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IMPLEMENTATION PLAN FOR DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7

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ABSTRACT

This document revises the original plan submitted in March 1991 for implementing the recommendations made by the Defense Nuclear Facilities Safety Board in their Recommendation 90-7** to the U.S. Department of Energy. Recommendation 90-7 addresses safety issues of concern for 24 single-shell, high-level radioactive waste tanks containing ferrocyanide compounds at the Hanford Site. The waste in these tanks is a potential safety concern because, under certain conditions involving elevated temperatures and low concentrations of nonparticipating diluents, ferrocyanide compounds in the presence of oxidizing materials can undergo a runaway (propagating) chemical reaction. This document describes those activities underway by the Hanford Site contractor responsible for waste tank safety that address each of the six parts of Defense Nuclear Facilities Safety Board Recommendation 90-7. This document also identifies the progress made on these activities since the beginning of the ferrocyanide safety program in September 1990. Revised schedules for planned activities are also included.*

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*Cash, R. J., 1991, *Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7*, WHC-EP-0415, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

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ACRONYMS

AEP	Aerosol Experts Panel
CASS	Computer Automated Surveillance System
CTMS	Continuous Temperature Monitoring System
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DSC	Differential Scanning Calorimetry
EA	Environmental Assessment
EDTA	Ethylenediaminetetraacetic Acid
EIS	Environmental Impact Statement
EM	Office of Environmental Restoration and Waste Management (DOE)
EM-50	Office of Technology Development (DOE)
EM-55	Demonstration Testing and Evaluation Division (DOE)
ERRA	Environmental Restoration and Remediation Action
FAI	Fauske and Associates, Incorporated
FSU	Florida State University
FTIR	Fourier Transform IR
FY	Fiscal Year
GAO	General Accounting Office
g-y	Gravity-Year
HDW-EIS	*Final Environmental Impact Statement, Disposal of Hanford Defense High-Level Transuranic and Tank Waste, Hanford Site, Richland, Washington*
HEPA	High-Efficiency Particulate Air
HLW	High-Level Radioactive Waste
IC	Ion Chromatography
IR	Infrared
LANL	Los Alamos National Laboratory
LOW	Liquid Observation Well
MIT	Multifunction Instrument Tree
PNL	Pacific Northwest Laboratory
PSO	Program Secretarial Officer
RL	U.S. Department of Energy, Richland Field Office
SA	Safety Assessment
SAR	Safety Analysis Report
SST	Single-Shell Tank
STG	Scanning Thermogravimetry
TAP	Tanks Advisory Panel
TC	Thermocouple
TRAC	Tracks Radioactive Components
TRU	Transuranic
TTX	Time-To-Explosion
USQ	Unreviewed Safety Question
Westinghouse Hanford	Westinghouse Hanford Company
XRD	X-Ray Diffraction

IMPLEMENTATION PLAN FOR DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7

1.0 INTRODUCTION

In March 1990, the Defense Nuclear Facilities Safety Board (DNFSB) gave the U.S. Department of Energy (DOE) its Recommendation 90-3 (DNFSB 1990a) regarding the safety of storing ferrocyanide-bearing high-level radioactive waste (HLW) in single-shell tanks (SST) 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 found that the plan was not adequately responsive. To strengthen their concerns, the DNFSB restated their position in Recommendation 90-7, consisting of six parts/recommendations (DNFSB 1990b). The DOE accepted the six recommendations and agreed to accelerate and expand its programs dealing with the HLW safety issues at the Hanford Site. The implementation plan for Recommendation 90-3 has been greatly expanded, and program elements have been accelerated to be responsive to DNFSB Recommendation 90-7 (Cash 1991). The plan for Recommendation 90-7 is believed to be responsive to Recommendation 90-3, and there is no separate plan for Recommendation 90-3 which has been superseded by Recommendation 90-7.

