safety Issue is to safely obtain samples of the tank contents and to analyze these samples. Task 1.2 of the logic diagram shows this to follow the development of Task 1.1. In fact, much of the Task 1.2 work has been in parallel with Task 1.1 and has been supported by waste simulant studies and other laboratory tests that are completed or now in progress.

The flow of work in Task 1.2 ensures the safe sampling of tank contents by definition of the sampling plan, the safety envelope, and sampling safety documentation for gas, auger, push-mode core sampling, and rotary-mode core sampling. This data collection task includes action to gather improved temperature measurements and physical sampling of the tank gas space, saltcake, and sludge materials. Results of analyses of waste samples will be used to compare actual tank contents with the model results and to refine and revise the predictive model (Task 1.3).

The endpoint of this task is to provide data to develop and validate a waste model and to ensure that the parameters affecting safety are supported to a high degree of assurance. This task will provide waste characterization for the following parameters in each waste tank:

- Ferrocyanide concentration and species
- Moisture concentration
- Concentration of heat producing isotopes (cesium and strontium)
- Energetics (heat of reaction).

NOTE: Core sample analysis is the only direct method of measuring ^{90}Sr (a major heat-producing isotope) concentrations in the waste.

Task 1.3 - Refine Hypothesis/Model

Actual tank samples are used to verify or refine the models developed to predict tank inventories and composition. Sample results will be used to guide the formulation of enhanced waste simulants, if required. Because the number of tank samples will be limited and difficult to work with, the use of enhanced waste simulants may be an effective way to measure the variation of important parameters and to validate the presence and importance of phenomena incorporated in the refined model. Iterations in the modeling and laboratory work have been necessary.

Task 1.4 - Define Tank Safety Criteria

The logic diagram allows establishing three possible options as the outcome of the previous efforts: (1) the zero option, which is a finding of allowable in situ safe storage; (2) mitigation; and (3) remediation. The safety criteria defined for in situ safe storage are reviewed in Section 4.2.

For implementing the steps in Task 1.0, some ferrocyanide tanks may be stabilized and isolated (shown in the logic diagram as Task A). This activity is the objective of a separate program. It addresses the Ferrocyanide Watch List tanks (currently six) that have not been stabilized by saltwell pumping. Saltwell pumping to reduce the free liquid in the waste is necessary to support the Tri-Party Agreement (Ecology et al. 1990, 1994) and is an action that could be needed to reduce liquid loss from a leaking tank. Reaching this decision point depends on authorization by DOE of the safety assessment prepared that shows pumping will not have deleterious effects on safe waste storage. Regardless of whether tank waste stabilization and isolation by saltwell pumping is conducted, the waste would still be evaluated for resolution of any concerns associated with the Ferrocyanide Safety Issue.

Task 1.5 Apply Criteria to Characterization Data, Tank by Tank

Waste criteria for ferrocyanide concentration, moisture content, and waste temperature are based on the results of ferrocyanide tank waste characterization by sample analysis, historical accounting, simulant waste studies, tank waste monitoring, and tank waste modeling. These criteria have been established and implemented to ensure that the waste is maintained in a safe condition (or is treated, if necessary) to ensure that it does not present a safety concern.

Task 1.6 Revise the Tank List

The Ferrocyanide Watch List will be revised after waste characterization for each of the tanks or group of tanks is completed, to include only those tanks that may have safety concerns involving ferrocyanide reactions. Ferrocyanide concentration (on an energy equivalent basis) will be used to evaluate each tank to determine if the tank should be on the Ferrocyanide Watch List.

Task 1.7 Upgrade Equipment, Facilities and Safety Documentation

Equipment upgrade needs are being evaluated for temperature measurement, moisture monitoring, and gas monitoring for ferrocyanide waste in Watch List tanks. Satisfactory completion of the activities will lead to Task 2.0, Implement Zero Option. However, Task 1.0 includes all planning and assessment activities, and actual equipment changes will be completed under Task 2.0.

Task 2.0 - Implement "Zero" Option

This important task includes two decision points that can result in three pathways. First, the results of Task 1.0 will be evaluated on a single tank (or on a group of tanks) basis, to determine if the zero option criteria can be met. Tanks meeting these requirements will be removed from the Ferrocyanide Watch List and, for these tanks, the Ferrocyanide Safety Issue would be resolved.

Remaining tanks, if any, will be evaluated to determine if upgrades in equipment, monitoring, and safety documentation can provide assurance of continued in situ safe storage. If so, implementing the upgrades and controlling tank conditions to those provided with the safety criteria will lead to resolving the safety issue for these tanks. Any tank not meeting the criteria (even with upgrades) will then be considered for Task 3.0, Mitigation, and/or Task 4.0, Remediation. Because these tasks will be costly and require a long time to implement, they will be considered only after reassessment and possible augmentation of Task 1.0 models and data.

Task 3.0 - Implement Mitigation

Mitigation approaches can be identified and evaluated for technical feasibility including safety risks, time for implementation, and effectiveness to pre-empt any identified pathways to hazards that may be determined on a tank-by-tank basis. An initial assessment of possible mitigation (and remediation) techniques was completed earlier (Babad et al. 1991). If implementing ferrocyanide mitigation becomes a mainstream path, the most promising approach will be selected and implemented. Appropriate control and surveillance equipment would be installed, and monitoring for adherence to surveillance criteria would be conducted.

The end point of this task is to take corrective action to mitigate (if remediation is judged to require an unacceptable time to implement) any imminent ferrocyanide safety concern identified in a particular tank or group of tanks while defining and evaluating (Task 1.0) the ferrocyanide safety concern.

Task 4.0 - Implement Remediation

Remediation approaches can be identified and evaluated for technical feasibility including safety risks, time for implementation, and effectiveness to pre-empt any identified pathways to hazards that may be determined on a tank-by-tank basis. If implementing ferrocyanide remediation becomes a mainstream path, the most promising approach will be selected and implemented. Remediation may be conducted without implementing mitigation to conserve resources, if any identified imminent safety concern can be resolved by remediation in a timely fashion. See Babad et al. (1991) for an evaluation of remediation concepts studied earlier.

4.2 SAFE STORAGE OF FERROCYANIDE WASTE

The in situ safe storage option (zero option) leaves the waste in the tanks in its present configuration without further treatment. Experiments on ferrocyanide waste simulants have shown that propagating reactions can be prevented by three conditions. Any one of these conditions is sufficient to ensure safety:

1. Sufficient water is present in the ferrocyanide waste to prevent or suppress a propagating reaction

2. The ferrocyanide and/or oxidant concentrations in the waste are too low to support propagating ferrocyanide reactions in a dry matrix

3. The waste temperature is maintained below that required for activating exothermic reactions.

4.2.1 Waste Characterization

The in situ safe storage approach requires characterization of the ferrocyanide waste for composition and reactivity. Characterization includes an historical accounting of the waste, determining flowsheet values of chemicals added to the tanks, obtaining waste samples, and analyses of the waste samples. In characterizing the energetics of the ferrocyanide waste, the presence of other inorganic reactive species (e.g., cyanide ion and sulfides) and organic reactants must be addressed. Organic reactants, if present at substantial concentrations, may also be covered by the Organic Tanks Safety Program at WHC (Babad and Turner 1993).

All credible reaction initiators during the "storage" period need to be considered. This includes any potentially energetic inorganic or class of organic species identified as present in the waste. They will be evaluated both as fuel and as potential initiators for other reactions. Possible initiation caused by performing work on the waste, such as auger sampling, core sampling (rotary and push-mode), and saltwell pumping activities, will be examined.

Implementing in situ safe storage for the ferrocyanide tanks will be done on a tank-by-tank basis as data become available for each tank. Monitoring and surveillance of certain waste properties may be required to ensure that the waste remains in a safe state. Parameters of interest include temperature, water content, radioactive species, and possibly other chemical species. Approval to remove a tank from the Watch List could require assurance that monitoring is in place or that tank conditions are static enough not to require monitoring on a frequent or continuous basis. Documentation that each tank is safe must be thorough and subject to peer review.

4.2.2 Moisture Content (Refer also to sections 5.1.5.3, 5.4.5.1, and 5.4.5.2)

Effects of Moisture. Adiabatic calorimetry and reaction propagation rate tests on ferrocyanide waste simulants have shown that sustained reactions cannot occur in waste containing more than 12 wt% water (Fauske 1992). Simulant containing the highest postulated ferrocyanide concentration could not be ignited or made to sustain a propagating reaction even when subjected to a strong ignition source. A moisture safety criteria has been developed that relates moisture concentration and ferrocyanide concentration. A description of the criteria and this relationship is provided in Section 4.3. Control can be achieved by monitoring the moisture content of the waste to ensure it exceeds this limit.

Moisture content of the simulants centrifuged to 30 equivalent gravity years ranged from 48 to 67 wt% (Jeppson and Wong 1993). These values are at least four times higher than the minimum required to inhibit propagating reactions. Analyses of core samples taken from actual ferrocyanide waste in the TY Farm in 1985 revealed the waste contained at least 40 wt% moisture even after the tanks had been interim stabilized by saltwell pumping. Three ferrocyanide tanks have been push-mode core sampled, 241-C-109, 241-C-112, and 241-T-107. Moisture in tank 241-C-109 samples ranged from 19 to 58 wt% for the three cores taken (Simpson et al. 1993a). Results from tank 241-C-112 samples showed moisture contents from 38 to 64 wt% (Simpson et al. 1993b). The core samples (subsegments) that contained the lowest moisture values were also low in total cyanide and they exhibited endotherms or low exotherms during differential scanning calorimetry (DSC) testing for energetics. Moisture determinations for the two tanks' core samples were completed more than 30 days after the core samples were obtained from the tanks. Loss of moisture from the samples undoubtedly occurred during this time. Note that all of these moisture measurements are substantially higher than the 12 wt% required to inhibit propagating reactions (Fauske 1992).

Laboratory investigations of the hydraulic properties of ferrocyanide waste were conducted in FY 1993 and are continuing in FY 1994. This work includes determining the retained moisture in the waste (i.e., the moisture content of drained waste as a function of waste depth). Preliminary results show the simulated waste retains considerable quantities of water, greater than 45 wt%, even after centrifugation.

Moisture Monitoring. In situ moisture measurement requires technology development and installation of special instrumentation into the tanks. Moisture monitors will be developed acknowledging that only a few tank risers will be accessible. A rationale will be established for an achievable number of moisture determinations that provide assurance of adequate moisture within the ferrocyanide waste. This may be accomplished by obtaining many moisture readings in a tank or by showing that a few moisture determinations are representative.

Possible types of instrumentation now being developed which may prove useful in making moisture measurements in the waste include the following:

- Near-infrared spectroscopy--A modified infrared (IR) probe is placed inside a tank to measure water content via near-infrared reflectance (Veltkamp 1993).

- Quantifying liquid observation well (LOW) neutron scans--A neutron probe with appropriate modifications and subsequent scan data may be used to determine wt% moisture. Computer modeling and actual deployment in ferrocyanide tanks are being used to determine the validity of this method (Watson 1993).

The feasibility for using in situ infrared to measure wt% moisture is being examined for WHC by the Center for Process Analytical Chemistry at the University of Washington. The method appears to be suitable for waste characterization of certain other analytes as well (Veltkamp 1993).

Computer modeling of the existing LOW neutron probe began in FY 1992 and is continuing. The theoretical feasibility for using data from this probe to quantify wt% moisture was established in FY 1992. In FY 1994 work will involve neutron probe scans of ferrocyanide tanks, preparing additional special-simulant-filled drums for moisture standards, and demonstrating the probe as an accurate and efficient moisture monitoring device. One obstacle of this technique may be that the probe only interrogates the waste to a radius of about 10 to 15 cm (4 to 6 in) around the LOW (Watson 1993).

4.2.3 Ferrocyanide Waste Energetics (Refer also to sections 5.4.5.1, 5.4.5.2 and 5.5.5.2)

A condition that ensures preclusion of ferrocyanide reactions of concern is low ferrocyanide concentration. Propagation experiments on simulants showed >15 wt% fuel (sodium nickel ferrocyanide as a stoichiometric mixture with a 3:1 ratio of sodium nitrate/sodium nitrite on a dry basis) was required to sustain a propagating reaction (Appendix B, Postma et al. 1994). The limiting concentration of ferrocyanide in actual ferrocyanide waste must be established by laboratory investigations. Sampling and subsequent analysis combined with modeling should provide the technical basis for removing several tanks from the Ferrocyanide Watch List that are considered to contain only small amounts of ferrocyanide. If this is not possible, a statistically designed sampling plan may be required to show that tanks originally containing appreciable inventories of ferrocyanide are below the concentration limit.

Methods have been developed for determining total cyanide (Pool 1993) and for cyanide speciation (Bryan et al. 1993) in ferrocyanide waste. The total cyanide analytical method is now approved for both PNL and WHC analytical laboratories. These activities began in FY 1992. The cyanide speciation techniques are expected to result in operational hot cell systems at both PNL and WHC by the end of FY 1994. More information on these techniques is presented in sections 5.4.5.3 and 5.5.5.1.

4.2.4 Temperature

Temperature is a secondary criterion for ensuring in situ safe storage of the ferrocyanide waste. A safety criterion of 90 °C (194 °F) has been selected. This is considerably lower than the temperature required to start a propagating reaction (~250 °C [482 °F]) and was set low to preclude rapid moisture loss via evaporation near the solution boiling point (approximately 120 °C [248 °F]). Current bulk temperatures for waste in the ferrocyanide tanks range between 19 and 54 °C (66 and 129 °F) (Meacham et al. 1994). Temperatures in the tanks have dropped steadily since the In Tank Solidification Program ended in the mid-1970's. The highest bulk temperature is currently in tank 241-BY-104, approximately 54 °C (129 °F). This temperature is considerably lower than the 90 °C (194 °F) maximum selected as a safety criterion. Prudent monitoring as specified in the Action Plan (Cash and Thurman 1991b) requires that actions be taken long before the waste temperature reaches 90 °C.

4.3 STATUS OF SAFETY ISSUE DOCUMENTATION

Safety and Environmental Assessments. The USQ process depends on an authorization basis that describes those aspects of the facility design basis and operational requirements relied on by DOE to authorize operation. The authorization basis is described in documents such as facility safety analysis reports (SARs) and other safety analyses, hazard classification documents, technical safety requirements, DOE-issued safety evaluation reports, and facility-specific commitments, such as the safety assessments (SAs) and most recently the Interim Safety Basis (ISB) (Wagoner 1993). The potential hazards of a ferrocyanide-nitrate/nitrite reaction were discovered to represent an inadequacy in the authorization basis. Before the USQ was closed, proposed intrusive activities that could have impacted the safety of the ferrocyanide tanks had to be thoroughly assessed for potential safety and environmental consequences. Furthermore, these activities could not be conducted without formal authorization from DOE. With closure of the USQ, all activities covered by the ISB can now be conducted without requesting DOE authorization. WHC policies and procedures must still be followed, however. Any proposed new activities that are not covered by the ISB must undergo a USQ screening in accordance with DOE Order 5480.21 (DOE 1991a) and WHC Management Requirements and Procedures Manual WHC-CM-1-3, Section 5.12 (WHC 1992). Those items judged to be an Unreviewed Safety Question using the USQ process would then have to undergo a thorough SA and EA evaluation, and DOE Program Secretarial Officer authorization would have to be obtained. If the screening does not result in a USQ finding, the work could then proceed in accordance with WHC management requirements and procedures (WHC 1992).

SAs are documents prepared to provide the technical basis to assess the safety of a proposed activity and to provide proper controls to maintain safety. The SA, along with an accompanying Environmental Assessment (EA) for that operation (or the generic EA if covered therein), provides the basis for authorization of the proposed activities. Recently the authorization basis for previously analyzed intrusive tank operations was combined into one document, the ISB. This document was approved by DOE in November 1993 (Wagoner 1993).

SAs have been completed for vapor space sampling of all ferrocyanide tanks, waste surface sampling, push-mode and rotary-mode core sampling, instrument tree installation in sound and leaker tanks, and removal of pumpable liquid from leaking tanks (interim stabilization).

A decision was made to revise the existing SA for installing instrument trees in sound (non-leaking) ferrocyanide tanks so that installation in assumed leaker tanks was addressed as well. A study to evaluate and identify alternative methods for installation of instrument trees in assumed leaker ferrocyanide tanks was completed. The previous method used relatively large volumes of water to sluice the tree through the waste. A concept that uses an ultra high-pressure device and minimal quantities of water was chosen for final testing and design. This document was first transmitted to DOE in April 1993, and several revisions have been made to incorporate DOE comments. The EA for installation of the instrument trees into assumed leaker tanks has been incorporated into a generic EA covering operations for Watch List tanks. This EA was approved by DOE-HQ in March and was issued with an accompanying Finding of No Significant Impact (FONSI) (Gerton 1994).

Hazard Assessment. In June 1991, the TAP requested that WHC prepare a position paper on the state of knowledge concerning the Ferrocyanide Safety Issue. The paper was to document what was known about continued safe storage of the ferrocyanide waste in the high-level waste tanks at the Hanford Site. The primary focus of the report was to assess if it was possible for a significant exothermic chemical reaction to occur in the tanks under existing conditions and whether the reaction could reach a runaway state in which radioactive aerosols would be expelled from the tank. The safety of continued storage is of interest for all long-term storage, mitigation, remediation, or treatment options because significant storage time will still accrue before options can be selected and completed that modify the waste form and render it safe, if some treatment process is required.

The ferrocyanide position paper represented a snapshot in time of: (1) what was known about ferrocyanide waste stored in underground tanks at the Hanford Site; (2) what this information means in terms of storage safety; (3) what key uncertainties exist; and (4) what must be done to resolve the safety issue. The position paper is an overview document with technical backup provided by the ferrocyanide hazards assessment document (Grigsby et al. 1992).

A draft position paper was issued November 27, 1991 for DOE and TAP review. Comments were received by May 1992 and the document was revised and cleared for public release in July 1992 (Postma et al. 1992). Updates of the position paper will be issued as significant new information becomes available and as results of core sample analyses are reported. To date, no updates have been issued because new findings and information are provided in the quarterly reports (Meacham et al. 1994).

The scope of the ferrocyanide hazards assessment task was to provide a technical assessment and updates of the ferrocyanide waste tank safety concerns and progress towards resolution of the Ferrocyanide Safety Issue. These assessments are based on information as it becomes available from the Ferrocyanide Safety Program. Contributions are included from Fauske and Associates, Inc. (FAI), LANL, PNL, WHC, and other sources.

The effort to update the ferrocyanide hazards assessment document was redirected in June 1993 toward developing safety criteria and a technical basis document supporting closure of the Ferrocyanide USQ. At that time, agreement was reached between DOE and WHC on the approach to be followed for closure of the USQ and for resolving the safety issue.

An updated ferrocyanide hazards assessment, now referred to as a technical basis document, will not be started until enough information is available for resolving the Ferrocyanide Safety Issue. Technical information from all Ferrocyanide Safety Program tasks will be incorporated into this document. The approach and key safety criteria that must be met for resolving the Ferrocyanide Safety Issue are addressed in Section 4.1. The objective of the technical data that will be presented is to show that in situ storage of the waste is safe and to designate those controls that must be implemented to ensure safety. The technical basis document will be completed in FY 1995 to support safety issue resolution for the four C Farm tanks. A revision of the document may be necessary in FY 1997 to support safety issue resolution for the remaining 14 tanks.

In September 1990, an Ad Hoc Task Force report recommended that studies be performed to provide information on: (1) the potential for a ferrocyanide-nitrate/nitrite explosion; (2) the conditions necessary in the tanks to initiate an explosion; and (3) the potential consequences of such an occurrence. The GAO advised the Secretary of Energy to implement these recommendations. A report describing the consequences from a hypothetical burn may be required to close out recommendation (3); however, documentation prepared addressing recommendations (1) and (2) has shown that the risk for an explosion is negligible. Since the consequences of incredible events do not have to be analyzed (WHC 1993b), there exists little technical justification for completion of a consequence report. A decision on the need for a consequence report will be made in June 1994, and a report will be written, if required, by September 1994.