This document describes the continuing strategy planned for investigating the physical and chemical characteristics of Hanford Site ferrocyanide waste. This document also outlines the actions necessary to lessen environmental and safety concerns associated with the storage of ferrocyanide waste. Updates to the original implementation plan (Cash 1991), including changes in strategy and schedule, are included to reflect new information as a result of modeling, chemical reaction studies and tank waste sampling activities. The current status of the ferrocyanide program is issued quarterly (Cash and Dukelow 1992c). This implementation plan will be revised as necessary. Activity Data Sheet 1110 in the *Environmental Restoration and Waste Management Five Year Plan* (DOE 1991a) outlines the budget and schedule for the ferrocyanide safety program. To assist the reader, the schedules are provided in Section 5.0 of this document.

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2.0 BACKGROUND AND STATUS

2.1 BACKGROUND

Radioactive waste forms from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940's. During the 1950's, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short period of time and to minimize the need for construction of additional storage tanks, Hanford Site scientists developed a process to scavenge ^{137}Cs from tank 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. Based upon existing information at the time, 24 tanks were assigned to the ferrocyanide list based upon the criterion that they contain inventories of at least 1,000 g-moles as the $Fe(CN)^{-4}$ 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 (430 °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-1980's 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 (SAR) applicable to the Hanford Site SSTs. The SARs have historically considered an explosion from fuel/nitrate reactions as an incredible event.

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 postulated that an explosion could occur during mechanical retrieval of saltcake or sludge from a waste tank. The EIS 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 short-term 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 advisory panel 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 (Westinghouse Hanford) to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident. On October 9, 1990, Secretary of Energy James D. Watkins announced that a supplemental EIS would be prepared containing an updated analysis of safety questions for the Hanford Site SSTs, including a ferrocyanide explosion (DOE 1990c).

The root cause of the ferrocyanide problem results from a combination of factors, beginning with the safety studies done as precursors to using the ferrocyanide scavenging flowsheets. These studies apparently did not include ultimate disposal of the ferrocyanide solids, and were evidently not performed to the conservative standards used today, since they did not point out 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 done, or were done to less conservative standards, to demonstrate that other chemicals would not increase the level of risk. Monitoring systems, such as temperature measurement instrumentation, were allowed to be disconnected and fall into disrepair since 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 done 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 raised about the assumed radioactive material source term (release fraction) resulting from a postulated explosion, and further evaluations highlighted questions about uncertainties in the chemical content of the waste tanks.

In October 1990 (Deaton 1990), the ferrocyanide issue was declared an Unreviewed Safety Question (USQ)* because the safety envelope for these tanks may no longer be bounded by the existing safety analysis report (RHO 1986). In 1990, using process knowledge, process records, transfer records, and log books, 24 tanks were identified at the Hanford Site as potentially containing

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*An Unreviewed Safety Question, as defined by DOE Orders 5480.5 (DOE 1986) and 5480.21 (DOE 1991b), 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."

1,000 g-mole (465 lb) or more of ferrocyanide [as the $Fe(CN)_6^{-4}$ anion]. All 24 tanks remain on the list of ferrocyanide watchlist tanks because of the USQ. Work in and around any of the ferrocyanide tanks requires detailed planning, including the preparation of 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 ferrocyanide 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.

The 24 tanks identified are listed in Table 2-1. Based upon more recent information (Borsheim and Simpson 1991), it is believed that six of the 24 tanks do not meet the 1,000 g-mole criterion. These tanks are shown in Table 2-1 as <1 in Column No. 3. 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 57 °C (135 °F) (Hanlon 1992). Each of these five tanks is estimated to contain from 36,000 g-moles (16,750 lb) to 83,000 g-moles (38,600 lb) of ferrocyanide, and have been assigned a high priority for installation of expanded tank monitoring capabilities. Temperatures in the remaining 19 tanks are below 38 °C (100 °F), and many contain 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) are estimated to contain a somewhat smaller ferrocyanide inventory, 25,000 g-moles (11,600 lb) to 33,000 g-moles (15,300 lbs), but are believed 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.

2.2 CURRENT STATUS OF THE FERROCYANIDE SAFETY ISSUE

This implementation plan has been revised to present the current status and planning for implementing each of the DNFSB safety recommendations. Increased knowledge resulting from initial engineering designs, research, and investigations has prompted changes in the original proposed approach and schedule for implementation of DNFSB recommendations. In some cases, the task scopes have been expanded or reduced as new technical information has become available. A summary of the progress achieved to date, a brief discussion of the problems encountered, and the approach for addressing each recommendation are presented in this plan. The schedules for the various tasks are presented in Section 5.0. A plan to address and remove the USQ on the ferrocyanide tanks is also being prepared and will be issued as a predecisional document* in January 1993.

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*Predecisional documents are those that require review and approval by DOE prior to public release. These documents may be preliminary in nature or in final form for program secretarial officer (PSO) approval.

2.2.1 What is Presently Known about Ferrocyanide Waste

Significant information and data have been acquired since the spring of 1990 on the safety of ferrocyanide waste in the Hanford Site high-level radioactive waste tanks. Concentrated ferrocyanide nitrate/nitrite chemical combinations can undergo an oxidation-reduction reaction. Laboratory tests on ferrocyanide compounds and waste simulants have demonstrated that these chemicals, when dry and relatively pure (i.e., near stoichiometric proportions with little or no diluents present), can react exothermically. On the other hand, it has been shown that the ferrocyanide-nitrate/nitrite reaction cannot propagate through waste if the reactants are sufficiently diluted by inert chemicals and/or by water. The actual tank waste hazards are not yet adequately understood because of a lack of tank data to this point in time. For a specific waste storage tank, the key parameters that govern waste reactivity are the following:

- The mass of ferrocyanide or other fuels present (inventory of ferrocyanide/other fuels)
- The portion of diluents present (concentration of ferrocyanide/other fuels)
- The proportion of water present (percent moisture in the ferrocyanide waste)
- The temperature of the stored waste.

Knowledge of these parameters on a tank-by-tank basis will provide a technical basis of whether or not the ferrocyanide waste would be reactive. While tanks 241-C-112 and 241-C-109 are the only recently sampled ferrocyanide tanks, historical records and laboratory tests with waste simulants provide evidence that ferrocyanide concentrations in the 24 tanks are too diluted by inert chemicals and water to support a propagating reaction. This conclusion assumes there are no local high ferrocyanide concentrations or hot spots. Even if the waste were to somehow dry out, evidence suggests that most of the tanks (20 of the 24) still contain ferrocyanide mixtures too dilute to support a propagating reaction. The four remaining tanks are in the C-Farm [241-C-108, -109, -111, and -112]. While the ferrocyanide waste in these tanks is believed to contain at least 50 wt% water, the simulant material representative of the C-Farm flowsheet does propagate when dry.

While variations of three flowsheets were used in the 1950's to perform the scavenging campaigns, some of the waste contents may now be different because of other wastes added to the tanks and possible aging effects by radiolysis and high pH. Therefore, the tanks are being treated individually in risk assessments and in drawing conclusions from tank core samples.

Results from thermal-hydraulic modeling conducted to date suggest that hot spots are incredible because the heat producing radionuclides must be concentrated over 100 fold into an unlikely configuration to cause a safety concern. For the shallow waste ferrocyanide tanks and/or those without saltcake, such as the C-, T-, and TY-Farms, the heat transfer away from a postulated hot spot should be significantly greater than tanks with more waste and/or a top saltcake (insulating) layer. The thermal load for the

ferrocyanide tanks is also proving to be much lower (up to 3 times lower in tanks analyzed to date) than originally estimated, based upon recent values calculated for six tanks. The new values are in the range of 0.7 to 3.2 kW (2,400 to 11,000 Btu/h). See Section 4.1.5 for more information on this subject.

Based upon current information on simulant testing and modeling of the ferrocyanide waste, the Aerosol Experts Panel (AEP) recently provided (March 1992) recommendations for aerosol testing. (See Section 4.4.5.5.) The consensus of the panel members was that any ferrocyanide reaction, if it did occur in the bulk of the tank waste, would result in only a slow burn. The slow burn would be expected to plug and rupture the passive High-Efficiency Particulate Air (HEPA) breather filter on the tank and cause a slow release of aerosols to the environment. The AEP recommended that small-scale tests be conducted to measure the rate of aerosol generation and the particle size distribution from ferrocyanide compositions of interest. The AEP also recommended that, if results of additional studies currently underway undermine this perception of slow burning, then the performance of large-scale tests and overburden participation in aerosol behavior would have to be evaluated. This topic is discussed in more detail in Section 4.4.5.5.