Closing the Ferrocyanide USQ. A draft of the Ferrocyanide USQ was submitted for DOE review on December 1, 1993. Closure of the Ferrocyanide USQ by January 31, 1994 was one of the initiatives to accelerate resolution of tank safety issues (O'Leary 1993). This date is seven months earlier than originally planned. Closure of the Ferrocyanide USQ by March 31, 1994 was also made a TPA milestone (TPA M-40-14) during renegotiation of the Tri-Party Agreement (Ecology et al. 1994). The steps that led to closure of the Ferrocyanide USQ are presented in Figure 4-3. The major effort was to determine three safety criteria for the safety categories or levels and provide technical bases for their selection. The criteria are formulated on the basis of defined safety categories, the safety objective, and an understanding of hazard phenomenology. After the criteria were quantified, available waste characterization data were evaluated in light of the criteria. The document that quantifies the work steps depicted in Figure 4-3 provides the basis for closure of the USQ (Postma et al. 1994).

In March 1994, the DOE approved a formal request from WHC (Alumkal 1994) to close the Ferrocyanide USQ (Sheridan 1994). A new safety envelope has been defined by Postma et al. (1994) which is reflected in an amendment to the Interim Safety Basis document (Wagoner 1993) for the tank farms.

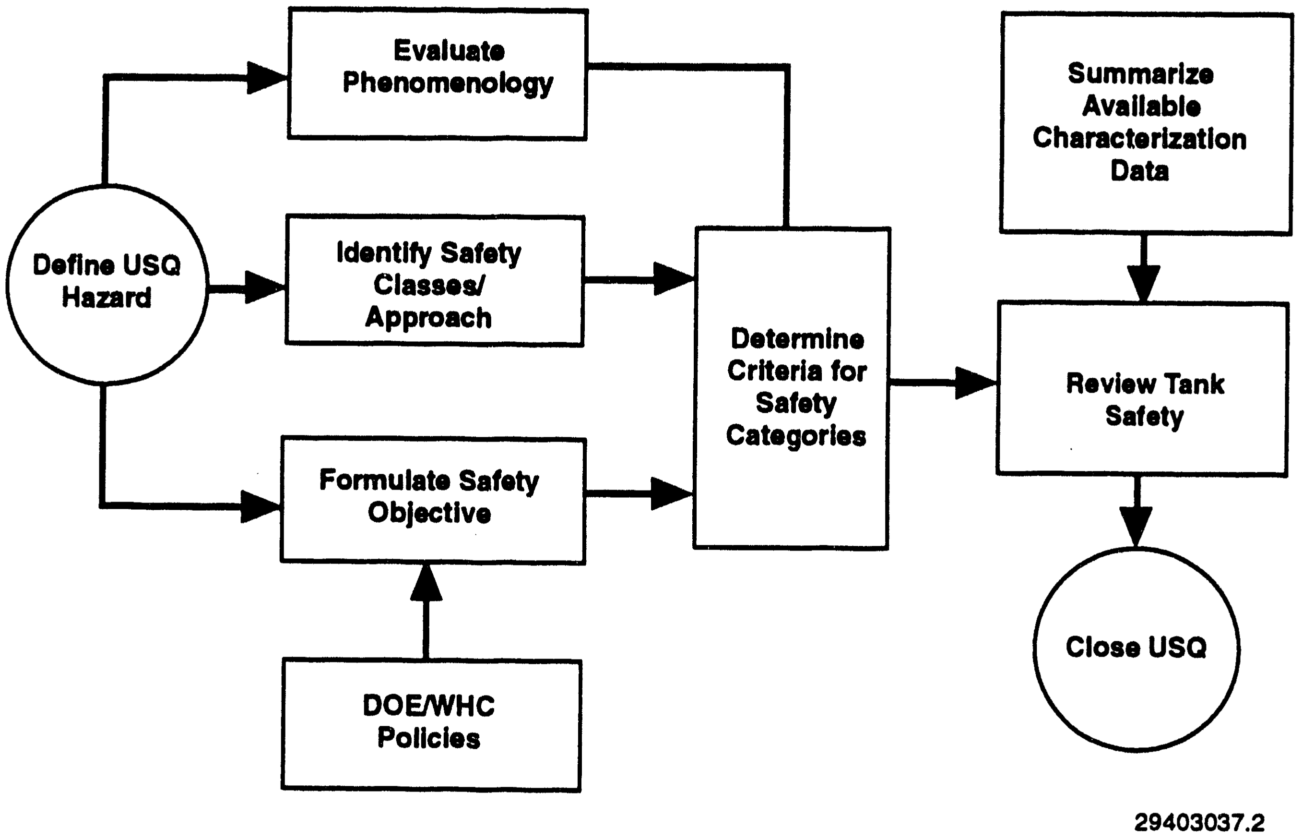
The waste parameters on which the criteria were established have been identified from known requirements for exothermic oxidation/reduction reactions. These are fuel, oxidant, and moisture concentrations, and waste temperature.

Each of the tanks were categorized into one of three possible levels:

1. **LEVEL 1 - <u>SAFE</u>**

Concentration of fuel:	≤ 8 wt% sodium nickel ferrocyanide on an energy equivalent basis
Concentration of water:	Not limiting
Concentration of oxidizers:	Not limiting
Temperature of waste:	Not limiting

Figure 4-3. Information Required for Closure of the Ferrocyanide USQ.



2. **LEVEL 2 - CONDITIONALLY SAFE**

Concentration of fuel:	>8 wt% sodium nickel ferrocyanide on an energy equivalent basis
Concentration of water:	≥0 to 24 wt% [The moisture criterion increases linearly from 0 at 8 wt% fuel to 24 wt% at 26 wt% fuel]
Concentration of oxidizers:	Not limiting
Temperature of waste:	≤90 °C (194 °F) [Temperature is not an independent criterion; see Section 6.2 of Postma et al. 1994]

3. **LEVEL 3 - UNSAFE**

Criteria for SAFE and CONDITIONALLY SAFE are not met; a modification in waste state is required to remove a tank from the UNSAFE category.

Numerical values for fuel, moisture, and temperature were chosen on the basis of theoretical studies and the results of experiments conducted on waste simulants (Postma et al. 1994).

The fuel criterion was determined on an energy equivalent basis that accounts for possible contributions from other potential fuel sources, such as sulfide or organics. The moisture criterion is not fixed at one value, but increases linearly from 0 at 8 wt% fuel, to 24 wt% at 26 wt% fuel. Temperature is not a primary criterion, and was set at 90 °C (194 °F) to preclude rapid moisture loss in the waste. Actions to cool the waste would be taken long before temperatures in the tank increased to 90 °C (Cash and Thurman 1991b).

The fuel and moisture criteria have safety factors of about 1.9 and 2.0, respectively, when compared to experimental results from propagation tests. The temperature criterion of 90 °C has a safety margin of 30 °C (86 °F), when compared to the boiling temperature of the interstitial liquid, about 120 °C (248 °F). More detailed discussions on criteria development and the conservatism inherent in the safety criteria are presented in *Ferrocyanide Safety Program: Safety Criteria for Ferrocyanide Watch List Tanks* (Postma et al. 1994).

- **Milestone Status**

  - **June 24, 1994**. Issue an Interim Safety Basis Level 1 report to DOE which provides the updated safety basis for safe operation of ferrocyanide tanks. The Level 1 ISB will cover previously analyzed operations for all Watch List tanks and includes updates (amendments) and more detailed analyses of intrusive tank operations.

- **July 29, 1994.** Issue an update of the ferrocyanide hazards assessment document. This milestone has been deferred to FY 1995. (See milestone for August 31, 1995.)

- **September 30, 1994.** Complete a final report, approved for public release, on effects and consequences of various in situ ferrocyanide tank waste burns (if required).

- **August 31, 1995.** Issue technical basis document supporting safety issue resolution for the four C Farm tanks. Recommend resolution of the Ferrocyanide Safety Issue for C Farm tanks.

- **February 29, 1996.** Receive DOE approval to remove the four C Farm tanks from the Watch List. Safety issue resolved for C Farm tanks.

- **January 31, 1997.** Revise the technical basis document to support safety issue resolution for the remaining 14 tanks. Recommend Ferrocyanide Safety Issue resolution for all remaining tanks.

- **September 30, 1997.** Receive DOE approval to remove all tanks from the Ferrocyanide Watch List, resolving the Ferrocyanide Safety Issue.

5.0 DESCRIPTION OF ACTIVITIES

This document section follows the general format of the revised DNFSB Implementation Plan (Borsheim et al. 1992). Each task activity is described relative to its application to one of the six DNFSB Recommendations (90-7.1 through 90-7.6). The specific recommendation is contained within the issue introduction or background subsection, followed by subsections giving the issue evaluation, baseline assumptions, and method to close the recommendation. The action plan subsection (if not already closed out) then briefly describes activities underway to respond to the recommendation. Note that the most comprehensive and current status of the work is provided in the Quarterly Reports on the Ferrocyanide Safety Program. The most recent report is for the period ending December 31, 1993 (Meacham et al. 1994).

5.1 ENHANCED TEMPERATURE MEASUREMENT

5.1.1 Background

When the DNFSB initially examined the Ferrocyanide Safety Issue, most of the ferrocyanide tanks did not have an adequate number of functioning TC elements to provide a complete vertical profile of the temperatures within the tanks, and limited information was available about the total heat generation rate of the waste. The DNFSB issued Recommendation 90-7.1, as follows:

> *"Immediate steps should be taken to add instrumentation as necessary to the single-shell tanks containing ferrocyanide that will establish whether hot spots exist or may develop in the future in the stored waste. The instrumentation should include, as a minimum, additional thermocouple trees. Trees should be introduced at several radial locations in all tanks containing substantial amounts of ferrocyanide, to measure the temperature as a function of elevation at these radii. The use of infrared techniques to survey the surface of waste in tanks should continue to be investigated as a priority matter, and on the assumption that this method will be found valuable, monitors based on it should be installed now in the ferrocyanide bearing tanks."*

This recommendation reflected their concern about the possibility of an undetected hot spot existing within the waste that might provide the necessary energy to promote an uncontrolled reaction or explosion.

Subsequent work in several areas has developed a broader knowledge base and has warranted several changes in the approach to implementing the recommendation. Originally, it was planned to add several temperature measurement instruments to each tank. This plan has been modified to ensure that there is at least one instrument tree with replaceable TCs or RTDs in each ferrocyanide tank. Additionally, there should be at least two operational temperature-sensing elements in the waste to ensure a true temperature measurement and one or more in the vapor space. The new data that have warranted this action include the following: (1) many of the TC elements in the existing trees have been returned to service and measured temperatures are as expected; (2) thermal modeling to date (McLaren 1993, McLaren and Cash 1993) and an enhanced process knowledge show that the waste is relatively homogeneous horizontally with respect to heat generation (thus a hot spot is most likely improbable); (3) any reasonable number of instrument trees would not be likely to detect a hot spot; and (4) new estimates o´ tank heat content based on tank temperatures show lower values than previous estimates. When completed, the new plan will result in having two instrument trees in all but three ferrocyanide tanks (241-BY-106, -111 and -112). Tank 241-BY-106 already contains an instrument tree with replaceable TC elements. Tanks 241-BY-111 and -112 had no operable instrument tree, and the waste temperatures were measured via a dedicated TC element installed in each tank's LOW. New instrument trees with replaceable temperature-sensing elements have now been installed in these two tanks. The existing instrument trees in the tanks will be monitored as well as the newly installed trees. It is expected that the older trees will eventually fail in a manner such that they cannot be repaired, and they will not be replaced.

5.1.2 Evaluation of Issue

Hot spots have been postulated to exist in the ferrocyanide tanks. Knowledge of the ferrocyanide scavenging process (the precipitates were easily suspended), indicates that the waste should be relatively evenly dispersed horizontally. Additional instrument trees to provide more than one vertical temperature profile and core sample analyses will confirm or refute this homogeneity. However, to date, the possibility of hot spots existing or developing in the future cannot be ruled out. Even if a hot spot is ruled out, prudent monitoring of temperatures is still planned. Therefore, the provision for having at least one instrument tree per tank, with replaceable temperature-sensing elements, is warranted, as is additional review of alternative methodologies, such as IR scanning, in parallel with further evaluation of the possibility and consequences of hot spots.

5.1.3 Baseline Assumptions

- Hot spots may exist in the ferrocyanide tanks. Prudent temperature monitoring is necessary even if hot spots do not exist.

- Use of instrument trees alone to detect hot spots is not practical because multiple (more than 10) trees per tank would be required to ensure coverage. The overall effort to install multiple new risers would be extensive. The work would include: (1) structural analyses for core drilling the tank dome to install the new risers; (2) a safety assessment for the dome coring and instrument tree placement; and (3) excavation, shielding and core drilling. As low as reasonably achievable radiation concerns would make this work expensive.

- IR technology can be made to function in high radiation fields for short time periods and has the sensitivity to detect hot spots of concern. (See Section 5.1.5.2.)

- Thermal modeling, by itself, will not be adequate to resolve the concern (i.e., field data such as measurements from new instrument trees and core sample analyses will also be required).

5.1.4 Method to Close Recommendation 90-7.1

Providing for at least one instrument tree with replaceable temperature-sensing elements (TCs or RTDs) in each ferrocyanide tank and connecting each element to TMACS should assure adequate temperature monitoring in the waste.

5.1.5 Action Plan

The tank monitoring and modeling activity includes four activities to respond to this recommendation. Subtasks for this activity are as follows:

1. **Installing new instrument trees**--The scope of this subtask has been changed as discussed in Section 5.1.5.1.

2. **Repairing and upgrading existing tank temperature monitoring instrumentation**--(This task has now been completed).

3. **Developing and analyzing thermal models for ferrocyanide tank temperatures and hot spots**--This task has been expanded to include estimating heat generation rates and thermal characteristics in additional tanks. See Section 5.1.5.2.

4. **Applying alternative tank monitoring technologies, such as moisture monitoring of the waste**--See Section 5.1.5.3.

5. **Investigating Cooling System Requirements**--This task will determine the best method for active cooling to control ferrocyanide waste temperatures if an increasing temperature trend is seen in a ferrocyanide tank--See Section 5.1.5.4.

5.1.5.1 Instrument Trees. A strategy initially was developed to provide the temperature instrumentation necessary to monitor conditions in five high-concern waste tanks on an expedited basis. The strategy was to: (1) repair the existing TC elements (where possible); (2) install new instrument trees that would be fabricated from existing drawings; and (3) install multifunctional instrument trees (MITs) in those tanks that only have a few risers available. The MITs would provide temperature monitoring, the capability for gas sampling at three elevations, possible pressure monitoring, and access for deployment of fiber optics inside the tanks, if desired. The instrument trees would provide temperature monitoring but may not provide the option to obtain any other needed data. This strategy was later revised to include only repair of TC elements in existing trees and installing new instrument trees in ferrocyanide waste tanks. A number of uncertainties concerning surveillance requirements were experienced with the early design and development of the MITs. Resolution of design and operational requirements resulted in substantial schedule delays and cost increases. In an effort to expedite the required ferrocyanide tank temperature measurement upgrades, it was decided to: 1) fabricate and install instrument trees in the tanks; and 2) determine how to take gas samples from the vapor space at a later date, if the installed capability for taking periodic or continuous gas samples is determined to be necessary. Currently, there are no plans to install MITs in the ferrocyanide tanks.

In fiscal years 1991 and 1992, the existing trees were evaluated and the TC elements were repaired and returned to service where possible. The evaluation consisted of taking field measurements on each TC element in the existing trees to determine the resistance and voltage across the junction and across each lead to ground. As reported in the DNFSB Quarterly Reports, 265 TCs were evaluated; and elements, determined to be failed or marginal in performance, were returned to service.

Installing instrument trees in the last four sound ferrocyanide tanks (241-BX-106, 241-BY-101*, 241-C-108, and 241-TX-118) was completed on July 30, 1993. Ten new instrument trees have (through FY 1993) been installed in tanks identified originally on the Ferrocyanide Watch List. A technique has been developed to install new trees in assumed leaking tanks using an ultra high-pressure water bore head, thereby minimizing the addition of water. The final report for the ultra high-pressure bore head testing has been disseminated for review and comments are being incorporated. Fabrication of the first four trees for the assumed leaker tanks has been completed. Delivery has been made for the ultra high-pressure equipment required to support instrument tree installations into the assumed leaker ferrocyanide tanks.

A heated vapor sampling tube has been added to the instrument tree design for the assumed leaker ferrocyanide tanks. The heated vapor sampling tube extends from outside the riser, through the TC tree and into the dome space of the tanks. The tube will be heated by circulating either hot water or hot gas around the sampling tube. This added feature to the new instrument trees may eliminate the need to install an additional vapor probe, which is currently required to obtain vapor space gas samples. Vapor sampling using the TC tree will reduce field efforts and the cost of vapor space characterization. The vapor sampling tube can also be used for monitoring pressure in the ferrocyanide tanks if deemed necessary.

* Note that tank 241-BY-101 has been removed from the Ferrocyanide Watch List.

Plans have moved ahead for installing the new instrument trees in assumed leaker tanks. The SA for installation of instrument trees into assumed leaker tanks was approved by DOE in March 1994.

- **Planned Work To Complete Program.** New instrument trees for the remaining five assumed leaker tanks will be fabricated with heated vapor sampling tubes and ultra high-pressure heads. The remaining new instrument trees will be fabricated and installed during CY 1994.

  The final report for the ultra high-pressure bore head testing was released in December 1993 (Hertelendy 1993). (WHC-SD-WM-RPT-132, *Final Test Report: Ultra-High Pressure Water as a Tool to Bore, Drill, Cut or Penetrate Hard Saltcake-Like Nuclear Waste.*)

- **Milestone Status**

  - **September 30, 1994.** Install 9 instrument trees into assumed leaker ferrocyanide tanks. This milestone also addresses the September 1994 TPA milestone (M-40-02B), installation of 6 instrument trees into ferrocyanide tanks.

  - **September 30, 1994.** Develop criteria for upgraded temperature monitoring capabilities in ferrocyanide tanks (TPA milestone M-40-02A).

  - **December 31, 1994.** Complete installation of instrument trees in assumed leaker ferrocyanide tanks. Replace existing TC elements in the remaining two ferrocyanide tanks as necessary (241-BY-105 and -BY-106).

5.1.5.2 Hot Spot Thermal Modeling. Radioactive materials in Hanford Site waste tanks generate heat. A concern, raised when the ferrocyanide tanks first became a safety issue, has been whether an exothermic excursion and local propagation could occur within the ferrocyanide waste if there was a sufficient concentration of ferrocyanide and a high enough temperature present. Not all ferrocyanide tanks have two instrument trees; consequently, it is questionable whether abnormal heat generation could exist in these tanks and not be detected. This task models and analyzes the available temperature data from the ferrocyanide tanks to determine the heat load and temperatures as a function of depth and horizontal location. Sensitivity and parametric analyses are included to determine the magnitude of hot spots that might exist within the waste and still not cause a propagating reaction to occur.

State-of-the-art validated computer codes are used in the modeling. They are benchmarked with existing data and employ two- and three-dimensional capabilities. Both steady-state and transient models are used. The work intent is to determine accurate heat loads for each ferrocyanide tank.

A more realistic SST heat load model has been developed that contains several improvements over previously used models. Refinements include: an experimentally measured value for soil conductivity, a curved dome space geometry, and use of a transient thermal history. Including radiant and convective heat transfer to the walls of the tank in the model offers minimal increased accuracy. The new model was used to develop a thermal profile of tank 241-BY-104 (McLaren 1993). Information derived from the analysis of tank 241-BY-104 was then used for correcting the thermal profile of ferrocyanide tanks that have previously been analyzed (McLaren and Cash 1993). The new model will also be used to reanalyze selected tanks, and to estimate the heat loads of the remaining ferrocyanide tanks.

The technical basis was developed for estimating integrated tank heat loads just using the tank vapor space temperatures. Calculations have shown that there is a correlation between total tank heat load and tank vapor space temperature. Tank vapor space temperature measurements may confer a more representative measure of tank heat load when only a few TC elements are located in the tank waste. Integrated tank heat loads for all the ferrocyanide tanks were calculated using tank vapor space temperature measurements. A report reviewing this work was publicly released in December 1993 as *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0709 (Crowe et al. 1993). Heat loads calculated from tank vapor space temperatures correlated closely with other methods previously used for calculating heat loads for selected ferrocyanide tanks. The heat load estimates calculated by this method were reported in Table A-1 of the last quarterly report, WHC-EP-0474-11 (Meacham et al. 1994).