2.2.2 Preliminary Conclusions on Continued In Situ Storage of Ferrocyanide Wastes

In situ safe storage of the ferrocyanide tank waste, as presently configured in the Hanford Site SSTs, is judged to be a viable option if an adequate dilution of the ferrocyanide waste by water and other inerts is confirmed (Grigsby et al. 1992; Postma et al. 1992; Cash et al. 1992). There are concerns, however, which need to be addressed by additional safety analyses and implemented in operational safety requirements. These areas of concern are as follows.

- Criteria for safe storage should be developed to guide tank management and surveillance operations. Key parameters are moisture content and temperature of the waste.
- Drying of the ferrocyanide waste by evaporation of water into dry air flowing through the vapor space of the tank should be monitored and controlled if a tank is placed on active ventilation for more than a few days. (See Section 4.1.5.5.2.)
- Tanks may need to be monitored for moisture and temperature on a routine basis to verify that safe storage conditions do not deteriorate with time.
- Control equipment should be installed to permit a quick response in the event that moisture levels or temperatures deviate from specified safe limits.
- Emergency preparedness procedures should be reevaluated with respect to the above.

2.2.3 Information That is Still Needed on the Ferrocyanide Safety Issue

The information gathered to date on the ferrocyanide safety issue has come largely from historical records and laboratory tests with specially prepared simulants that attempt to duplicate the chemical flowsheets used during the 1950's. Chemical and physical properties of the actual waste in the tanks at this time are lacking and need to be obtained and/or monitored. New, reliable instrumentation for monitoring waste temperatures, moisture contents, and possibly other tank properties must be installed, and tank waste must be characterized. Key data that must still be obtained* from the ferrocyanide tanks are listed below.

- Analyses of ferrocyanide tank waste are required to confirm expected ferrocyanide compositions as a function of waste depth as part of the evaluation of the potential for hot spots.

- Thermal analyses of tank waste samples are needed to determine whether the actual wastes could lead to a propagating reaction under postulated accident conditions.

- The expected high retention of moisture by nickel ferrocyanide compounds must be verified for various postulated accident scenarios.

- Compositional limits that prevent propagating reactions (currently determined from thermodynamic analyses and waste simulant tests) should be confirmed by experiment with simulant compositions based on actual waste analyses.

- The potential for hot spots, or regions of highly concentrated ferrocyanide compounds and heat-producing radionuclides, needs further study to determine if they can exist and, if hot spots are possible, under what conditions. Resolution of the hot spot issue may require waste sampling and monitoring, as well as the waste tank thermal modeling already underway.

- Chemical changes that could or have occurred during long-term storage need to be evaluated further to determine how such changes may affect the reactivity of the ferrocyanide waste. Radiolysis and/or high pH chemical reactions may have degraded and removed a significant fraction of the nickel ferrocyanide compounds.

- If hot spots are deemed credible, a method to detect and/or control them needs to be developed.

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*The rotary drilling core sampling technique must be developed and deployed so that the ferrocyanide tanks containing overlying salt cake can be sampled. See Section 4.4.5.1.

Table 2-1. Ferrocyanide Tank Data Summary.

Tank	Waste Processing Source	FeCN Content (1,000 g-moles)	^{137}Cs (Ci) Decayed To January 1991			^{90}Sr (Ci) Decayed To January 1991		Stabilization Status			Solids Volume/Height (kgal/ft)			Supernate Above Solids	Liquid Levels (ft)		Maximum Temperature As Of November 1992
		(1)	Total (2)	Total (3)	FeCN sludge content only (1)	(3)	FeCN sludge content only (1)	Interim stabilized	Saltwell jet pumped (end date)	Contains LOW	Total (4)	FeCN sludge (5)	FeCN sludge (1)	(4)	DT/MT ZC/FIC	LOW (neutron/ gamma)	°C (°F)
BX-102	U Plant	<1		2.6 E+05	--	1.7 E+05	--	Y	N	N	96/3.5	NM	0	N	2.5	--	21 (70)
BX-106	U Plant	<1		6.1 E+06	--	1.7 E+06	--	N	N	N	31/1.6	NM	0	Y	1.0	--	21 (70)
BX-110	U Plant	<1		4.4 E+05	--	2.6 E+05	--	Y	N	N	198/6.6	NM	0	Y	5.6	--	20 (69)
BX-111	U Plant	<1	1.5 E+05	4.4 E+05	--	2.6 E+05	--	N	N	Y	211/7.0	NM	0	Y	6.6	7.5/7.4	22 (71)
BY-101	U Plant	<1	3.9 E+04	5.2 E+05	--	3.5 E+05	--	Y	Y (1/84)	Y	387/12.3	NM	0	N	2.6	4.9/5.6	24 (76)
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	P	Y	400/12.7	NM	212/7.0	N	10.0	11.9/11.3	28 (82)
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 (11/84)	Y	406/12.9	244/8.0	260/8.5	N	4.0	7.0/6.7	54 (130) 46 (115)[6]
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	N	Y	503/15.9	213/7.1	96/3.5	N	--	13.6/14.8	46 (114) 49 (120)[6]
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	N	Y	642/20.1	111/4.0	228/7.5	N	--	18.5/18.6	55 (131)
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 (7/79)	Y	266/8.7	172/5.8	158/5.4	N	--	5.1/5.6	36 (96)
BY-108	U Plant	58		2.6 E+05	2.1 E+05	5.2 E+04	2.6 E+05	Y	Y (12/84)	N	228/7.5	201/6.7	208/6.9	N	4.8	--	43 (110)
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 (12/84)	Y	398/12.7	211/7.0	225/7.4	N	5.0	6.2/5.9	49 (121) 44 (111)[6]
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 (11/84)	Y	459/14.5	26/1.4	14/1.1	N	2.3	6.8/4.0	30 (86) (LOW)
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 (5/84)	Y	291/9.4	NM	7/0.7	N	1.6	2.8/3.1	28 (83) (LOW)
C-108	In Farm	25		4.0 E+00	6.5 E+04	2.6 E+04	5.9 E+02	Y	N	N	66/2.6	79/3.0	77/3.0	N	1.6	--	27 (80)
C-109	In Farm	30		5.2 E+03	1.1 E+05	7.0 E+01	3.8 E+03	Y	N	N	62/2.5	90/3.3	109/3.9	Y	1.6	--	28 (82) 27 (81)[6]
C-111	In Farm	33		4.3 E+03	1.4 E+04	8.6 E+04	8.1 E+02	Y	N	N	57/2.3	95/3.5	98/3.6	N	1.3	--	26 (79)
C-112	In Farm	31		3.5 E+03	1.3 E+05	4.3 E+04	1.4 E+03	Y	N	N	104/3.8	46/2.0	84/3.2	N	--	--	29 (84) 30 (86)[6]
T-101	U Plant	<1		2.6 E+04	--	1.7 E+03	--	N	N	N	103/3.7	NM	0	Y	3.7	--	24 (76)
T-107	U Plant	5		--	7.8 E+03	3.5 E+04	1.3 E+04	N	N	N	171/5.8	201/6.7	212/7.0	Y	5.1	--	21 (70)
TX-118	U and T Plants	<3	5.3 E+04	9.0 E+05	--	1.0 E+06	--	Y	Y (2/83)	Y	347/11.1	6/0.6	--	N	3.3	4.4/4.8	26 (78)
TY-101	T Plant	23		7.0 E+03	4.2 E+04	1.7 E+04	3.7 E+04	Y	Y (2/83)	N	118/4.2	183/6.2	151/5.2	N	1.4	--	19 (67)
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 (12/82)	Y	162/5.5	188/6.3	179/6.0	N	4.7	4.9/4.1	22 (71)
TY-104	T Plant	12		1.7 E+03	2.1 E+04	7.0 E+03	1.9 E+04	Y	N	N	43/1.9	74/2.9	75/2.9	Y	2.0	--	20 (68)
	Total	630															