A study was performed and a position paper issued (Dickinson et al. 1993, WHC-EP-0648, Rev. 0) discussing the probability of a hot spot within a ferrocyanide tank that could raise the waste temperature to 120 °C (248 °F), the approximate boiling point of the waste solution. The report used results from several analyses to describe the concentration factors required for such a hot spot and the mechanism for forming one. The report concluded that the existence or formation of a hot spot of this magnitude was improbable.

Using infrared scanning to detect a postulated hot spot was also addressed in the position paper. Developing an infrared scanning system for use in the Hanford Site waste tanks has been reported in the DNFSB Quarterly Reports. This work culminated in the demonstration of the scanning system in a nonferrocyanide tank, 241-S-110. The position paper concluded that while infrared scans of the tanks may produce useful information concerning the lateral heat distribution within the tank, and thus could be used to investigate anomalies, the possibility of hot spots actually existing is too low to warrant the use of infrared scans for routine surveillance. The report on the infrared scans of tank 241-S-110, *Application of Infrared Imaging in Ferrocyanide Tanks*, (Efferding et al. 1993) was submitted for DOE review (WHC-EP-0593).

- **Planned Work To Complete Program.** Deve   ent of the improved heat transfer/heat load model has been completed an a report was issued (McLaren 1993). Heat load analyses of all ferrocyanide tanks will be performed in FY 1994. Existing analyses will be updated by using the correction factors being developed. Reports of the new analyses will be prepared and issued.

Comments received from DOE and other reviewers will be addressed in an update of the report *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Waste by Hot Spots* (Dickinson et al. 1993). Additional analyses, taking into account other possible drying mechanisms, will be included in the report update.

- **Milestone Status**

  - **December 30, 1993.** Complete thermal hydraulic analyses (using the updated model) of tank 241-BY-104 to determine heat load and conductivities of the waste contents and issue a report, available to the public, on the results of the analysis. The scope of this milestone has been reduced to one tank (from four tanks) and the date slipped from September 17, 1993 because of delays in developing the updated heat transfer/heat load model. The delays resulted from incorporating refinements in the soil thermal conductivities as a function of moisture content and determining the transient thermal history of the tanks. The report, WHC-EP-0669, *Ferrocyanide Safety Program: Updated Thermal Analysis Model for Ferrocyanide Tanks with Application to Tank 241-BY-104* (McLaren 1993), was released on schedule.

  - **December 30, 1993.** Complete and issue a report, available to the public, of corrected thermal analyses of six ferrocyanide tanks (241-BY-105, -106, -108, -110, 111, and 241-C-109). This milestone was slipped from November 26, 1993 because of delays in developing the updated heat transfer/heat load model. The report *Ferrocyanide Safety Program: Heat Loads and Thermal Characteristics of Selected Tanks* (McLaren and Cash 1993) has been issued.

  - **May 31, 1994.** Complete additional analyses and issue an update of the report *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Waste by Hot Spots* (Dickinson et al. 1993), approved for public release.

  - **June 30, 1994.** Complete thermal hydraulic analyses of heat loads for nine ferrocyanide tanks (241-BY-103, -105, -106, -107, -108, -110, -111, and 241-C-109 and -112) and issue a report available to the public.

- **September 30, 1994.** Complete thermal hydraulic analyses of heat loads for all remaining ferrocyanide tanks and issue report available to the public.

5.1.5.3 Estimation of Waste Moisture Content. Various techniques for measuring moisture in the tank waste are being investigated. They include use of a neutron probe in a LOW or in a cone penetrometer pushed into the waste, measuring surface moisture using infrared techniques, electrical measurements using an induction coil, phase change probes using thaw/freeze cycling and temperature measurement in the tank, and time domain reflectometry. Only the first two techniques are currently being funded by the Ferrocyanide Program; these are described below. A white paper evaluating all of these techniques titled *Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools*, (Meacham et al. 1993) has been publicly released.

Determination of moisture concentrations in the ferrocyanide waste tanks is being pursued using data analysis and modification of existing surveillance systems (neutron probes in LOWs). Well-logging techniques coupled with computer modeling are being developed and applied to an existing neutron probe to assess this probe and to determine information about moisture levels, material interfaces, and other waste characteristics. The existing neutron probe, used routinely to determine tank liquid levels, is inserted into closed-bottom LOWs to access tank contents. Development of a new, improved neutron-diffusion-based detector system is being investigated. This improved technique would be used primarily to determine the vertical moisture concentration profile within the ferrocyanide tanks.

Moisture measurement using neutron diffusion is an established technology. The technique uses a neutron source and one or more neutron detectors. The thermal neutrons reaching a detector originate as fast neutrons from the source and are slowed or absorbed by the medium. Because hydrogen atoms are the most effective at slowing down neutrons, the detector response is a strong function of the surrounding moisture concentration.

The source-to-detector spacing of a neutron probe may be adjusted with the addition of source extenders. The variation in source-to-detector spacing affects the near- and far-field response of the detector, and determines whether the system performs as a moisture gauge or as a neutron log. Source extenders are not currently used with the neutron probe for liquid level detection via the LOW. Computer modeling of the existing neutron probe system revealed that, in its current configuration, it responds most like a moisture gauge. Calculations also revealed that the probe would operate as a neutron log with the addition of an appropriate length source extender.

Preliminary interpretations of neutron scans obtained in three ferrocyanide tanks (241-BY-107, 241-BY-110, and 241-BY-111) have been completed. To relate the axial counting rates observed in these scans to an axial moisture concentration profile, the probe response was modeled to best estimate 241-BY-104 tank saltcake and tank sludge for different water concentrations. If the detector system were fully calibrated and the modeled waste composition were representative of the tank material, it should be possible to predict moisture concentrations based on the near- or far-field detector response alone. Further improvement in the moisture prediction is usually gained by using the ratio of these two responses. This ratio will often reduce or cancel some systematic uncertainties in the measurement as well as correct for some near-borehole effects.

Interpreting the scan data obtained from the saltcake region of each tank is complicated by the fact that the LOW insertion through the hardened saltcake requires that a water lance be used to create an opening. In-tank photographs of many LOWs show a saltcake entrance hole larger than the LOW, leaving an annular air gap around the LOW. The observed annular air gap affects the responses of the detectors. It should be possible to correct for such an air annulus using modeling in conjunction with experimental tests. In addition, modeling has shown that developing a detector with a thermal neutron shield (epithermal neutron detector) would be less sensitive to the air gap and should allow more accurate moisture determination. The fact remains, however, that the gap contains less waste and the waste may be drier because of its increased surface area exposed to air in the tank.

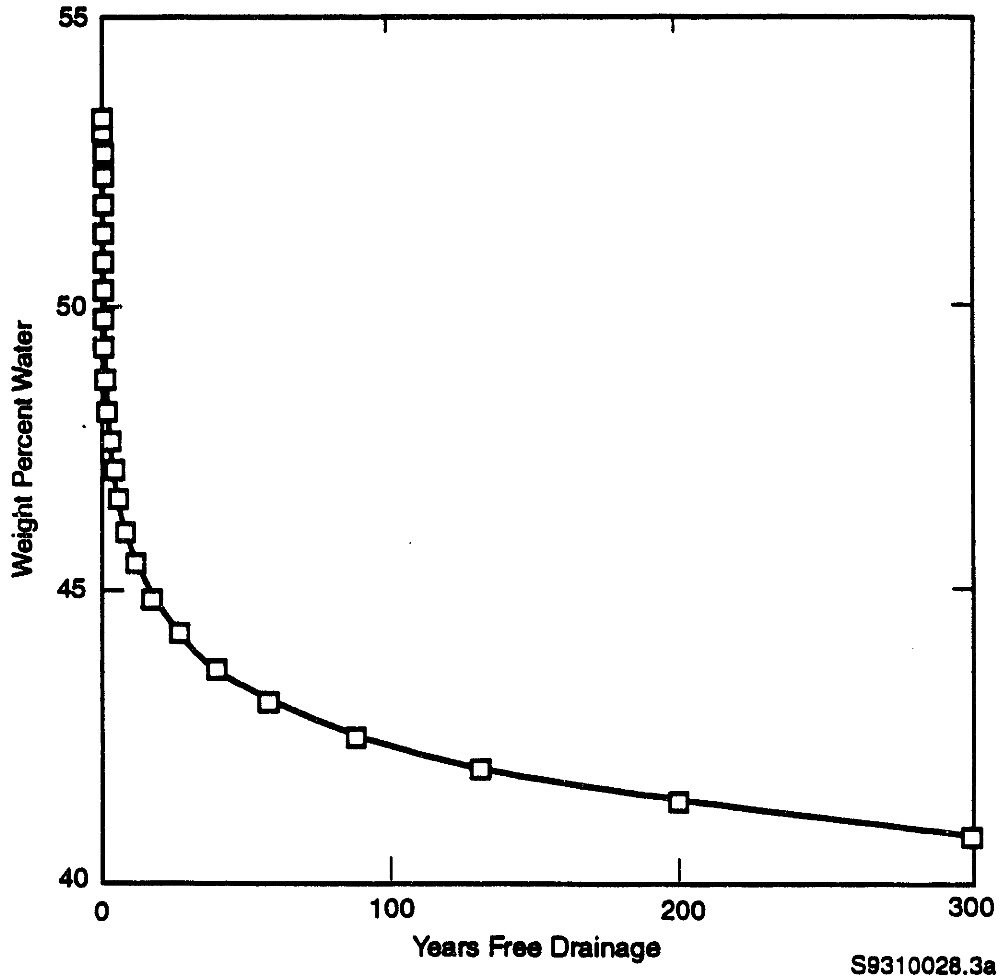
The University of Washington's Center for Process Analytical Chemistry (CPAC) has completed a Phase 1 study of the feasibility of measuring saltcake surface moisture with optical scattering techniques (Veltkamp 1993). Scattering comparison studies for three spectral regions (visible, near-infrared [NIR], and mid-infrared) on a 241-BY-104 saltcake simulant, indicated that the NIR region produced the best moisture sensitivity and the simplest (one parameter) calibration model. Over a range of 0 to 20 wt% moisture, the NIR calibration model predicted water within 0.5 wt%. Issues such as particulate size and material matrix changes will be explored in the Phase 2 work. The Phase 2 work will also include a full-scale demonstration experiment that indicates feasibility at tank scale dimensions for noncontact sensing.

A spectrometer system with a fiber optic probe is being delivered to WHC by the Savannah River Site (SRS) laboratory. The plan is to integrate the CPAC NIR calibration model with this system for a remote probe moisture sensing system. Nonradioactive (cold) materials will be used to feature test this system. The remote fiber optic probe system has potential application in hot cells and with in situ waste tank cone penetrometer systems.

A preliminary modeling analysis was performed to evaluate ferrocyanide sludge water loss as a result of gravity drainage. The model simulated flow of a highly concentrated solution of nitrate salts through an unsaturated porous medium. Data from the small column and centrifugation experiments (reported in Section 5.4.5.2) are being used to estimate the hydraulic properties that control liquid flow in the sludge. Figure 5-1 shows water remaining as a function of time for a 2.44-m (8-ft)-deep sludge layer. The model indicated that the sludge would still contain 40 wt% water even after 200 to 300 years of drainage.

The modeling results are still tentative because consolidation processes and possible evaporative loss of water were not included. Other studies have demonstrated that sludge shrinks by consolidation as it drains liquid. The current unsaturated flow analysis, however, presumes that the sludge matrix remains rigid. Moreover, sludge would dry out at the surface of a profile if exposed to an atmosphere of sufficiently low relative humidity. This modeling study did not consider evaporation at the surface if the relative humidity is less than saturation.

Figure 5-1. Water Concentration at the Surface of a 2.44-m (8-ft) Column of Ferrocyanide Sludge as a Function of Drainage Time.



- **Planned Work to Complete Program.** An experimental test area in which to complete the final development, testing, and calibration of a prototype neutron diffusion-based moisture measurement system is being set up. This will allow necessary, controlled experimental measurements to be made.

  Development of two neutron probes with different source-to-detector spacings will be completed and the probes will be used to scan for moisture content in the ferrocyanide tanks. A single probe with two detectors may be developed later if it is necessary to reduce the time required for scanning LOWs.

The possibility will be investigated of using a pulsed neutron source for obtaining additional information about the surrounding medium. A simulant more representative of the neutronic properties of ferrocyanide waste will be identified and used to obtain probe data as a final check for the Monte Carlo Neutron Photon (MCNP) model.

Integrating the SRS NIR system with the CPAC calibration model and identifying materials for cold feature testing will be initiated. The Phase 2 work scope that started in FY 1993 will be completed and a report expanding on the Phase 1 work (Veltkamp 1993) will be issued for public availability. The Phase 2 studies will optimize the calibration model and evaluate the effects of matrix interferences on moisture sensitivities.

The CPAC surface moisture monitoring concept will proceed through Phase 3 studies and final evaluation made. If the concept appears feasible, a prototype monitoring system will be initially installed in a hot cell. If the concept is successful, an evaluation will be made as to the advisability of installing a prototype into a tank, taking the Ferrocyanide Safety Program surveillance needs into consideration.

Drainage modeling will continue, and will be expanded to include moisture loss from the waste surface. The work will be reported in a document cleared for public release.

Overall, the various concepts for moisture monitoring will be evaluated, the monitoring needs evaluated from a surveillance requirement standpoint, and a decision made as to what systems should be deployed.

Frequency of moisture measurement will be established and appropriate administrative systems developed to detect potential decreasing amounts of moisture.

- **Milestone Status**

  - **March 31, 1994.** Complete the Phase 2 surface monitoring interference study/scaleup report.

  - **September 30, 1994.** Complete Phase 3 surface monitoring work and provide a report.

  - **September 30, 1994.** Provide a working prototype neutron probe system for moisture monitoring with documentation.

  - **September 30, 1995.** Complete first phase of neutron moisture monitoring installation and initiate monitoring.

- **September 30, 1995.** Complete surface moisture measuring development work and in-tank demonstration, if warranted.

- **September 30, 1996.** Complete installation of neutron moisture monitoring equipment.

- **September 30, 1996.** Initiate installation of surface moisture monitoring equipment if demonstration is successful and if need is warranted.

- **September 30, 1997.** Complete installation of surface moisture monitoring system.

5.1.5.4 Cooling System Requirements. If an increasing temperature trend develops, leading to undesirable high temperatures in a ferrocyanide waste tank, a method for controlling the temperature to prevent the loss of moisture would be required. Immediate emergency actions that would be taken are described in the *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991b). Types of cooling systems might include, but are not limited to: (1) forced ventilation of the tank, using an existing or new exhauster system; (2) air conditioning air to the tank; (3) adding humid air or mist; and (4) adding water to the tank. Systems (2), (3), or (4) might also require that an exhauster system be installed on the tank. For tanks with large amounts of solids, the cooling provided by the exhauster might not allow the temperature to be controlled at the bottom of the waste. Adding water to the tank is undesirable because it could potentially add radioactive waste to the soil, assuming the tank leaked. Adding humid air to the tank has the advantage in maintaining a higher moisture level which by itself (if it reached the lower part of the waste) would prevent the occurrence of any exothermic reaction. Air conditioning might provide the necessary cooling where a standard exhauster is not sufficient.

- **Planned Work for Completion of Program.** An engineering study may be performed to determine the best method for preventing a potential exothermic reaction in the event of increasing temperatures in a ferrocyanide tank. The results of the engineering study would lead to a decision whether to design and purchase a cooling system as a contingency measure.

- **Milestone Status**

  - **September 30, 1995.** Complete an engineering study (if required) to identify the best system for controlling an increasing tank temperature.

  - **January 31, 1996.** Decide whether a cooling system should be available as a contingency action. Initiate fabrication/purchase of the cooling system, as required.

- **September 30, 1997.** Fabricate and install cooling systems (if required).

5.2 CONTINUOUS TEMPERATURE MONITORING

5.2.1 Background

All Hanford SSTs were equipped originally with thermometers or TCs for temperature measurement. By 1989, many of the TC elements were inoperable, and the "good" TCs were being manually read by operators, generally on a 1-, 3-, or 6-month interval. As a result, there were many missed and inaccurate readings. Thus, a reliable and consistent temperature database for the ferrocyanide tanks was not available.

The TC reading frequency for the ferrocyanide tanks was increased to weekly in October 1990. The additional readings, coupled with the temperature upgrade program (see Section 5.1.5.1), improved the temperature database and reduced scatter considerably. However, the reliance on operators for scheduled manual readings still resulted in many questionable readings. A project was started to provide continuous, direct temperature readouts and alarms to a continuously manned station. As a first phase, strip chart recorders were placed on two of the higher temperature ferrocyanide tanks (241-BY-106, -110) in March 1991.

The need for improved temperature measurements was recognized by the DNFSB and led to Recommendation 90-7.2:

> *"The temperature sensors referred to above should have continuous recorded readouts and alarms that would signal at a permanently manned location any abnormally high temperatures and any failed temperature instrumentation."*

5.2.2 Evaluation of Issue

It is agreed that continuous temperature monitoring of the ferrocyanide tanks with readout and alarms in a permanently manned location is needed. Even when the tanks are removed from the Watch List, it is expected that continuous temperature surveillance will continue, although not dictated by the safety criteria to ensure in situ safe storage. Prudent management of the tanks, especially the SSTs, requires that the upgraded instrumentation be surveilled until the waste is finally removed from the tanks. See Section 5.6.4 for the plan for response to increasing ferrocyanide tank temperatures.

5.2.3 Baseline Assumptions

- Temperature measurements provide valuable information, although the measurements provide only one (or two) vertical profiles in the tank waste.
- The temperature-sensing elements (TCs or RTDs) should be read automatically, to eliminate the errors introduced by manual readings.
- The temperature readings need to be timely and accurate; they must initiate an alarm if preset limits from a baseline are exceeded.

5.2.4 Method to Close Recommendation 90-7.2

Connecting the temperature-sensing elements in the radioactive waste (both existing and from new instrument trees) to TMACS will provide the necessary temperature monitoring. (See also Section 5.1.5.1 for provisions for new instrument trees.)

5.2.5 Action Plan

The objective of this task is to have continuous and more accurate temperature monitoring, data logging (recording), and alarms on all ferrocyanide tanks with readouts at the Computer Automated Surveillance System (CASS) in the 2750E Building (200 East Area), which is manned 24 hours per day. Until completed, temperature readings on the ferrocyanide tanks will continue to be taken manually on a weekly basis. (Weekly is defined as 7 days, not to exceed 12 days, between any successive readings of an individual tank.) The enhanced monitoring will significantly improve the accuracy, precision, and detection of potential changes in temperature.

The scope of this task has not changed from the initial implementation plan. Delays have been experienced in completing the installation for all tanks, primarily because of tank farm entry restrictions. Using supplied fresh air has been imposed, first for work within the 241-C Tank Farm, and since early 1992 for work around all ferrocyanide tanks.
An Administrative Hold placed on tank farms activities on August 12, 1993 to allow a re-examination of tank farm conduct-of-operations and safety procedures has also delayed completion of this task.

5.2.5.1 Tank Monitoring and Control System (TMACS). This task provides the continuous monitoring of currently installed (and operable) temperature-sensing elements for the ferrocyanide tanks. New instrument trees will be connected to the system as they are installed in each tank, resulting in continuous monitoring of all trees in ferrocyanide tanks. All data are collected automatically at the continuously manned CASS Operator Control Station. The monitoring system is independent of the CASS and is capable of displaying data to an operator on request. Trend data on selected points are available for display in numeric or graphic form.

The system, which became operational in September 1991, has the capacity to assign alarms for change in the value of any temperature point. Alarms, if they occur, trigger an audible annunciator and are logged immediately to hard copy. An alarm summary display provides a list of the most recent alarms in order of occurrence. Each alarm can be identified by point and time of occurrence. Operator acknowledgement of the alarm will silence the audible annunciator.

Signal conditioning and multiplexing are performed locally at each tank. This eliminates the need to transmit low-level signals to the tank farm boundary and reduces cable runs. Electronic noise, extension wire corrosion, and thermal gradients are thereby reduced.

Five BY Farm tanks were first connected to the system in September 1991. Currently all Ferrocyanide Watch List tanks in the 241-BY, 241-TY and 241-TX tank farms have been connected to TMACS (including four new instrument trees installed in 241-BY farm). Thirteen ferrocyanide tanks (16 trees and two LOW TC elements) are monitored by the TMACS. Temperature readings from the working TC elements in these tanks are being recorded continuously. The design has been completed for connecting the ferrocyanide tanks in the 241-BX, 241-C and 241-T tank farms, but final installation has been impacted by the Tank Farm Administrative Hold.

- **Planned Work To Complete Program.** Construction has resumed in C, T, and BX Farms, and the initial TMACS installation will be completed by September 1994.

- **Milestone Status**

  - **September 30, 1994.** Complete installation of the TMACS for the four ferrocyanide tanks in C Farm, one tank in T Farm, and two tanks in BX Farm. Ferrocyanide tanks recently removed (BX-110, BY-101, and T-101) or scheduled to be removed (BX-102 and -106) will also be connected, but not until FY 1995.

  - **December 31, 1994.** Complete installation of the TMACS for new TC trees installed during FY 1994. The completion of the TMACS installations is also a TPA milestone (M-40-02).

5.3 COVER GAS MONITORING

5.3.1 Background

Concerns that flammable gases might be present in the ferrocyanide tanks led to DNFSB Recommendation 90-7.3:

"Instrumentation should also be installed to monitor the composition of cover gas in the tanks, to establish if flammable gas is present."

All ferrocyanide tanks, like most SSTs, are passively ventilated to the atmosphere via individual high-efficiency particulate air breather filters. The "breathing" is dependent on changes in barometric pressure and differences in temperature between the waste tank and the outside air. The pressure change causes a small volume of stagnant air to be replaced with fresh air, which helps control the concentration of chemical vapors inside the tanks. The tank vapor space does not have any normal capability for sampling; therefore, a riser must be opened to obtain gas samples. The tank waste is expected to produce small amounts of hydrogen (H_2) via radiolysis of water, but at only a small rate because of the low fission product inventory. Sampling of the ferrocyanide tanks to date has shown only trace amounts of hydrogen and sometimes other flammable gases.

In general, the vapor spaces of the waste tanks are poorly characterized. Several SSTs emit noxious gases, with ammonia being fairly common. It has been postulated that ferrocyanide tanks could emit hydrogen cyanide gas, from degradation of cyanide compounds, although results to date show less than detectable (<2 ppm) levels. The normal practice before work begins around or in an SST has been to sample the work space and vapor space, if a riser is opened, with a combustible gas analyzer and other gas detection devices (e.g., volatile organic monitors and Dräger™ tubes) as directed by WHC Industrial Hygiene. Supplied breathing air is initially used if a tank riser is opened. Until recently, all work on any ferrocyanide tank required that workers use supplied breathing air. This requirement has been reduced or eliminated using information gained from gas sampling efforts.

5.3.2 Evaluation of Issue

The vapor space within the ferrocyanide tanks must be sampled for flammable gases before performing any intrusive activities in the tanks. This control has been included in all safety assessments written for such activities (e.g., core/surface sampling, and thermocouple tree installation). To date, there is no indication that continuous monitoring for compositional changes is needed. However, if periodic, or cyclic, venting of the ferrocyanide tanks does occur, sampling of the tanks that has been done to date may not have detected all potential concentrations of flammable gases. Note that there has been no indication from gas sampling or tank level measurements that cyclic venting occurs in these tanks.

5.3.3 Baseline Assumptions

- Flammable gases are assumed to be present until proven otherwise.
- Noxious gases are assumed to be present until proven otherwise.

- Vapor space and thermal modeling have shown that stratification is improbable, and that hydrogen gas levels from radiolysis alone are not high enough to be in the flammable range. Organic vapors may still be above the lower flammability limit (LFL), however.

5.3.4 Method to Close Recommendation 90-7.3

This recommendation may be closed when the vapor spaces of all the ferrocyanide tanks have been sampled and found to be below concern for flammability. The issue of the need for continuous monitoring will also be resolved. A study will be performed to examine the potential for periodic, or cyclic, venting of flammable gases. This study and past sample analyses will address the question of how fast the gas composition within a given tank may change. If characterization of the tanks demonstrates that the fuel value is below the proposed 8% limit (Section 4.3), flammable gases will not be a concern as it applies to the ferrocyanide program but, instead, will be addressed by the flammable gas program. If it is deemed necessary to install continuous gas monitoring, those results will be evaluated and used as they apply to the proposed safe storage limits with respect to fuel and moisture.

5.3.5 Action Plan

The intent of this task is to provide intermittent gas sampling for the ferrocyanide tanks and to determine whether continuous monitoring is required. The safety assessments for intrusive activities (such as core drilling and TC tree installation) require sampling for flammable and noxious gases.

The frequency of gas sampling and/or the need for continuous monitoring will be determined after most of the ferrocyanide tanks have been sampled and the data analyzed for gas content, concentration, and distribution. An evaluation will be completed to determine which gases may need to be continuously monitored and whether a prototype monitor should be installed in certain tanks. To date, no evidence exists that continuous monitoring is necessary for any gas.

5.3.5.1 Interim Flammable Gas Monitoring. The effort to conduct flammable and toxic gas monitoring and analyses in the ferrocyanide tanks is continuing. Most of this effort was transferred to the Tank Vapor Issue Resolution Program, which is coordinating interim gas monitoring of the ferrocyanide tanks. Tank vapor spaces are measured for flammability using a commercial combustible gas monitor (calibrated with pentane gas) and are monitored for potential toxic gases using an organic vapor monitor and Dräger™ tubes as required by the safety assessments and work procedures for a particular activity. Development and validation of alternative technologies for vapor space characterization are in progress using Summa canisters and specific absorption tubes. The initial vapor space sampling was done in several tank locations; i.e., from two widely separated risers and at three elevations in the vapor space. Review of the sample data indicated that sampling from one riser was adequate and the number of sample elevations may also be reduced in the future.

To date, the vapor spaces in 15 of the ferrocyanide tanks have been sampled. In two of the tanks the combustible gas analyzer reading was reported as 1% of the LFL, and the reading was reported as <1% in all other ferrocyanide tanks sampled. The maximum reading reported for the organic vapor monitor was 350 ppm (~0.035 vol. %) in tank 241-BY-110, and all other tanks had readings at least an order of magnitude lower. Ammonia has been detected in several of the sampled tanks; the maximum reported value was estimated as 612 ppm, again in tank 241-BY-110. The measured values in the other tanks ranged from <2 ppm to 250 ppm. Hydrogen cyanide measurements with Dräger™ tube monitoring have all been below 2 ppm, the detection limit for that method. (The NIOSH recommended 8-hr threshold limit value time-weighted average exposure limit for HCN is 4.7 ppm.) This method is adequate for field use. Two tanks, 241-C-108 and -111, have been sampled and analyzed for HCN with a more sensitive method as part of a larger characterization program, and both were reported as less than 0.04 ppb; i.e., <40 parts per trillion.

- **Planned Work to Complete Program.** Flammable gas sampling and selected noxious gas monitoring will be done, as required, to support planned core sampling and instrument tree installation.

- **Milestone Status**

  - **September 30, 1994.** Complete vapor space sampling of remaining ferrocyanide tanks, as required, to support various field activities.

  - **September 30, 1995.** Complete vapor space sampling of remaining ferrocyanide tanks. This milestone addresses the November 1995 TPA milestone M-40-03.

5.3.5.2 Continuous Gas Monitoring. Options for installing a gas monitoring capability on the new instrument trees have been reviewed and a heated vapor sampling tube has been added to the design of future trees for ferrocyanide tanks (see Section 5.1.5.1). This will allow vapor space sampling on a continuous or intermittent basis. However, a definitive decision to monitor continuously or just occasionally has not been made. The need for continuous gas monitoring will be addressed in a study that will address the potential for cyclic venting and the possibility of accumulating flammable gases. Evaluation of gas samples secured to date for tanks 241-BY-101, -104, -110, -111, -112; 241-BX-106, -110, -111; 241-C-108, -109, -111, -112; 241-T-101, -107; and 241-TX-118 has indicated no need to continuously monitor for specific gases.

The possibility that localized concentrations or stratification of gases exist in the tanks has been evaluated. This concern is being addressed through the sampling effort described in Section 5.3.5.1. A modeling effort to determine airflow patterns in the vapor space of tank 241-C-109 was conducted to evaluate the amount of mixing and the local gas concentrations that could occur. The results of this analysis were used to evaluate the hazards and risks involved during sampling and other intrusive activities within this and other ferrocyanide tanks.

The results of this study have shown that the gases in the tank are well mixed and follow Graham's law for gaseous diffusion. A significant exchange of tank gases with fresh air occurs frequently and the accumulation of flammable gases is precluded based on the natural breathing rates of the tanks from changes in barometric pressure. Thermal convection was shown to provide a well-mixed vapor space within the tanks. This task has been completed and a report, WHC-SD-WM-ER-183, Rev. 0 (Wood 1993), issued.

An analysis of a second tank was deemed unnecessary because of the well-mixed environment calculated for the first tank. This study, however, did not address the possibility of cyclic venting and flammable gases accumulating for short periods of time before fresh air exchange occurred.

- **Planned Work to Complete Program.** A study will be completed to evaluate potential sources of flammable gases including possible cyclic venting. The study will determine if continuous gas monitoring equipment is needed. A decision on the need for continuous vapor space monitoring of some or all of the ferrocyanide tanks will be made and documented based on sampling data. If recommended, continuous gas monitoring will be implemented. However, if characterization of the tank waste demonstrates that the fuel value is below the proposed 8 wt% limit, no continuous gas monitoring will be performed by the Ferrocyanide Safety Program.

- **Milestone Status**

  - **March 31, 1994.** Complete a study to evaluate whether continuous monitoring is required. This task is on schedule.

  - **September 30, 1995.** Develop and design continuous monitoring equipment (if required).

  - **September 30, 1997.** Complete installation of continuous gas monitoring equipment on six tanks (if required).

5.3.5.3 Tank Pressure Monitoring. Public Law 101-510, Section 3137 (Wyden Bill), requires that "...the Secretary of Energy shall identify which single-shell tanks...may have a serious potential for release of high-level waste due to uncontrolled increases of... pressure. After completing such identification, the Secretary shall determine whether continuous monitoring is being carried out to detect a release or excessive...pressure at each tank so identified. If such monitoring is not being carried out, as soon as practicable the Secretary shall install such monitoring...". The ferrocyanide tanks initially were so identified, but the capability for pressure monitoring does not exist on the tanks. Because the ferrocyanide in these tanks is believed to be wet, the possibility of a rapid reaction that would generate a pressure wave is considered highly unlikely and most likely incredible. Sufficient knowledge about the safety of the Ferrocyanide Watch List tanks exists at this time to justify closure of the USQ, which DOE approved in early March 1994. Characterization (core sampling) of most of the tanks, however, is required to resolve the Ferrocyanide Safety Issue.

Characterization of all ferrocyanide tanks is now scheduled to be complete by September 1995. It is anticipated that this characterization will place all ferrocyanide tanks into the SAFE category, a condition sufficient to remove them from the Watch List. Therefore, it is very likely that pressure monitoring will not be necessary nor required. It would take several years to install pressure monitoring instrumentation and the readout capability for the CASS Control Room. Another study is being conducted that will evaluate the potential for the generation of flammable gases that might cause pressurization of a tank. If the results of this study show that 25% of the LFL cannot be exceeded, a recommendation will be made that no pressure monitoring be installed.

- **Planned work for Completion of the Program:** Complete a study on evaluation of gas generation and the need for continuous pressure monitoring.

- **Milestone Status**

  - **July 29, 1994.** Complete studies to determine whether continuous pressure monitoring is required for some or all ferrocyanide tanks.

  - **September 30, 1995.** Install the first phase of pressure monitoring instrumentation (if required).

  - **September 30, 1996.** Install pressure monitoring instrumentation and readout capability on all applicable ferrocyanide tanks (if required).

5.4 FERROCYANIDE WASTE CHARACTERIZATION

5.4.1 Background

The ferrocyanide sludge was deposited in the SSTs in the mid-1950s. Sampling and analysis of the sludge since that time have been limited. The 241-TY Tank Farm (which contains T Plant flowsheet sludge) was core sampled in 1985 (Weiss 1986); thus, some data on these tanks, including total cyanide analyses on two archived sample composites (Winters 1988), were available when the DNFSB first reviewed the Ferrocyanide Safety Issue. The DNFSB Recommendation 90-7.4, which follows, reflects their concern over the lack of analyses of the actual tank waste:

> *"The program of sampling the contents of these tanks should be greatly accelerated. The proposed schedule whereby analysis of two core samples from each single shell tank is to be completed by September 1998 is seriously*

> *inadequate in light of the uncertainties as to safety of these tanks. Furthermore, additional samples are required at several radii and at a range of elevations for the tanks containing substantial amounts of ferrocyanide."*

An extensive core sampling program for the ferrocyanide tanks has been initiated, with three tanks (241-C-112, -C-109 and -T-107) sampled to date. Two surface (saltcake) samples from tank 241-BY-104 were also secured and analyzed.

Ferrocyanide tank core samples are being analyzed to provide characterization of physical, chemical, and radiological properties to support: (1) the resolution of the Ferrocyanide Safety Issue; and (2) the design of retrieval, pretreatment and disposal systems as required for all SST samples. All core samples are normally full waste-depth; thus, a vertical profile of the waste is secured at the sample location. The desire to secure multiple samples across the tank area is tempered by the following considerations: (1) only a limited number of entry risers are available; (2) Hanford Site analytical facilities (hot cells and labs) for handling these highly radioactive samples have a limited capacity; and (3) the safety screening suite of analyses for a typical set of ferrocyanide core samples is estimated to cost approximately $300,000.

5.4.2 Evaluation of Issue

It is agreed that sampling and characterization of the ferrocyanide tanks is required to adequately resolve the safety issues. The current schedule for ferrocyanide tank sampling shows completion of sampling from all ferrocyanide tanks by the end of FY 1995 (DOE 1994). A data quality objectives (DQO) document, *Data Requirements for the Ferrocyanide Safety Issue Developed Through the Data Quality Objectives (DQO) Process* (Buck et al. 1993), was prepared that provides a statistical basis for the number of cores required to characterize the ferrocyanide tank waste. The number of cores required to determine the fuel and moisture values for each ferrocyanide tank is two full-depth cores, taken from representative areas of the tank. Each core consists of 48-cm (19-in.) segments or portions thereof depending on the depth of the waste in the tank. The sludge layer in these cores will be divided into four 12- cm (4.75-in.) subsegments for each 48-cm (19-in.) segment. If the tank contains a saltcake layer, the saltcake segments will be divided into only two subsegments. Process flowsheet knowledge, tank historical data, and results obtained from tests with ferrocyanide sludge simulants are used to supplement the core sample results.

Ideally, the bulk of the data regarding the behavior of ferrocyanide waste would be obtained from actual waste samples. However, the scarcity of tank samples has necessitated the use of waste simulants to perform studies on energetics, kinetics, aging, and rheological properties. In addition, it is more cost effective and timely to work with simulants. Problems encountered in working with actual waste, in addition to the obvious ones of working with highly radioactive materials, include the fact that in many of the samples (as demonstrated by the 241-C-109 and -112 core samples) the waste no longer contains the original high concentrations of analytes of concern. The waste has aged, and aging data may be difficult to obtain from the tank samples (except perhaps by spiking with a flowsheet simulant). Detailed historical analyses and an extensive technical review were performed during development of the simulants. There is a laboratory task (see Section 5.5.5.1) to compare the physical and chemical properties of ferrocyanide waste simulants with the results of actual tank waste. If discrepancies are found, the safety implications will be evaluated and further work performed as necessary.

5.4.3 Baseline Assumptions

- Some waste forms are reactive and capable of propagating reactions above some onset temperature [currently estimated from simulants to be >245 °C (473 °F) (Postma et al. 1994)], unless shown otherwise.
- Even if reactive, stored ferrocyanide waste cannot reach this onset temperature from the present storage temperature (≤55 °C), unless the moisture content of the waste drops below the safety criteria limit for moisture (see Section 4.3), and some heat source is present to cause the tank to heat up. Studies of moisture transport in ferrocyanide tanks have concluded that the ferrocyanide sludge will retain a moisture content greater than 40 wt% (see Section 5.1.5.3), even if the tanks leak or are saltwell pumped (Grigsby et al. 1992, Postma et al. 1994).
- The most reactive ferrocyanide sludges are those from the In Farm scavenging flowsheet; these are stored in the four 241-C Farm ferrocyanide tanks. T Plant flowsheet ferrocyanide sludge exhibits chemical and physical behavior similar to U Plant flowsheet sludge because their compositions are comparable (Fauske 1993, Jeppson and Wong 1993).
- The DQO process has been used to establish the requirements for safety screening sampling and analysis for the Ferrocyanide Watch List tanks (Buck et al. 1993, Babad and Redus 1994). Other DQO analyses are planned; (e.g., for waste retrieval) and the DQO sampling needs for all tank issues will be combined to allow the most efficient use of sampling and analytical resources.
- Waste simulants and modeling assumptions are conservative estimates appropriate for use in closing the USQ and resolving the Ferrocyanide Safety Issue.

5.4.4 Method to Close Recommendation 90-7.4

It is anticipated that the sampling and analysis of the In Farm scavenging flowsheet tanks, several U Plant scavenging flowsheet tanks (including some BY-Farm tanks), and at least one

T Plant scavenging flowsheet tank, in combination with simulant studies of all flowsheets, will establish the maximum reactivity of these ferrocyanide sludges. When these analyses and evaluations are completed, sufficient information may be available to resolve the Ferrocyanide Safety Issue. The present schedule for core sampling calls for obtaining cores from all of the ferrocyanide tanks by September 30, 1995. However, the waste in many of the U Plant flowsheet tanks, for example, may exhibit very similar chemical and physical properties. If this is the case, it may not be necessary to obtain cores from each ferrocyanide tank, and resolving the safety issue could proceed ahead of schedule.

5.4.5 Action Plan

Characterization of the chemical and physical properties of ferrocyanide tank waste is necessary to: (1) determine the chemical reactivity of the waste; (2) guide chemical reaction studies; (3) provide a basis for determining the probability and consequences of any postulated uncontrolled ferrocyanide reaction; and (4) allow application of the study results to resolve the Ferrocyanide Safety Issue. Knowledge of the relative vertical position of various waste constituents is also important to determine the extent of safety concerns.

Work in progress to characterize the ferrocyanide tank contents includes full waste-depth core sampling and analysis. Additionally, infrared reflectance spectroscopy is being developed for more rapid waste analyses for ferrocyanide/ferricyanide and other anticipated key analytes. Note that tank characterization work is also underway using flowsheet simulants (see Section 5.4.5.2).

Initial core sampling efforts focused on the 241-C Farm ferrocyanide tanks because flowsheet analysis and simulant testing indicate the In Farm scavenged waste is likely to be much more reactive than other ferrocyanide waste produced by the U Plant and T Plant flowsheets. The 241-C Farm waste is also amenable to push-mode core sampling.

5.4.5.1 Ferrocyanide Tank Waste Sampling and Characterization. Important materials present in ferrocyanide waste consist of fuel (e.g., ferrocyanides, sulfides, and reduced carbon species such as organic complexants), oxidants (e.g., nitrates and nitrites), and inerts or diluents (e.g., water, phosphates, sulfates, carbonates, oxides, and hydroxides). The location of fission products, such as ^{137}Cs and ^{90}Sr, is important because these isotopes act as heat sources that can raise and maintain the temperature of the tank contents and because they are source terms if a radiological release occurs. The water content of the waste is important because of its high heat capacity and heat of vaporization; water is also an effective inerting material and prevents sustained combustion. Wet ferrocyanide material (expected to have precipitated in the tanks with 50 wt% or greater water) will neither react nor propagate. This material would have to be dried by some undefined mechanism to reach a condition at which it could burn or propagate if heated to temperatures above 245 °C (473 °F). Other materials (e.g., nickel, copper, lead, and rare earths) may be important as potential catalysts, but have not been identified as such in a PNL screening (Scheele et al. 1993); refer to Section 5.5.5.1.