1. Borsheim, G. L., Simpson, B. C. An Assessment of the Inventories of Ferrocyanide Watchlist Tanks, WHC-SD-WM-ER-133, Westinghouse Hanford Company, Richland, Washington, 1991.
2. Keele, B. D., et al., Application of Cadmium Telluride Gamma Ray Spectrometer to Remote Characterization of High-Level Radioactive Waste Tanks, WHC-SA-1196-A, Westinghouse Hanford Company, Richland, Washington, 1991.
3. Jungfleish, F. M., TRAC: A Preliminary Estimation of Waste Tank Inventories in Hanford Tanks Through 1980, SD-WM-TI-057, Rockwell Hanford Operations, Richland, Washington, 1984.
4. Hanlon, B. M. Tank Farm Surveillance and Waste Tank Summary Report for April 1992, WHC-EP-0182-49, Westinghouse Hanford Company, Richland, Washington, 1992.
5. Anderson, J. D., A History of the 200 Area Tank Farms, WHC-MR-0132, Westinghouse Hanford Company, Richland, Washington, 1990.

6. Readings from new TC trees installed in September 1992; Tank 241-BY-105 already had two TC trees.

DT = Dip tubes
FeCN = Ferrocyanide
FIC = Food Instruments Corporation (Auto Tape)
LOW = Liquid observation well (thermocouple)
MT = Manual tape
N = No
NM = Not measured
P = Partially
Y = Yes
ZC = Zip cord

The information above and the current plans for obtaining more data are discussed in this implementation plan. The major focus is on improved tank monitoring and characterization of actual tank waste. The concepts for resolution/closure of the ferrocyanide tank safety issue are provided in a series of logic diagrams, with accompanying narrative provided in *The Fiscal Year 1992 Program Plan for Evaluation of Ferrocyanide in the Hanford Site Waste Tanks* (Cash and Dukelow 1992b). The logic diagrams may change as additional information is obtained, or as requirements for closure are changed.

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3.0 OBJECTIVES

The objectives of this implementation plan are to (1) specifically show how each of the six parts of DNFSB Recommendation 90-7 (DOE 1990b) is being addressed; (2) describe and status the associated program activities for each part of the recommendation; and (3) provide the schedule for future activities.

The overall approach taken in addressing the ferrocyanide safety issue includes short- and long-term safety analyses, management and control of tank storage operations, collection and analysis of tank historical information, removal of possible liquid from SSTs, interim waste tank stabilization and, ultimately, waste remediation and final disposal. The principal objective of this work is to gain a thorough understanding of ferrocyanide tank waste and the reactive behavior of its constituents so that the following can occur: (1) the ferrocyanide tanks can be maintained in a safe condition with minimal risk of an accident; (2) one or more strategies can be selected to ensure interim safe storage until retrieval of the wastes from the tanks for ultimate disposal; (3) the USQ on the ferrocyanide tanks can be closed out; and (4) ultimate disposal options can be identified, developed, and implemented.

To gain a thorough understanding of the ferrocyanide tank waste and the reactive behavior of its constituents, chemical reaction experiments are underway using simulated ferrocyanide waste sludge that have been produced based on flowsheets used during the scavenging campaigns of the 1950's. Three major flowsheets were used to produce sludges that varied in composition of ferrocyanide and diluents (Borsheim and Simpson 1991). The experiments are described in more detail in Section 4.5. Aerosol modeling to determine onsite and offsite dose consequences is planned as are possible tests to experimentally validate the aerosol source terms and aerosol particle size distribution. This information will be used to bound the worst-case accident scenario.

Instrumentation presently available on many of the ferrocyanide tanks includes equipment originally installed when the tanks were constructed. Although some new capabilities, such as liquid observation wells (LOW), were installed on some of the tanks, obtainable tank data are limited and sometimes suspect. In addition, the physical properties and exact chemical makeup of the waste are not well known because so many additions and transfers occurred since the original ferrocyanide scavenging campaigns were completed in the mid-1950's. Chemical and physical changes may have occurred within the waste over the 35-plus years of storage.