Both rotary-mode core sampling and push-mode core sampling will be available in March 1994 for obtaining core samples from the Watch List tanks. Tanks without saltcake and with relatively soft waste solids can be core sampled by the push-mode method. If a hard saltcake layer is present, rotary-mode core sampling will be used.

Cores are normally full-depth, taken in 48-cm (19-in.) segments starting above the top of the expected solids level and working down to the tank bottom. The specification requires that the bottom segment be a full 48-cm (19-in.) core segment. A sample analysis test plan is prepared to specify the analytes of concern and what laboratory procedures will be used. The plan also specifies how the segments will be handled for analysis (e.g., whether subsegments are prepared for analysis, how to prepare material from the segment with material from other segments to form a core composite, and how to blend and analyze material for the segment analysis). The core sample segments from the first three ferrocyanide tanks were analyzed by quarter-segment, i.e., the 48-cm (19-in.) segments were separated into 12-cm (4.75-in.) samples for analysis to be sure that any peak ferrocyanide concentrations were captured. The DQO documents (Buck et al. 1993, Babad and Redus 1994) require that future core samples of the ferrocyanide sludge also be analyzed by quarter-segment.

The priority for sampling ferrocyanide tanks has now been changed to reflect the need to determine the reactive properties of the contents. In response to DNFSB Recommendation 93-5 (Conway 1993) to expedite sampling and analyses required to address safety issues in the Hanford Site Watch List tanks, the analysis plans for future ferrocyanide tank core samples (and the plans for other Watch List tanks) have been revised (DOE 1994). The Watch List tanks have been given priority for core sampling and the number of required analytes was reduced and refocused on safety-related properties (Babad and Redus 1994).

The source of ferrocyanide material in both of the 241-C farm tanks sampled to date was the In Farm scavenging flowsheet. This material is expected to yield higher ferrocyanide concentrations than either the U Plant or T Plant scavenging flowsheets. The analytical results from these samples and their interpretation were reported in Simpson et al. 1993a and 1993b, and in the applicable DNFSB Quarterly Reports. To summarize, the results for samples from both tanks showed that: (1) the waste material contains appreciable moisture (greater than 19 wt%*); (2) the fuel content is such that the waste will not support a propagating exothermic reaction even when dry (the maximum measured exotherm for any

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* One sample from tank 241-C-109 showed only 19 wt% moisture. Moisture values from this tank's core samples ranged from 19 to 58 wt% for the three cores taken (Simpson et al. 1993a). Results from tank 241-C-112 samples showed moisture contents from 38 to 64 wt% (Simpson et al. 1993b). The samples found to contain the lowest moisture values were also found to be very low in total cyanide and exhibited endotherms or only small exotherms during testing for energetics. Moisture determinations for samples from the two tanks were completed more than 30 days after the core samples were obtained from the tanks, and some moisture loss in the samples was expected.

sample or subsample was -12 cal/g, well below the level of concern limit of -115 cal/g); and (3) although it appears that the bulk of the precipitated nickel ferrocyanide has degraded [the calculated ferrocyanide contents, based on the analytical results, are only about 13 to 19% of the estimated original tank inventories], the ^{137}Cs is still retained in the solids. Thus, the ^{137}Cs may still be present as $NaCsNiFe(CN)_6$.

Three, four-segment cores were taken from tank 241-T-107. The analytical report has been received and a data interpretation report is now being prepared. The most significant item noted is that none of the core samples or subsamples exhibited an exotherm. This is the first tank containing material from the U Plant scavenging flowsheet to be core sampled for the Ferrocyanide Safety Program.

Two surface samples were taken by auger from tank 241-BY-104 in June 1992. These samples from the saltcake overlying the ferrocyanide sludge were taken primarily to provide information on the fuel value and energetics of the waste as input to the safety evaluation for rotary-mode core sampling. The applicable analyses were reported in Neskas and Borsheim (1993). Briefly, the results showed that propagating reactions could not be initiated in the samples (maximum exotherm of -41 cal/g), and the total cyanide content was quite low (~40-80 ppm) as expected. This surface crust contained 15 to 17 wt% water, and the material was not rigid and crumbled easily. (The task to test the surface hardness of the 241-BY-104 saltcake with a penetrometer was canceled when testing of the technique indicated that it would yield only an order of magnitude approximation of the saltcake shear strength).

Work was performed early in the Ferrocyanide Safety Program to use existing gamma scan data from the available ferrocyanide tank LOWs to estimate ^{137}Cs concentrations as a function of waste elevation. An improved gamma detector was built and multiple scans were made in each of the 12 tanks containing a LOW. The results were reported in Keele (1991) and Keele et al. (1991), and no additional work has been performed to further enhance the gamma scanning. The effort here has been concentrated on the LOW neutron scanning reported in Section 5.1.5.3.

Development and design work began in July 1991 to demonstrate that rotary-mode core sampling of saltcake waste tanks can be done without producing unacceptably high bit temperatures. No viable concept has been found to date to provide direct reading of the rotary bit temperature. Therefore, a safety envelope was established by laboratory testing with simulants under conditions controlled by operational procedures. Core sampling of ferrocyanide tanks that contain saltcake was deferred until the rotary-mode core sample truck is available for field use. The schedule for its deployment has been established, and the first tank (241-C-106, the high heat load tank, not a ferrocyanide tank) will be sampled in April-May 1994, followed by tank 241-BY-104 in June 1994. Operability test procedures began in mid-August, but have been impacted by the Tank Farm Administrative Hold. Push-mode core sampling was also suspended by the Administrative Hold, but it is also expected to resume by April 1994 starting with tank 241-C-111.

- **Planned Work To Complete Program.** Review of the 241-T-107 sample analysis data will continue and a data interpretation report will be issued. Push-mode core sampling is expected to resume as work to resolve the poor core-recovery issue is completed. Efforts to prepare the rotary-mode core sample system for field use will continue. It is presently anticipated that push-mode core sampling will resume in April 1994. Rotary-mode is expected to begin in April 1994, and all core sampling of Watch List tanks is scheduled to be completed by the end of FY 1995.

- **Milestone Status**

  - **August 5, 1994.** Complete interpretation of ferrocyanide tank 241-T-107 analytical data and issue a report cleared for public release. This milestone was deferred from September 1993 because of delays in core sampling and laboratory data analysis. Poor core recovery and difficulties with interpretation of the scattered data have also delayed completion of this milestone.

  - **September 30, 1994.** Two full-length push-mode core samples from three additional ferrocyanide tanks were originally planned in FY 1993. The following order for sampling in the tanks was planned: 241-C-111, -108, and 241-BX-102. Problems with poor sample recovery and the Tank Farm Administrative Hold have delayed completion of this milestone until FY 1994, and only two tanks (241-C-111 and -108) will be sampled by push-mode. Tank 241-BX-102 is one of two tanks expected to be removed from the Watch List (Alumkal 1993).

  - **September 30, 1994.** Secure rotary-core samples from three ferrocyanide tanks (241-BY-104, -106, and -105).

  - **March 31, 1995.** Complete data interpretation reports, available for public release, for five ferrocyanide tanks (241-C-111, -C-108, 241-BY-104, -BY-106, -BY-105). Completion of the reports for the C Farm ferrocyanide tanks should allow WHC to recommend that the Ferrocyanide Safety Issue be resolved for the four C Farm tanks.

  - **August 31, 1995.** Recommend to DOE that the Ferrocyanide Safety Issue is resolved for the four C Farm tanks.

  - **September 30, 1995.** Obtain core samples from the remaining ferrocyanide tanks.

- **February 29, 1996.** Receive DOE approval that the safety issue is resolved for the four C Farm ferrocyanide tanks and these tanks can be removed from the Watch List.

- **June 28, 1996.** Complete data interpretation reports, available for public release, for the remaining ferrocyanide tanks.

- **January 31, 1997.** Recommend to DOE that the safety issue is resolved for the remaining ferrocyanide tanks.

- **September 30, 1997.** Receive DOE approval that the Ferrocyanide Safety Issue is resolved for the remaining ferrocyanide tanks and these tanks can be removed from the Watch List.

5.4.5.2 Simulated Ferrocyanide Waste Preparation and Characterization. Ferrocyanide waste simulants have been and continue to be prepared and analyzed to determine their composition, physical properties, and chemical reaction properties. These simulants conservatively represent the ferrocyanide waste originally placed in the ferrocyanide tanks. The analytical results from these simulants, along with analyses of actual tank waste samples, waste tank monitoring, and waste modeling, provide information to characterize with assurance any safety concerns of the sludge in each of the ferrocyanide tanks. The results are providing a technical basis for: (1) safety measures taken; (2) decisions on appropriate actions leading to closure of the Ferrocyanide USQ; and (3) resolving the Ferrocyanide Safety Issue.

Five waste simulants (without radioactive species) are used to represent the variety of waste produced in the mid-1950s and stored in SSTs. The waste produced at the Hanford U Plant is represented by U Plant 1 and U Plant 2 test mixtures. The U Plant 1 waste simulant represents 41 of 59 batches and the U Plant 2 simulant represents 9 of 59 batches of U Plant waste. The average U Plant batch volume was about 2,300,000 L (600,000 gal). The other nine batches of U Plant waste have a ferrocyanide concentration between that of U Plant 1 and U Plant 2. A test mixture representing these batches will not be prepared and tested. In Farm flowsheet waste (stored in four C Farm tanks) is represented by the In Farm 1 and In Farm 2 test mixtures. The In Farm 1 test mixture is representative of one batch (expected to have the greatest ferrocyanide concentration) of the 29 In Farm batches processed in the 1950s. In Farm 2 is representative of 11 intermediate ferrocyanide concentration batches of the 29 In Farm batches. An average size In Farm batch was approximately 1,500,000 L (400,000 gal). It should be noted that six of the 29 In Farm scavenging batches did not contain any ferrocyanide, but sodium sulfide was added to enhance precipitation of ^{60}Co.

A T Plant simulant was prepared for testing to represent the six T Plant batches produced. An average-sized T Plant batch was 2,098,000 L (554,000 gal). The T Plant ferrocyanide sludge is stored in three TY Farm tanks.

Three main departures from the actual processes used in the 1950s were made in the laboratory scavenging preparation method to produce the ferrocyanide waste simulants. These changes are as follows: (1) the solution concentrations were adjusted to include nitrite at a 1:3 mole ratio of nitrite/nitrate, to account for nitrite buildup over time in the waste by radiolysis of nitrate; (2) the waste simulants prepared or being prepared for characterization do not contain the radioactive isotopes present in actual waste, because of the difficulty in working with radioactive materials; and (3) the settled waste simulants from the laboratory scavenging process were centrifuged at a force of approximately 2,000 g to mimic an equivalent 30-gravity-year settling period.

A report documenting the analyses and characterization of the U Plant and In Farm simulants was issued in January 1993 (Jeppson and Wong 1993). The T Plant simulant fractions and supernatant prepared have also been analyzed for chemical composition, chemical reactivity (Fauske 1993), and physical properties. A report on the chemical and physical properties is now being prepared. The results indicate that the T Plant bottom fraction contains little fuel and the dried top fraction simulant contains ~9 wt% disodium mononickel ferrocyanide and excess nitrate/nitrite. The fuel in the T Plant simulant is much less concentrated than the In Farm simulants. The cesium content of the supernatant was less than 0.1 ppm.

The X-ray diffraction analysis of the T Plant simulant fractions indicated that iron ferrocyanide $Fe_4[Fe(CN)_6]_3$ was the only identifiable crystalline species in the top fraction and bismuth phosphate was the only identifiable crystalline species in the bottom fraction.

Moisture retention and movement within the ferrocyanide waste and overlaying saltcakes in waste tanks are important to the demonstration of safe storage conditions within the tanks. Studies are presently underway to model (Section 5.1.5.3) and test these water migration characteristics with simulated tank waste. Laboratory work includes measurement of hydraulic conductivity for saturated and unsaturated flow conditions, measurement of air entry pressures and determination of water retention at various drainage pressures. These parameters are then used to model water drainage at tank conditions. The modeling and testing will be expanded to include moisture loss from the waste surface by evaporation as a function of relative humidity. Initial parameters will be determined by waste simulants, and later by tank waste samples when the test methods are verified. However, it may not be possible to measure all needed parameters (such as hydraulic conductivity) on the actual waste samples as recovered. This task will evaluate use of related data and correlations to provide the best estimates for the needed parameters.

Several tests are continuing to determine the amount of moisture remaining in the simulants for free-flowing drainage, such as a tank leak or saltwell pumping of liquids for tank stabilization. A free-flowing liquid drainage test using In Farm 2 top fraction simulant at one atmosphere pressure has been underway for over 20 months. The initial water content of the simulant was 53 wt%. Calculations from the measured liquid drained to date indicate that the remaining material still has a water content of about 48 wt%. Liquid is continuing to drain slowly from this material, but the curve has started to flatten out. Some consolidation of the sludge has been observed. Other smaller tests are continuing at various hydraulic pressures in hopes of reaching equilibrium conditions more quickly.

A vented scoping centrifugation test conducted on In Farm 2 simulant at 10 gravities centrifugal force with fritted porous media (30 μm-sized openings) resulted in a final water content of 47 wt%. An additional vented test conducted at 20 gravities indicated an end point of 46 wt% water. This identifies a final water content that is well above the 12 wt% minimum water content required to prevent propagation of the most concentrated ferrocyanide simulant (Fauske 1992). Results to date show the ferrocyanide sludge drains slowly even under increased hydraulic pressure or centrifugation.

- **Planned Work to Complete Program.** A ferrocyanide waste simulant based on characterization of actual tank waste samples will be prepared, analyzed, and tested. Simulant drainage and centrifugation tests will continue. The effects of relative humidity in air on the loss and absorption of moisture by the waste will be evaluated under surface-to-volume ratios representative of the SSTs.

  A report, available for public release, will be prepared and issued on the three methods used for drying the ferrocyanide waste simulants. This evaluation was completed in FY 1993 (Cash et al. 1993) to determine how well each method measured the amount of bound water still present in the ferrocyanide sludge matrix. Temperatures in the range of 160 to 190 °C (320 to 374 °F) are required before bound water begins to come off a heated sample. The three methods included: (1) heating to 120 °C (248 °F) in air at atmospheric pressure for 18 hr; (2) heating to 105 °C (221 °F) in air at atmospheric pressure for 24 hr; and (3) heating to 60 °C (140 °F) under vacuum at 35 mm mercury absolute for 24 hr.

- **Milestone Status**

  - **March 31, 1994.** Issue a report, available for public release, on the evaluation of the three waste simulant drying methods.

  - **May 31, 1994.** Issue a report, available for public release, on the chemical and physical properties of the T Plant ferrocyanide waste simulant.

  - **September 30, 1994.** Complete drainage tests on ferrocyanide waste simulants and issue a report, available for public release, on modeling and moisture retention by ferrocyanide sludge.

  - **September 30, 1994.** Issue a report, available for public release, on the effects of relative humidity on moisture retention in ferrocyanide waste.

- **September 30, 1995.** Complete waste simulant studies and issue a final report, available for public release.

5.4.5.3 Waste Analysis Using Infrared Spectroscopy. The objective of this activity is to develop and demonstrate Fourier Transform Infrared (FTIR) spectroscopy as a qualitative and quantitative method for measuring key analytes in ferrocyanide tank waste. Immediate application includes scanning of core samples shortly after they are extruded from the core sampling apparatus in a hot cell. The method also has application to waste samples that have been treated with a special solution to dissolve all solids. Later, application to in situ tank measurements may be possible. Techniques for remote sensing via optical fibers in a laboratory hood or hot cell are being pursued as prime means of remote measurement. Analytes of interest include ferrocyanide, ferricyanide, cyanide, water, sulfate, nitrate, nitrite, phosphate, aluminate and organic compounds such as ethylenediaminetetraacetic acid (EDTA) and hydroxyethylenediaminetriacetic acid (HEDTA). Raman spectroscopy which was partially funded by the Ferrocyanide Safety Program in previous years is now under the direction of the Characterization Program at Hanford; funding is no longer provided by the Ferrocyanide Safety Program. Progress on the Raman program is reported in Crawford et al. (1993). Two hot cell campaigns were completed with actual waste tank materials. Data were obtained that demonstrates the potential for a hot cell Raman spectroscopy system; ferrocyanide sensitivity was less than expected but other analytes were readily identified.

Infrared spectroscopy is a promising technology for determining the chemical makeup of various materials. Its application to tank waste sludges has been proposed as a means of rapidly determining the chemical composition of the waste directly or after a sample is put into solution. PNL has developed two solution (wet) methods for future application in a hot cell based on FTIR spectroscopy and ion chromatography (IC) (Bryan et al. 1993). Their procedures, with applicable hardware, will be implemented and used to analyze core sample material from various ferrocyanide tanks. The PNL task includes the initial training and supervision of analysts performing analyses of waste samples and ultimately transferring validated procedures to the PNL and WHC laboratories.

Direct FTIR spectroscopy without using wet methods is being developed at the WHC analytical laboratories, concentrating on those analytes important to the Ferrocyanide Safety Program. However, it is recognized that the spectroscopy of solids only interrogates the surface layer of the solids. Infrared spectral data will be generated using near-infrared fiber optic probes and light guides and beam directing modules in a noncontact configuration. The system will be calibrated using known standards, and system performance of the two light conduits will be compared. The most promising system will be installed and tested in a hot cell with the objective of validating the method for routine use in analyzing ferrocyanide and other waste tank samples in a hot cell.

Infrared, particularly near-infrared, is very sensitive to moisture. The Savannah River Site (SRS) laboratory has fabricated a moisture analyzer that will also be tested and validated as part of this activity using simulated and actual tank waste.

- **Planned Work to Complete Program.** This activity is a continuation of work started in FY 1993 by the Characterization Program. The Raman spectroscopy development work was transferred to the Characterization Program starting in FY 1994, and the FTIR spectroscopy program, which is more sensitive and has direct application to ferrocyanide waste, is now partially supported by the Ferrocyanide Safety Program. The better method for light transmission, fiber optics or light guides and beam directing modules, will be determined by evaluating both techniques. As quickly as possible, the fiber optic probe or the diffuse reflectance sampler and associated light pipe will be tested inside a hood and then a hot cell with simulant waste and actual tank waste. Spectral data will be collected with known standards and compared against the simulants and real waste. Once validated, operating procedures will be certified and transfer of operations to the analytical laboratories at WHC and PNL will be effected.

  A similar approach will be taken with the SRS moisture analyzer to determine its capabilities and sensitivities to water in standard samples, simulants, and actual tank waste. If validated, the unit would be applied to routine moisture analysis of ferrocyanide (and other) waste samples in hot cells at PNL and WHC.

- **Milestone Status**

  - **September 30, 1993.** Transmit a report, cleared for public release, on development and deployment of Raman spectroscopy to analyze actual waste in a hot cell. A report was prepared in September and issued as a cleared document in December 1993 (Crawford et al. 1993).

  - **September 30, 1994.** Complete hot cell demonstration of FTIR spectroscopy for key ferrocyanide waste analytes, including water, and issue a cleared report of FY 1994 test results.

  - **September 30, 1995:** Complete development of solids speciation methods using FTIR and validation of techniques and procedures for routine application in the WHC and PNL analytical laboratories. Issue a final report, cleared for public release, on this task's activities.

5.5 CHEMICAL REACTION STUDIES

5.5.1 Background

Chemical reaction characteristics of the broad spectra of ferrocyanide waste stored in Hanford Site underground tanks are needed to assess the GAO postulation (Peach 1990). The GAO concluded that the source term from a ferrocyanide accident scenario involving a temperature excursion or explosion could result in consequences greater than those described in the HDW-EIS (DOE 1987). The lack of data on the chemical properties of the actual ferrocyanide waste was the basis for DNFSB Recommendation 90-7.5, which follows:

> *"The schedule for the program on study of the chemical properties and explosive behavior of the waste in these tanks is indefinite and does not reflect the urgent need for a comprehensive and definitive assessment of the probability of a violent chemical reaction. The study should be extended to other metallic compounds of ferrocyanide that are known or believed to be present in the tanks, so that conclusions can be generalized as to the range of temperature and other properties needed for a rapid chemical reaction with sodium nitrate."*

Core sampling and analyses of waste from the ferrocyanide tanks are being pursued in a safe manner and on a high-priority basis (See also Section 5.4).

The schedule for determining the chemical properties and potential explosive behavior of ferrocyanide waste was changed to reduce the time for evaluating the Ferrocyanide USQ. Initial efforts were directed toward characterization of dicesium mononickel ferrocyanide [$Cs_2NiFe(CN)_6$] (Cady and Scheele 1992). However, since early 1991, chemical reaction studies have focused mainly on disodium mononickel ferrocyanide [$Na_2NiFe(CN)_6$] (because that is the major ferrocyanide precipitate), on actual waste tank samples, and on five simulated compositions of flowsheet variations used in the 1950's to produce the waste. Additional studies were made or begun to: (1) determine the chemical form of the cyanide compounds in the waste at the present time; (2) determine reaction mechanisms and kinetics; (3) determine the effects of other fuels present in the waste, such as sulfides and organics; (4) determine the effects of possible catalysts and initiators, water, and other diluents on the behavior of the waste; and (5) identify the effects of increasing the ferrocyanide reaction mass. Studies also have been initiated to determine the temperatures at which various reactions begin with respect to gas release, heat release, and propagation, and rates for dry and moist ferrocyanide sludges.

Information for these studies is gathered from historical data, laboratory studies on ferrocyanide simulants produced by the three flowsheets used during the 1950s, and actual waste samples as they become available from the tanks. These waste studies, along with modeling studies, tank waste temperatures, and moisture determinations, support the preparation of safety documentation for core sampling and tank farm operations. The information was also used to support closure of the Ferrocyanide USQ (Postma et al. 1994).

5.5.2 Evaluation of Issue

At present, there are 18 Hanford Site waste storage tanks (Borsheim and Simpson 1991) that may contain at least 1,000 g-moles (465 lb) of ferrocyanide mixed with sodium nitrate/sodium nitrite. Many of these tanks have been saltwell pumped to remove most of the drainable liquid, but none have exhibited signs of increasing temperature, much less propagating reactions.

Laboratory tests have demonstrated that near-stoichiometric mixtures of concentrated (undiluted) sodium nickel ferrocyanide and nitrate/nitrite chemicals, when dry, exhibit exothermic behavior that starts to release heat at temperatures as low as 220 to 240 °C (428 to 465 °F). Waste studies addressing DNFSB Recommendation 90-7.5 are being conducted to determine: (1) the quantities of water and other diluents expected in the ferrocyanide waste; (2) actual species of cyanide present; and (3) effects of solid diluents, water, additional fuel sources (e.g., sodium acetate, other organics, and sulfides), and the presence of possible catalysts on waste reactivity.

The bulk (about 66%) of the ferrocyanide sludges placed into the Hanford Site waste storage tanks was produced by the U Plant flowsheet process. Simulated sludges produced from this flowsheet have shown no propagating tendencies even when dried and heated above 400 °C (752 °F). Propagation testing of 70 g of the more concentrated (and dried) U Plant simulant (U Plant 2, bottom fraction) with external heating to approximately 270 °C (518 °F) showed sufficient reaction to raise the sample temperature to 620 °C (1148 °F) (Fauske 1992). Although self heating at temperatures above about 280 °C (536 °F), the mixture will not propagate. The potential for aerosol generation from heating of this material is very low.

About 26% of the ferrocyanide sludge stored in the Hanford Site waste storage tanks was produced by the In Farm flowsheet. The In-Farm sludge simulant (preparation included centrifuging at approximately 2000 g for an equivalent 30 gravity-years settling time) did not propagate when the moisture content was 12 wt% or greater (Fauske 1992). Centrifuged In-Farm sludge simulant has a free* water content of about 50 wt%. Dry (0 wt% free water) In-Farm sludge exhibits propagation rates up to 10 cm/min starting at about 245 to 250 °C (473 to 482 °F) when external heat is applied. Reaction temperatures up to 1200 °C (2192 °F) can be produced. These tests show the importance of water in preventing ferrocyanide reactions and ensuring that the ferrocyanide waste is stored safely. The ferrocyanide sludges in the tanks are all believed to contain appreciable amounts of water.

The T Plant simulant was tested in FY 1993 (Fauske 1993). Chemical analyses were completed in December 1993, and physical analyses will be completed by the end of March 1994. The concentration of ferrocyanide was found to be slightly higher than the U Plant 2 concentration, but much lower than that in the In Farm 1 simulant. Fauske and Associates conducted adiabatic calorimetry tests on the T Plant simulant and found that it too would not propagate even when dry. The T Plant flowsheet accounts for about 8% of the total ferrocyanide waste added to the tanks.

*Free water is water removed by vacuum drying as opposed to "bound" water that remains after vacuum drying at 60 °C (140 °F) for 24 hr. See Glossary on page vii.

Effects of catalysts, initiators, and other fuels have been studied by PNL (Scheele et al. 1993). None of the candidate materials tested had a significant effect on lowering the initiation temperature except when milligram quantities of the material were exposed to high temperatures (>300 °C [572 °F]) to measure changes in the time to explosion. The presence of possible catalysts in the waste is not considered a safety issue for the ferrocyanide tanks. Diluent effects are very pronounced as seen with tests using non-stoichiometric amounts of fuel or oxidizer. Excess material, including water and non-reacting solids, diminish the energy release because these materials must be heated as well to the temperature experienced by the reactants. Experiments at FAI and PNL have shown this dramatic effect very clearly.

Compositions of actual waste samples must continue to be determined under present storage conditions and be compared to simulant behaviors to provide a firm basis for waste modeling.

5.5.3 Baseline Assumptions

- The waste in each tank or groups of similar tanks must be evaluated/characterized independently.

- Complete characterization of the waste by extensive core sampling of the waste in each tank is impractical.

- Adequate waste characterization can be done by limited core sampling using the DQO process for the Ferrocyanide Safety Issue (Buck et al. 1993), and by data acquired from tank monitoring, modeling, historical records, and simulant studies.

- One of the following conditions must be established to ensure safety (see Postma et al. 1994).

  - the concentration of fuel in the waste must be below 8 wt% sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] on an energy equivalent basis, calculated on a dry basis. This ensures that the waste is in the <u>SAFE</u> category; see also Section 4.3.

  - If the concentration of fuel is greater than 8 wt% equivalent sodium nickel ferrocyanide, then the free water content of the waste must vary linearly from 0 at 8 wt% fuel up to 24 wt% for 26 wt% fuel. This ensures that the waste is in the <u>CONDITIONALLY SAFE</u> category (Section 4.3).

5.5.4 Method to Close Recommendation 90-7.5

The method of closure for this recommendation is to determine, through ferrocyanide simulant testing and actual waste testing and analysis, the reactive properties for the range of ferrocyanide waste concentrations in the Hanford Site tanks and to validate the criteria for safe storage. Ferrocyanide sludges in the tanks were produced by three different flowsheets, resulting in variations in chemical compositions. The extent of sludge mixing and changes caused by later additions of waste on top of ferrocyanide sludges is being studied. The present form and quantity of ferrocyanide in the tanks is being determined as core samples become available. Extrapolations to unsampled tanks are also being made. The moisture content of the sludge is an important parameter that dramatically affects the reactivity of the ferrocyanide; therefore the water content of the waste must be measured and possibly monitored in situ on a frequent basis in the tanks. The simulant having the greatest ferrocyanide concentration (In-Farm 1) also contains excess oxidant, and has been shown not to react when exposed to an intense ignition source as long as the moisture content is greater than 12 wt% (Fauske 1992). When completely dry, this simulant has been shown not to deflagrate, but does propagate at a rate of 5 to 10 cm (2 to 4 in.) per minute. It is unlikely that any ferrocyanide waste exists in the tanks with a moisture content of less than 15 wt% (or much higher in most cases). In-Farm sludge centrifuged at approximately 2000 g for an equivalent 30 gravity-years settling time has a moisture content of about 50 wt%. Other tests are also underway or have been completed that show water is retained in the waste simulants at values greater than 40 wt% (Sections 5.1.5.3 and 5.4.5.2). Moisture analysis of ferrocyanide core samples analyzed to date also show high moisture numbers (Simpson et al. 1993a, 1993b). See also Section 5.4.5.1).

5.5.5 Action Plan

Ferrocyanide waste studies are underway, as described below, to accomplish the following.

1. Characterize the various types of ferrocyanide waste added to the tanks, using the five flowsheet simulants and real waste samples as they become available, to determine their potential reactive properties (energy content per unit mass and the kinetics of reactions).

2. Identify changes to the waste forms (from oxidation, reduction, hydrolysis, and/or radiolysis) that may have occurred during in-tank storage over the last three plus decades, including potential effects on the waste reactivity.

3. Identify changes to the waste forms that may have occurred from exposure to other waste forms added to the tanks either before or after the ferrocyanide waste additions (e.g., high-pH waste from decladding operations and evaporator bottoms were added to many of the ferrocyanide tanks after the 1950s). This may have affected the ferrocyanide waste and, thus, changed the waste reactivity.

4. Determine the effects of other waste materials added to the tanks, such as organic complexants, on ferrocyanide waste reactivity (e.g., some waste constituents may act as initiators or as additional fuel, or as diluent material).

5. Perform safety evaluations and recommend courses of action (See Section 4.3.).

Information for these studies is gathered from historical data, laboratory studies on ferrocyanide simulants produced by the three flowsheets (and their variations) used during the 1950's, and actual waste samples (as they become available from the tanks). These waste studies, along with modeling studies and measurements of tank waste temperatures, moisture, cesium content, and flammable gas have supported the preparation of safety documentation for core sampling, tank farm operations, closure of the Ferrocyanide USQ, and ultimately for resolution of the Ferrocyanide Safety Issue.

Chemical reaction studies on ferrocyanide waste simulants have been, and in some cases are still being, conducted by WHC, FAI, PNL, LANL, and Washington State University (WSU). Westinghouse Hanford and PNL have produced flowsheet simulant materials for testing and characterization. PNL also administered the subcontract with LANL, completed in FY 1993. In FY 1992, LANL completed chemical reaction sensitivity tests on ferrocyanide waste simulants to identify what stimuli (emphasizing non-thermal) may cause a reaction to occur (Cady 1993). FAI is conducting adiabatic calorimetry and propagation tests on these same replicated flowsheet materials. The FAI scope of work was expanded in FY 1993 to include selected aerosol studies and special studies for modeling of potential hot spots and tank waste rheology. WSU completed real time x-ray diffraction studies with stoichiometric mixtures of sodium nickel ferrocyanide with sodium nitrate/nitrite heated to reaction temperatures and above (Dodds and Thomson 1993).

5.5.5.1 Chemical Reaction Studies at Pacific Northwest Laboratory

Chemical reaction studies are continuing at PNL using flowsheet simulant materials. Waste studies addressing DNFSB Recommendation 90-7.5 are being conducted to determine: (1) the aging effects (hydrolysis and radiolysis) from more than 35 years of storage in the tanks; (2) the speciation of cyanides found in the actual tank waste; (3) the influence of chemical interactions and physical changes on the solubility of sodium and cesium nickel ferrocyanides; (4) possible mechanisms that may have allowed mixing of the ferrocyanide sludge with caustic solutions added to the tanks at a later time; and (5) comparisons of simulated waste with actual ferrocyanide waste.

Aging Studies. A series of hydrolysis screening studies were conducted with dried In Farm 1 ferrocyanide flowsheet simulant. A report reviewing progress in FY 1993 on demonstrating the concept of waste aging has been issued, *Ferrocyanide Safety Project: Task 3 Ferrocyanide Aging Studies FY 1993 Annual Report* (Lilga et al. 1993).

Hydrolysis of ferrocyanide can occur by dissociation of cyanide ion from the ferrocyanide anion:

$$Fe(CN)_6^{4-} + H_2O \rightleftharpoons Fe(CN)_5(H_2O)^{3-} + CN^-$$

$$CN^- + 2\,H_2O \rightleftharpoons NH_3 + HCO_2^-$$

Samples of the In Farm simulant were contacted with 4 M NaOH [which removes nickel from sodium nickel ferrocyanide as insoluble nickel hydroxide, $Ni(OH)_2$, and produces soluble ferrocyanide as $Na_4Fe(CN_6)$] for three weeks at 90 °C (194 °F) in a field of 1.43 x 10^5 Rad/hour. An identical reaction mixture was heated to 90 °C outside the gamma irradiation source as a control. The final reaction solutions were analyzed for ammonia using a solution ammonia selective electrode technique. The analytical data indicate that the radiation field increased the ammonia concentration in solution by nearly an order of magnitude. These results strongly suggest that gamma radiation promotes the hydrolysis of ferrocyanide, possibly by facilitating the dissociation of cyanide from the ferrocyanide complex. Additional tests are underway at a pH of 10, where dissolution of the sodium nickel ferrocyanide does not occur, to see how fast hydrolysis occurs in a radiation field. This environment may be more typical for tanks that did not receive evaporator bottoms waste.

Cyanide Speciation. *Cyanide Speciation Studies - FY 1993 Annual Report*, a report summarizing the progress on cyanide speciation was issued at the end of FY 1993 (Bryan et al. 1993). Two solution techniques were developed as analytical methods. These methods are based on Fourier Transform infrared (FTIR) spectroscopy and ion chromatography (IC) analytical techniques. Both methods are able to quantify cyanide species at a concentration down to 0.1 wt%.

The effect of potential interferences on the speciation analyses by other constituents present in the dissolved ferrocyanide waste is under investigation. Tests already concluded have shown that cyanide speciation is insensitive to inorganic constituents, including nitrate, carbonate, hydroxide, and phosphate.

The effect of organic constituents, which could be present in ferrocyanide waste, are also being investigated for their potential interferences on the cyanide species analyses. The presence of various organic species had no appreciable effect on the measured concentration of ferrocyanide. However, if ferricyanide is present, several organic constituents may have a major effect on the measured concentration of ferricyanide. Ferricyanide has not been detected in actual tank waste samples. When purposely added to the simulants, ferricyanide was found to degrade to ferrocyanide because of iron or other chemicals also present.

Organic compounds that showed dramatic ferricyanide-to-ferrocyanide conversion [nitrilotriacetic acid, HEDTA, EDTA, iminodiacetic acid, glycine, and ethylenediamine] all contain organic amine functionalities within their molecular structure. Several of the non-amine complexes also showed some ferricyanide to ferrocyanide conversion. They included sodium oxalate, sodium glycolate, and n-butanol. Even though these conversion rates are relatively slow when compared to the amine based conversion, ample time has passed during waste storage for the reduction of ferricyanide to ferrocyanide to occur. It should be noted that there has been no indication that ferricyanide was ever present in the scavenging precipitate or in waste samples analyzed to date. Reactivity tests conducted with ferricyanide show no significant difference from those conducted with ferrocyanide.

Sodium and Cesium Nickel Ferrocyanide Solubilities Studies. The behavior of sodium-cesium nickel ferrocyanide compounds in caustic waste solutions is being examined in FY 1994, because cesium present in precipitated nickel ferrocyanide has been found to remain insoluble after exposure to strong caustic ($OH^- \geq 4$ M) solutions. Phenomena being studied include aqueous interaction and ion-association parameters of hydroxide, sodium, cesium, and nickel with ferrocyanide. The solubility product for sodium-cesium nickel ferrocyanide compounds is also being determined.

A separate study is investigating cesium uptake/retention capabilities of the ferrocyanide-sludge matrix. At issue is whether heat-producing ^{137}Cs can concentrate in regions within the waste under tank conditions. Cesium solubility/uptake work is scheduled for completion in FY 1995.

Microconvection Modeling. Microconvection is the term being applied to mixing at the solids/liquid interface (and within the waste) of the 22.9-m (75-ft)-diameter, non-agitated waste tanks. *Ferrocyanide Safety Program: Computational Analysis of Fluid Flow and Zonal Deposition in Ferrocyanide Single-Shell Tanks*, a report on microconvection modeling was issued at the end of FY 1993 (McGrail et al. 1993). Computer simulations predicted that microconvective mixing could occur in ferrocyanide tanks because of fluid density gradients and/or thermal gradients.

A stability analysis was performed for a dense fluid layer overlying a porous medium saturated by a less dense fluid. Given several assumptions, it was found that the configuration is unconditionally unstable and independent of the properties of the porous medium or the magnitude of the fluid density difference, as long as the density difference was not zero. It was shown that finger-like convection will always occur in the system under consideration. If this configuration occurred in the tanks, the fluid contents would tend to mix. Maximum velocity estimates for the finger-like convection are approximately 3 m/yr for sludge with 50% porosity. Thermal convective mixing was predicted to be much slower, about 10^{-5} to 10^{-2} m/yr.

The effects of diffusion and fluid convection on redistribution of ^{137}Cs were also evaluated. The report concluded that diffusion and fluid convection could not result in a hot spot of concern. The maximum concentration factor predicted by the model for ^{137}Cs was 10 times the average tank concentration. The predicted maximum local temperature rise because of a concentrated zone of this magnitude would be about 5 °C (41 °F).

The microconvection modeling work will continue in FY 1994 and be completed by September 30, 1994. In FY 1994, the single solute model developed in FY 1993 will be extended to include a complete aqueous speciation and dissolution/precipitation chemical model. The transport model will also be extended to support multiple chemical species. It is anticipated that the chemical model will be based on a free energy minimization algorithm to compute the equilibrium distribution of aqueous species and dissolution/precipitation of solid phases.

Comparison of Simulated and Actual Ferrocyanide Waste. A task comparing measured physical and chemical properties of ferrocyanide waste simulants with actual waste tank sample properties was begun in FY 1994. These comparisons will facilitate design and verification of analytical models involving waste aging, energetics, water retention, and microconvection. Among the parameters to be compared are rheological properties, thermal properties, nickel content, and diluent (i.e., nonreactive material) concentrations. Measurements of some parameters on actual waste samples will require development of hot cell deployable analytical techniques. This task will be completed in FY 1995.

Simulations will be run on a hypothetical waste tank using thermodynamic data from ferrocyanide aging and solubility studies currently in progress. Mass balance calculations will be done to predict total amounts of sodium nickel ferrocyanide that could be dissolved given a range of physical properties for the waste and buoyancy-driven fluid convection.

- **Planned Work To Complete Program.**

  The radiolysis and hydrolysis experiments will be continued using the most reactive ferrocyanide flowsheet simulant (In Farm 1). Temperature and pH will be evaluated during gamma pit radiolysis experiments to determine rates of hydrolysis under projected tank waste conditions as they existed for the years immediately after ferrocyanide waste scavenging. This tank activity is expected to be completed in FY 1995.

  Cesium solubility experiments will be conducted to determine solubility products for various sodium-cesium nickel ferrocyanide compounds. The ability of the ferrocyanide sludge matrix to retain/exchange cesium will be determined. These studies will be completed in FY 1995.

  Cyanide speciation analytical methods development, including IC methods and solution IR methods, will continue until the validated techniques and procedures can be routinely applied to samples in the analytical laboratories at both PNL and WHC. The studies will include the determination of interferences and corrections or work-arounds that may be encountered in developing analytical methods for actual waste samples. Completion of this phase is expected by the end of FY 1994. Work will also continue at WHC on solids speciation methods using FTIR and possibly Raman spectroscopy. These methods will be explored further using ferrocyanide waste simulants and actual waste samples. If sensitivity and accuracy of the techniques are deemed acceptable, the methods will be adapted for routine analysis in the PNL and WHC analytical laboratories. This activity is scheduled for completion in FY 1995.

Microconvection modeling studies have been expanded and information that contains key physical and chemical properties of waste as described above for FY 1994 will be assembled. This task is expected to be completed by September 30, 1994.

Comparisons of physical and chemical properties of ferrocyanide waste simulants and actual tank waste samples will be made. Information gained from these comparisons will be used to improve waste aging, water retention, and microconvection analytical models. The comparison studies will be completed in FY 1995.

- **Milestone Status**

  - **September 30, 1994.** Issue the final PNL report, cleared for public release, on FY-1994 hydrolysis and radiolysis aging experiments with ferrocyanide waste materials.

  - **September 30, 1994.** Issue the final PNL report, cleared for public release, on solution IR and IC cyanoferrate speciation activities and application for routine measurements in the analytical laboratory.