To learn what is in the tanks and to continuously monitor their conditions, an accelerated characterization and research program is underway. The purpose of the ferrocyanide program is to provide sample analyses of all 24 tanks by the end of fiscal year (FY) 1997, so that tank contents and properties can be determined and the principal objectives can be achieved.

Activities that are underway to address each part of DNFSB Recommendation 90-7 are detailed and discussed separately in Section 4.0. A schedule for these activities is shown in Section 5.0.

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4.0 IMPLEMENTATION TASK ACTIVITIES

4.1 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.1 (ENHANCED TEMPERATURE MEASUREMENT)

"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."

4.1.1 Background

The recommendations were made at a time when there was a significant concern over the possibility of an undetected hot spot existing within the waste that might provide the necessary energy to promote an uncontrolled reaction or explosion. Most of the ferrocyanide tanks did not have an adequate number of thermocouples (TC) functioning to provide even one complete vertical profile of the temperatures within the tanks, and little was known about the reliability of the heat content estimates.

Subsequent work in several areas has developed a broader knowledge base and has warranted several changes in approach to implement 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 TC tree with replaceable TCs in each ferrocyanide tank. Additionally, there should be at least two operational TCs 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 thermocouple elements in the existing trees have been returned to service and measured temperatures are as expected; (2) thermal modeling to date (McLaren 1992c) 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 TC trees would not be likely to detect a hot spot; and (4) new estimates of tank heat content based on tank temperatures show lower values than previous estimates. When completed, the new plan will result in having two TC trees in all but three ferrocyanide tanks (241-BY-106, -111 and -112). Tank 241-BY-106 already contains a TC tree with replaceable TCs; tanks 241-BY-111 and -112 currently have no operable TC tree. The tank 241-BY-111 and -112 waste temperatures are being measured via a dedicated TC installed in the tank LOWs. The existing TC trees in the tanks will be monitored as well as the newly installed trees. It is expected that the older TC trees will eventually fail in a manner that cannot be repaired and will not be replaced.

4.1.2 Evaluation of Issue

Hot spots have been postulated to exist in the ferrocyanide tanks. Knowledge of the ferrocyanide process (the precipitates were easily suspended) indicates that the waste should be relatively evenly dispersed horizontally. Additional TC 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. Therefore, the provision of at least one TC tree per tank, with replaceable TCs, is warranted, as is additional review of alternative methodologies, such as infrared (IR) scanning, in parallel with further evaluation of the possibility and consequences of hot spots.

4.1.3 Baseline Assumptions

- "Hot spots" may exist in the ferrocyanide tanks.

- Use of TC trees alone to detect "hot spots" is not practical because up to 75 TC 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 TC tree placement; and (3) excavation, shielding and core drilling. As low as reasonably achievable concerns would make this work expensive. (See Section 4.1.5.4.)

- IR technology can be made to function in high radiation fields for short periods of time and has the sensitivity to detect hot spots of concern. (See Section 4.1.5.5.1.)

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

4.1.4 Method to Close Recommendation 90-7.1

The provision of at least one TC tree with replaceable TCs in each ferrocyanide tank and the connection of each TC to the continuous temperature monitoring system is expected to provide adequate temperature monitoring in the waste. Completion of a planned hot spot position paper will determine whether a hot spot is a credible event (see Section 4.1.5.4). If a hot spot is credible, IR scanning will initially be used (as appropriate) to determine if there are any existing hot spots and to validate the modeling. IR scanning can be used on an established frequency if there is a mechanism postulated for hot spots developing and if it is determined that additional monitoring is necessary. If an alternative technology for hot spot monitoring is identified, its application will be pursued as warranted.

4.1.5 Action Plan

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

1. **Installation of new instrument trees**--The scope of this subtask has been changed as discussed in Section 4.1.5.1.

2. **Repair and upgrades to existing tank temperature monitoring instrumentation**--This task has now been completed. See Section 4.1.5.3.