  - **September 30, 1994.** Issue a publicly available progress report on FY 1994 work on the solubility of sodium-cesium nickel ferrocyanide compounds, with recommendations on future work for FY 1995.

  - **September 30, 1994.** Issue a final PNL report, cleared for public release, on microconvection modeling and the effects projected to have occurred in the tank waste from this phenomenon during the years of storage.

  - **September 30, 1994.** Issue a final PNL report, available for public release, on results of cesium uptake studies.

  - **September 30, 1994.** Issue a progress report, available to the public, on FY 1994 studies comparing chemical and physical parameters of ferrocyanide waste simulants with actual waste samples. The report will include recommendations on future work for FY 1995.

- **September 30, 1995.** Issue the final PNL report, available for public release, integrating all Ferrocyanide Safety Program hydrolysis and radiolysis aging activities.

- **September 30, 1995.** Issue a final report, available to the public, on the solubility of sodium-cesium nickel ferrocyanide compounds under waste tank conditions.

- **September 30, 1995.** Issue a final report, available to the public, on studies comparing chemical and physical parameters of ferrocyanide waste simulants with actual tank waste samples.

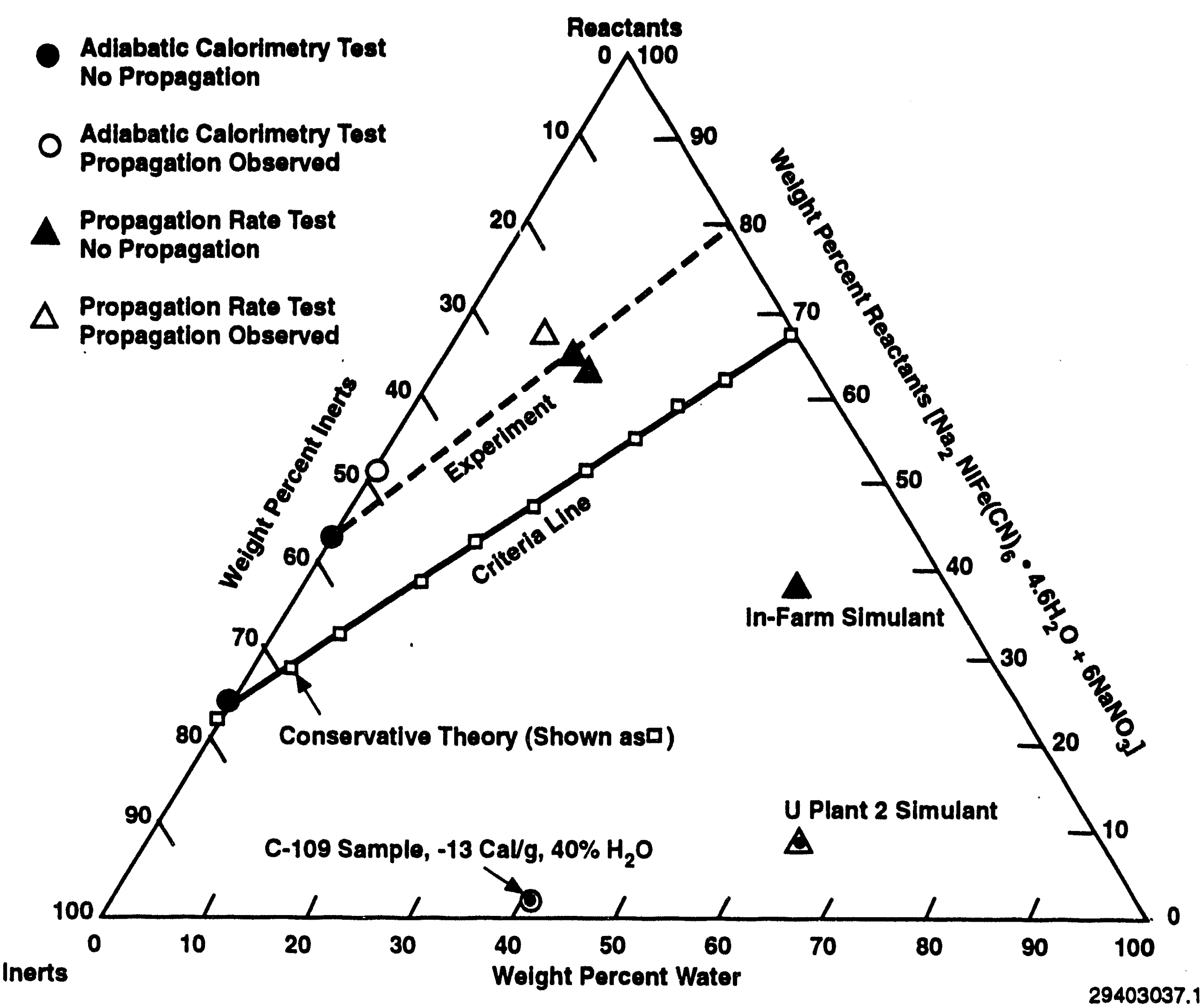
5.5.5.2 Ferrocyanide Adiabatic Calorimetry and Propagation Studies

Ferrocyanide adiabatic calorimetry and propagation tests are continuing at FAI under contract to WHC. The results of these tests are being used to help determine if Hanford Site ferrocyanide waste could ignite and burn to spread and involve additional waste from a potential ignition point, and to determine the potential for release of radioactive species under various postulated accident scenarios. Tests are being conducted with dried and partially dried simulant to evaluate safety consequences associated with reactions of various concentrations of ferrocyanide. The propagation velocity and reaction temperatures are key parameters in determining the safety consequences of postulated burns, including a potential release of radioactivity from tank confinement.

Because the composition of the waste in the storage tanks may vary and is not known at all locations, ranges of material compositions are being tested. Present work is focused on the T Plant and the most reactive In Farm 1 simulants. Sludge produced by the In Farm flowsheet was placed in four C Farm tanks and represents about 26% of the total ferrocyanide used in the Hanford scavenging processes. Sludge produced by the T Plant flowsheet was placed in three TY Farm tanks and represents about 8% of the total ferrocyanide used. Adiabatic calorimeter tests have also been initiated to determine the experimental line that separates propagating from non-propagating ferrocyanide mixtures as shown in the triangular diagram, Figure 5-2. Two series of tests are being conducted: one series to define more precisely the fuel concentration under dry conditions (0% free water in Figure 5-2) that just propagates; and the other that defines the position of the experimental line in Figure 5-2.

Four tests were recently conducted at FAI to determine the minimum concentration of sodium nickel ferrocyanide required to sustain a propagating reaction. In Farm 2 simulant was mixed with sodium nitrate or alumina to concentrations of 15 and 18 wt% $Na_2NiFe(CN)_6$, on a dry basis; i.e., two tests at each fuel value, one with sodium nitrate and the other with alumina, were conducted (Appendix B, Postma et al. 1994). The two dilutions containing 15 wt% $Na_2NiFe(CN)_6$ [43% reactants] did not propagate. However, simulant dilutions containing 18 wt% $Na_2NiFe(CN)_6$ [52% reactants] did propagate. These experiments were conducted to determine an empirical value for the fuel concentration criterion for sodium nickel ferrocyanide and gave the experimental point at 0% water in Figure 5-2; see also Section 4.3. Additional tests will be conducted during FY 1994 to confirm the empirical line in Figure 5-2.

Figure 5-2. Comparison of Theoretical and Experimental Propagation Limits (Postma et al. 1994)



The present concentration of ferrocyanide in the sludge is expected to be significantly less than that in the original precipitate because ferrocyanide has been shown to hydrolyze, breaking down into ammonia and sodium formate which in turn goes to sodium carbonate under radiological conditions in the tanks (see Section 5.5.5.1). Core sample results of C Farm tank waste show that the waste's total cyanide concentration is considerably lower than that for the In Farm simulants being tested (Simpson et al. 1993a, 1993b).

T Plant simulant was prepared and sent to FAI for adiabatic calorimetry tests. The ferrocyanide concentration in the upper fraction of T Plant simulant was found to be similar to the U Plant simulant in composition and exothermic behavior. The lower fraction did not exhibit exothermic properties during DSC tests (see Fauske 1993).

- **Planned Work to Complete Program.** The screening tests described above will be conducted in the first half of FY 1994 to determine propagation limits for ferrocyanide simulants as a function of ferrocyanide concentration and moisture content (Figure 5-2). Additional parametric and some ferrocyanide/organic tests will be specified and initiated at FAI. The residue from aerosol testing using In Farm 1 samples will be analyzed to identify reaction products. The fraction of cesium released during the aerosol tests will also be determined. Adiabatic calorimeter studies on ferrocyanide simulant sludges spiked with organics will continue.

- **Milestone Status**

  - **July 30, 1993.** Complete report on T Plant calorimetry and propagation tests and U Plant dryout tests. This report was completed by FAI on July 28, 1993. The report will be cleared for public release and issued in March 1994.

  - **September 30, 1993.** Complete organic calorimetry scanning tests. These tests were completed on schedule and a report, cleared for public release, will be issued early in 1994.*

  - **September 30, 1993.** Complete theoretical evaluations on hot spots and tank waste dryout. Conduct confirmatory tests and provide a report that supports USQ closure. This report was completed by FAI in November 1993 (Fauske and Cash 1993). The report was cleared for public release in November 1993.

  - **December 15, 1993.** Complete report on conditions necessary for ferrocyanide - nitrate/nitrite propagation. This report was completed

*This work is part of the Organic Tanks Safety Program and is not shown in the Section 6 schedules.

by FAI in November 1993 (Fauske and Epstein 1993). The report will be prepared for public release and issued in March 1994.

- **June 30, 1994.** Complete screening tests of In Farm 1 simulant at FAI by varying ferrocyanide and water compositions to define the empirical line that divides propagating and non-propagating mixtures on the triangle diagram (Figure 5-2). Issue a report for public distribution (if required) by September 30, 1994.

- **March 31, 1995.** Complete parametric aerosol tests at FAI (if required) that provide source terms for determining consequences of hypothetical ferrocyanide burns in a ferrocyanide tank.

- **September 30, 1995.** Complete FY 1995 ferrocyanide calorimetry and propagation test program at FAI as specified by WHC and prepare reports, available for public release, that support resolution of the Ferrocyanide Safety Issue.

- **September 30, 1996.** Complete FAI support for Ferrocyanide Safety Issue resolution.

5.6 EMERGENCY RESPONSE PLANNING

Emergency response planning is necessary to specify appropriate actions required in case there are abnormal conditions that develop in the ferrocyanide tanks. The DNFSB emphasized that fact in their Recommendation 90-7.6 as follows:

> *"The Board had recommended 'that an action plan be developed for the measures to be taken to neutralize the conditions that may be signaled by alarms.' Two types of measures are implied: actions to respond to unexpected degradation of a tank or its contents, and actions to be taken if an explosion were to occur. Your implementation plan stated that 'the current contingency plans . . . will be reviewed and revised if needed.' We do not consider that this proposed implementation of the Board's recommendation is adequately responsive. It is recommended that a written action plan founded on demonstrated principles be prepared as soon as possible, that would respond to indications of onset of abnormal temperatures or other unusual conditions in a ferrocyanide-bearing tank, to counter any perceived growth in hazard.*
> *A separate emergency plan should be formulated and instituted, covering measures that would be taken in event of an explosion or other event leading to an airborne release of radioactive material from the tanks, and that would protect personnel both on and off the Hanford Site. The Board believes that even though it is considered that the probability is small that such an event will occur, prudence dictates that steps be taken at this time to prepare the means to mitigate the unacceptable results that could ensue."*

5.6.1 Background

Subsequent to the issuance of this recommendation by the DNFSB, WHC has: (1) prepared and issued an action plan to respond to developing abnormal conditions in a ferrocyanide tank; (2) prepared and issued emergency documents to respond to a release from a ferrocyanide tank; and (3) conducted field exercises (in conjunction with other Hanford Site emergency organizations) to test the Hanford Site ability to respond to such emergency conditions.

The temperature and moisture content of the waste are key safety control parameters for tanks with the potential for an exothermic reaction. The ferrocyanide tanks have estimated heat loadings of less than 4 kW (11,000 Btu/h) (Crowe et al. 1993), and dissipate their heat via natural circulation (i.e., convection and radiation to the tank headspace and conduction to the surrounding earth). Temperatures in 13 of the 20 ferrocyanide tanks are monitored continuously, while the remaining 7 tanks are monitored weekly. The highest temperature observed in any of the tanks is less than 55 °C (131 °F). This is well below the minimum exothermic reaction temperature of approximately 220 °C (428 °F) observed in the laboratory under ideal conditions (Hallen et al. 1992) for stoichiometric mixtures of ferrocyanide and oxidant, even with additional fuel (5 mole% EDTA) present and no additional diluents.

The moisture content of the ferrocyanide waste layers is postulated to be ≥40 wt%, based on: (1) ferrocyanide tank samples taken before 1986; (2) moisture analysis results from samples taken from tanks 241-C-112 and -C-109 in 1992; and (3) recent flowsheet simulant investigations, which show at least 45 wt% moisture for simulants centrifuged at >2000 g and simulant drainability tests. However, no moisture surveillance system is currently installed for monitoring the tanks. See Section 5.1.5.3 for work in progress to estimate the tank waste moisture content.

5.6.2 Evaluation of Issue

It is prudent to preplan responses to abnormal conditions that may develop in the ferrocyanide tanks. Likewise, additional definition of the probable consequences of potential release events and planning to respond to such events are necessary.

5.6.3 Baseline Assumptions

- Control of waste temperatures and the moisture content of ferrocyanide waste will preclude propagating reactions.
- Temperature excursions within the waste, although highly unlikely, may be possible until proven otherwise.

- Loss of significant moisture from a ferrocyanide tank is to be considered a problem until demonstrated otherwise.

- Thermal response of the ferrocyanide tanks is slow.

5.6.4 Method to Close Recommendation 90-7.6

The *Action Plan for Response to Abnormal Conditions in Hanford Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991a) was prepared in response to DNFSB Recommendation 90-7.6. The action plan describes the steps to be taken if a temperature increase trend above the tank temperature baseline is measured in any of the ferrocyanide tanks. The document was revised in December 1991 and reissued as WHC-EP-0407, Rev. 1 (Cash and Thurman 1991b) to include the monitoring criteria and responses for abnormal levels of flammable and toxic gases, as well as the reporting requirements, if established criteria are exceeded.

In addition, the *Tank Farm Stabilization Plan For Emergency Response* (WHC 1991) was issued in March 1991. If a radioactive release from a ferrocyanide tank were to occur, it would be detected by one or more radiation monitoring systems. Significant airborne or ground surface releases that spread beyond the immediate tank or tank farm would be detected by the tank farm area radiation detectors. These monitoring systems are on all tank farms. An emergency involving an underground radioactive waste storage tank is a unique event with potentially serious consequences both onsite and offsite. The *Stabilization Plan* analyzed the potential effects of an event involving one of these tanks, and additional steps were prescribed so that emergency personnel can take mitigating actions in a timely fashion. The *Stabilization Plan* includes predetermined mitigative actions for terminating the emergency phase and providing a transition to the recovery phase. Acknowledging that an event could range from minor to major releases, the *Stabilization Plan* addresses responses in four distinct and defined steps that cover a broad range of consequences. The *Stabilization Plan* provides quick, preplanned actions that can be used to stabilize an emergency event at an underground radioactive waste storage tank.

Emergency event recognition and classification; protective action recommendations; and emergency notification emergency plan implementing procedures for response to tank farm emergencies were completed and issued in June 1992. Training has been conducted and an exercise was completed to validate the effectiveness of the procedures and training.

All actions with respect to emergency planning, emergency event recognition, protective action recommendations, and emergency response procedures have been completed. Further revisions and occasional validation exercises will be accomplished as part of the normal WHC and DOE emergency planning efforts. No further reporting on these issues is planned and this part of DNFSB Recommendation 90-7.6 is considered complete and closed.

DOE considers this recommendation to be closed with the proviso that the abnormal conditions response plan and emergency plans are: (1) reviewed on a periodic basis; (2) revised and updated as required to incorporate any additional controls determined appropriate by the ongoing Waste Tank Safety Program investigations (e.g., the "Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide," will be updated in May 1994); and (3) validation exercises for various waste tank accident scenarios are conducted (exercises for the tank farms are conducted every two years).

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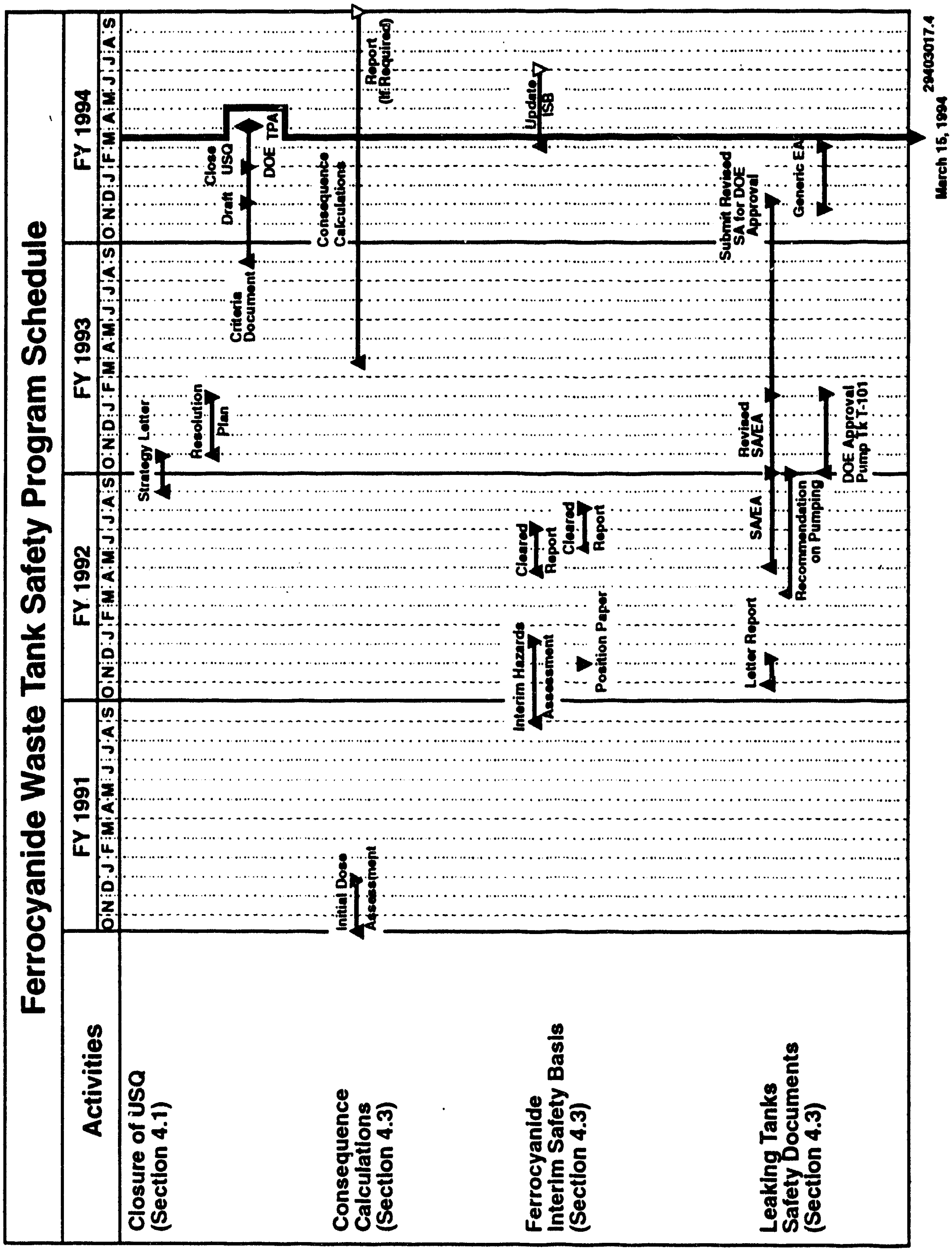
6.0 PROGRAM SCHEDULES AND MILESTONES

Two sets of schedules (Figures 6-1 and 6-2) are presented in this section. The scope of some of the program activities has changed since the FY 1992 program plan was released and progress should be tracked against the new schedules presented here. The first set of schedules reviews milestones for FY 1991 through FY 1994; these have been statused through March 15, 1994. A status line was drawn showing the progress completed on each activity. Actions that have started or been completed are indicated by triangles that are filled in. Work indicated by open triangles has either not started or has not been completed. Diamonds indicate a TPA milestone.

The second set of schedules reviews out-year milestones for FY 1994 through the expected end of the program in FY 1997. The sequence and anticipated completion dates of the major milestones leading to safety issue resolution are presented. Reports tracking progress against these schedules will be published quarterly.

Figure 6-1. Ferrocyanide Waste Tank Safety Program Schedule. (Sheet 1 of 4)



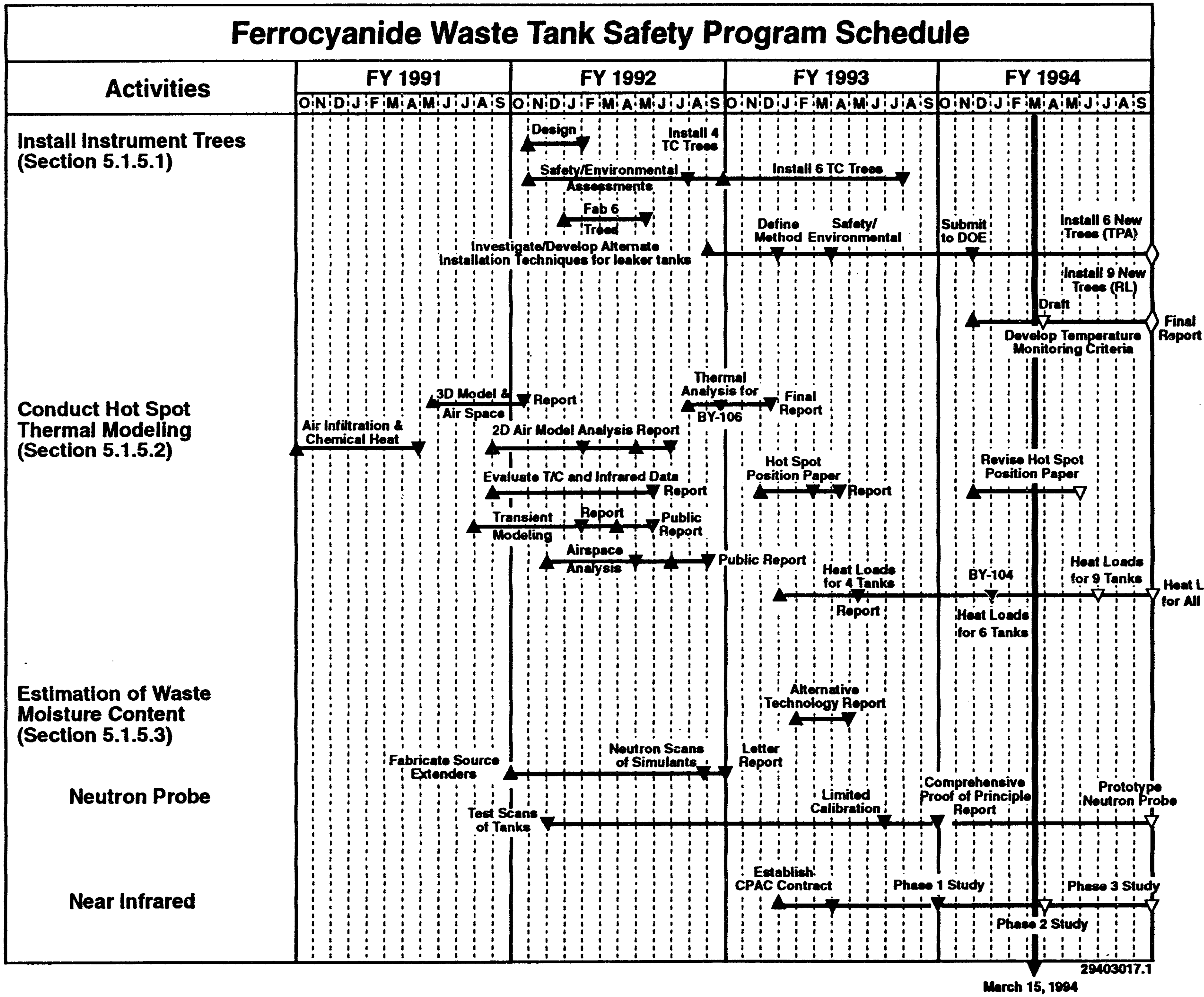


Figure 6-1. Ferrocyanide Waste Tank Safety Program Schedule. (Sheet 2 of 4)

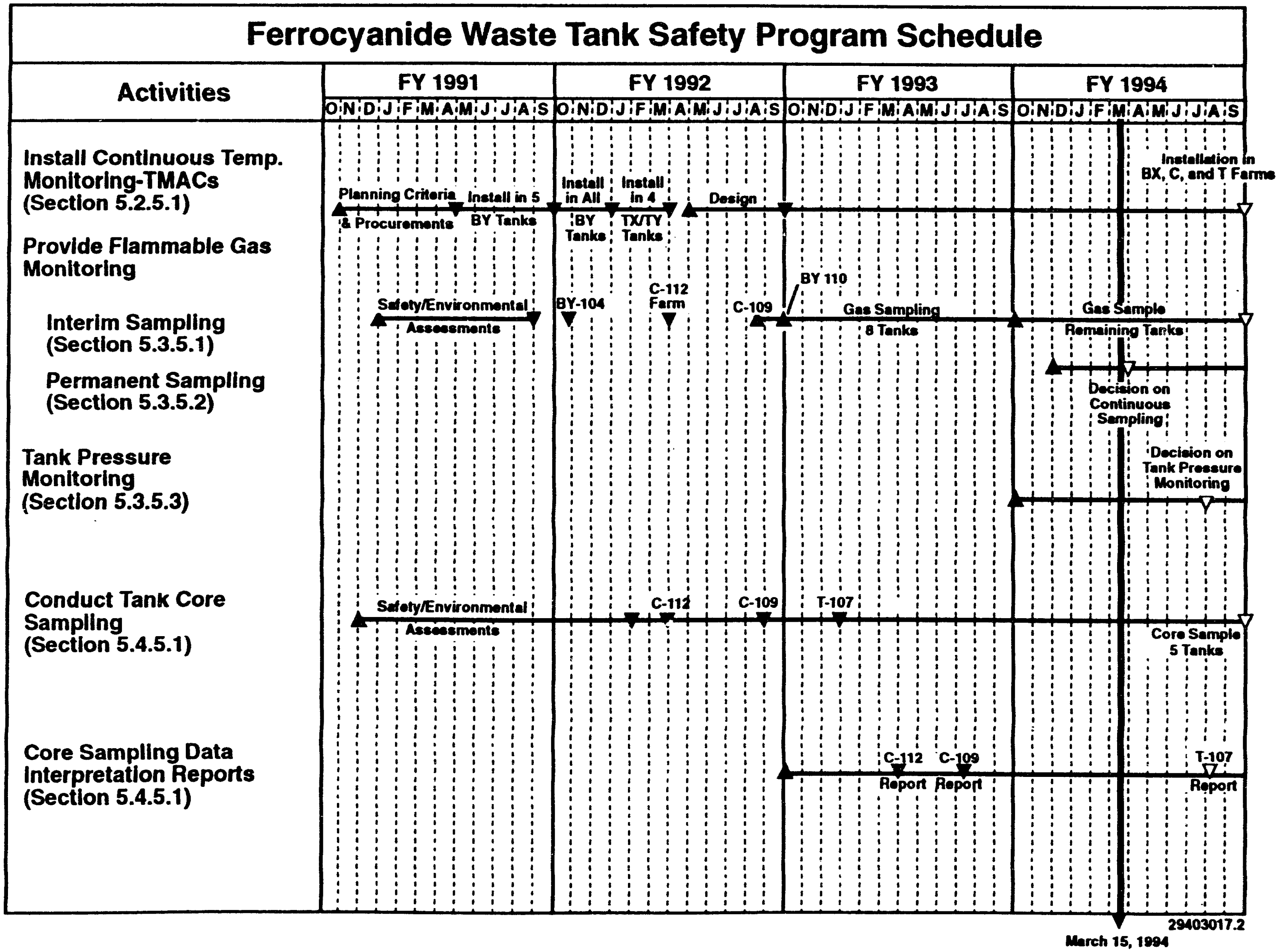


Figure 6-1. Ferrocyanide Waste Tank Safety Program Schedule. (Sheet 3 of 4)

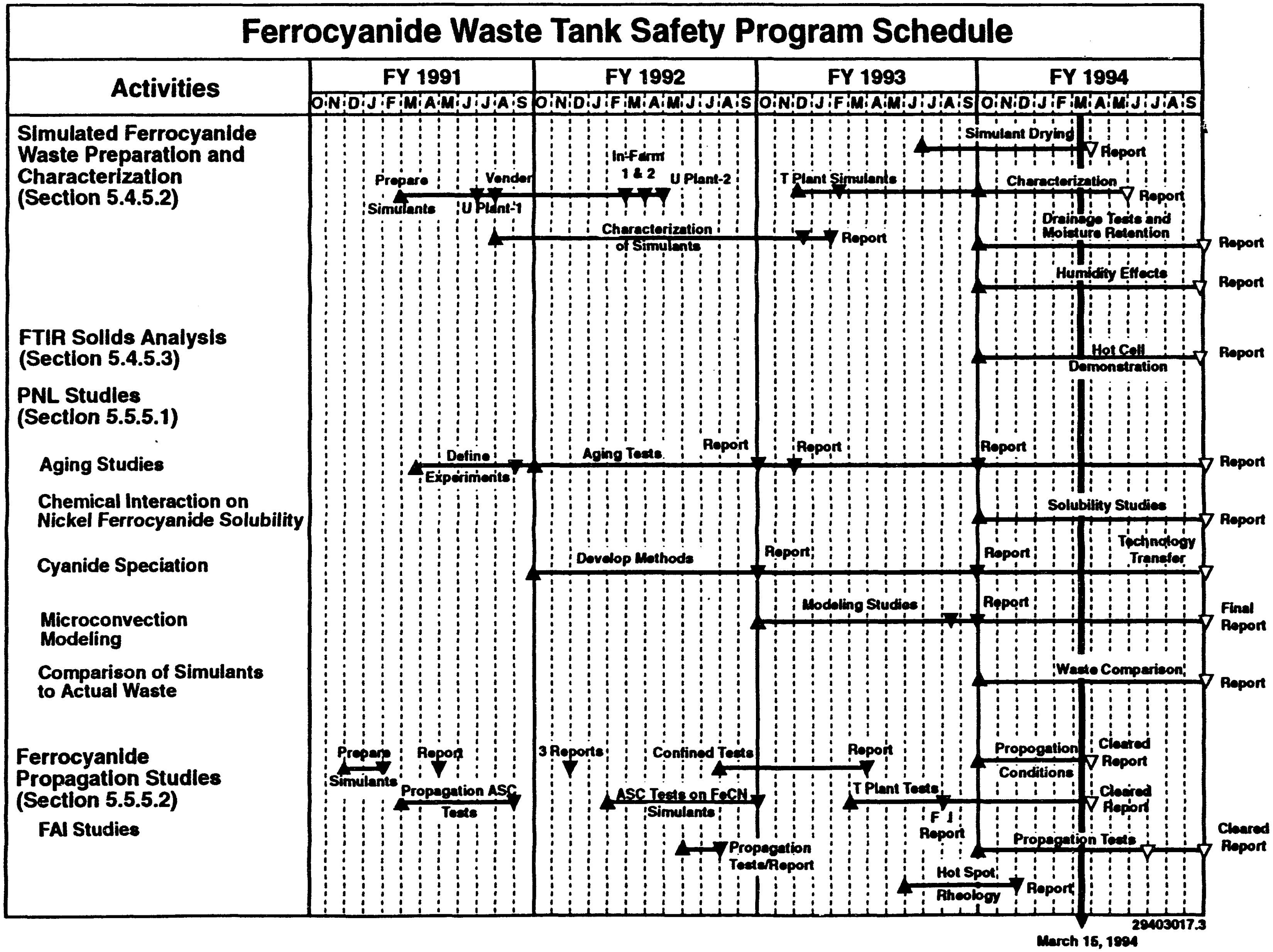


Figure 6-1. Ferrocyanide Waste Tank Safety Program Schedule. (Sheet 4 of 4)

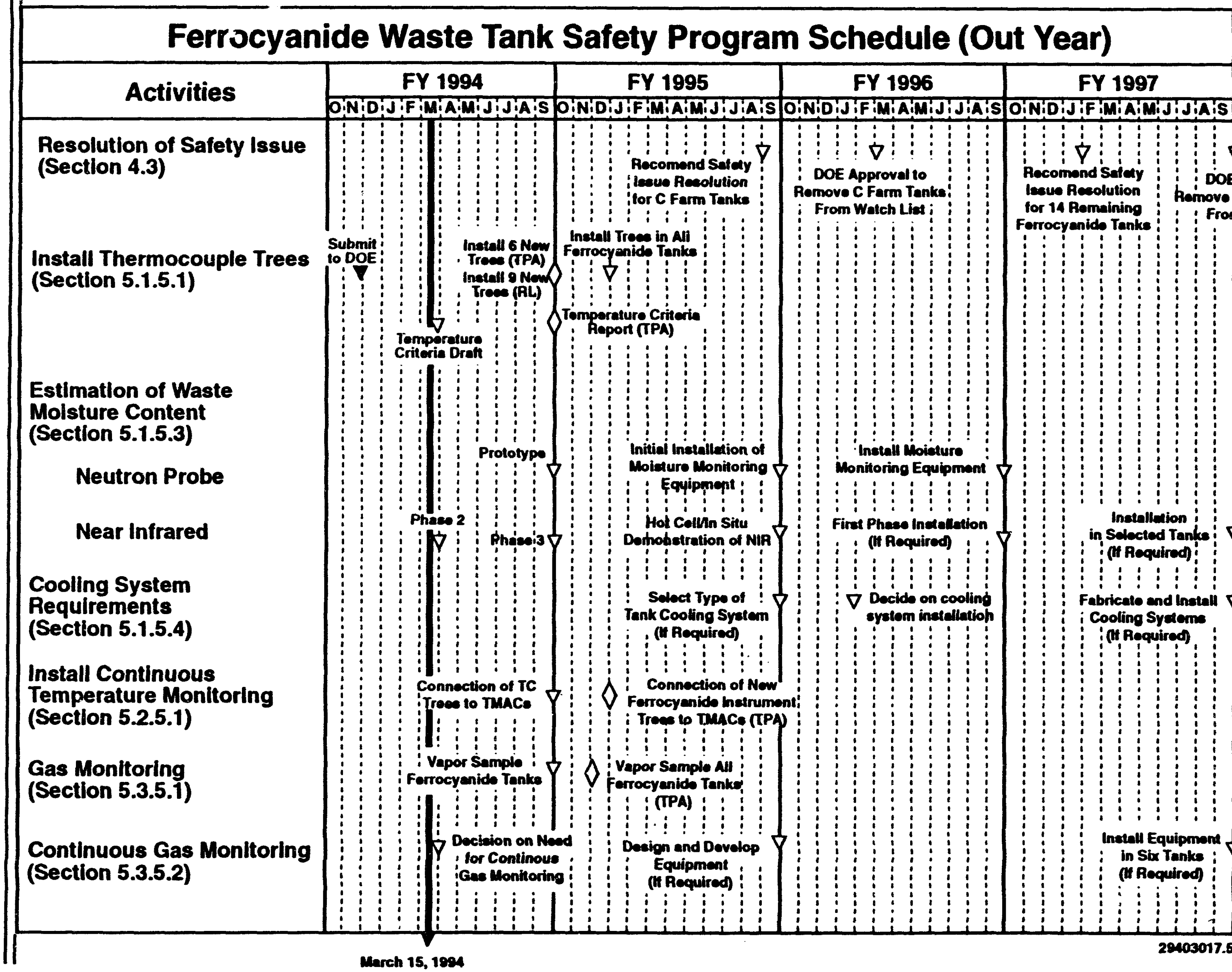


Figure 6-2. Ferrocyanide Waste Tank Safety Program Schedule (Out Year). (Sheet 1 of 2)

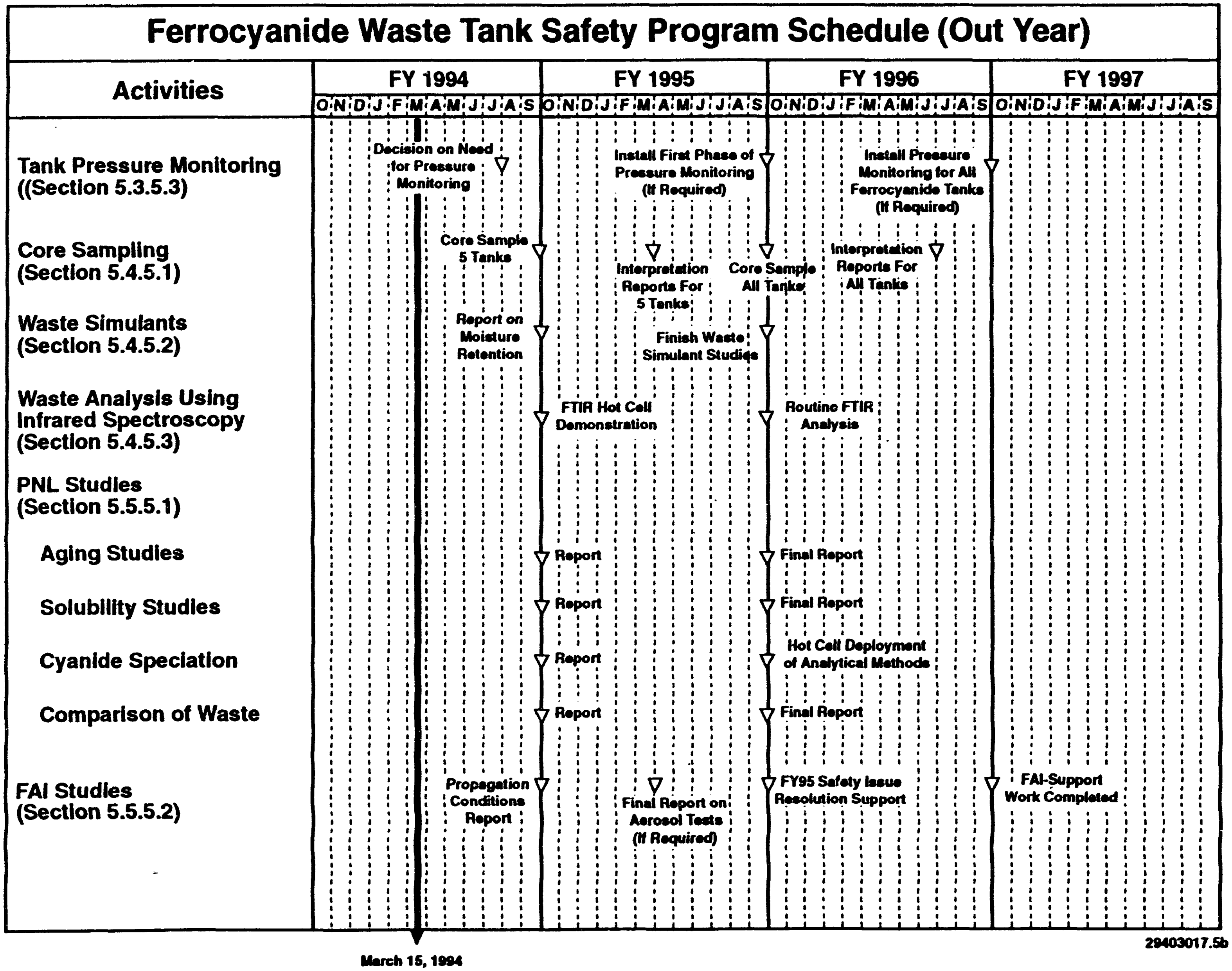


Figure 6-2. Ferrocyanide Waste Tank Safety Program Schedule (Out Year). (Sheet 2 of 2)

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