3. **Application of alternative tank monitoring technologies, such as IR imaging, and moisture monitoring of the waste**--The extent of the scanning effort will be determined when a position paper is completed on the credibility of the formation of a hot spot. See Sections 4.1.5.4 and 4.1.5.5.

4. **Development and analyses of thermal models for ferrocyanide tank temperatures and hot spots**--This task has been expanded to include the estimation of heat generation rates and thermal characteristics in additional tanks. See Section 4.1.5.4.

4.1.5.1 Thermocouple Trees. The FY 1992 workscope for installation of TC trees was to update a standard tree design, fabricate, and install one additional TC tree in each of the following tanks: 241-C-109, 241-C-112, 241-BY-104, and 241-BY-110. This provided two TC trees for each of these four tanks, spaced as far apart inside the tanks as available riser space allowed. The presence of two TC trees in each tank will not in itself verify that a "hot spot" does not exist. It will, however, help confirm the thermal modeling that is being performed and add to knowledge of the temperature profiles and homogeneity in the tanks, as well as the reliability of existing TCs.

Existing design drawings have been updated to allow fabrication of the TC trees. Fabrication and installation of the first four TC trees were completed in September 1992.

The safety assessment (SA) to establish controls and address the safety issues raised by installation of TC trees into nonleaking tanks has been completed. The *National Environmental Policy Act of 1969* documentation process [i.e., environmental assessment (EA) and finding of no significant impact] for the identified workscope was also approved by DOE. Chemical compatibility reviews, seismic analysis, TC tree installation work plans, and much other work was done in conjunction with the SA. To install equipment such as TC trees into waste tanks, water is normally used to sluice the equipment through the waste (and saltcake) to the desired location. The SA was delayed because Westinghouse Hanford believed additional alternatives for installation should be reviewed before up to 5,700 L (1,500 gals) of water was added to assumed leaker tanks. It was subsequently decided (by Westinghouse Hanford) to limit the SA to the 11 (now 10 with the declaration of Tank 241-T-101 as a leaker in October 1992) tanks considered to be sound. For the assumed leaker tanks, alternatives are being examined for installation using minimum amounts of water. For installation of the new TC trees into

leaker tanks, either a new technique would be used or justification would be developed for use of water for installation. A second SA and EA will be written and submitted for approval for TC tree installation into leaker tanks to accomplish that objective. The SA for TC tree installation into leaker tanks is scheduled to be completed by September 1, 1993.

Based upon the experience gained from installing the four thermocouple trees in September 1992, where only 70-260 gallons of water were used, and from information obtained from the State of Washington, it may be possible to install TC trees in assumed leaker tanks using only minimum quantities of hot water. In that case only minor revisions to the existing SA and EA would be required to include leaker tanks. These documents would again require approval by the PSO.

There are 10 sound tanks that are included in the initial SA and EA. TC trees have been installed in four of these tanks. It is projected that TC trees for the remaining six sound tanks will be installed by July 30, 1993.

When appropriate documentation is prepared and approved for the assumed leaker tanks, the remaining TC trees will be installed as indicated in the Figure 5-1 schedule. Further acceleration of the installation of TC trees will be difficult because of the large manpower resources required for installation and the present restrictions imposed by fresh air respiratory requirements. A typical TC tree installation requires a crew of about 12 people to support installation. The TC tree installation must compete with other high priority work, such as ferrocyanide program vapor space and core sampling, in addition to the rest of the Tank Farm programs. The TC tree installation schedule will be revised as conditions change.

The new TCs in 241-BY-104 and 241-BY-110 were be connected to the continuous temperature monitoring system (CTMS) in November, 1992. Additional new TCs will be connected to the CTMS as the system is installed in C, T, and BX Farms or within about three months after the TCs are installed. Presently, the C Farm CTMS is not expected to be operational until July 1993. The TCs from the new trees in C Farm will be connected as soon as the CTMS is available in that tank farm. (See Section 4.2.2.)

Progress on identified milestones is as follows.

- **September 30, 1992:** Install new TC trees in tanks 241-C-109 and -112, 241-BY-104 and -110. This action is complete

The following future milestones have been established.

- **March 30, 1993:** Submit safety and environmental documentation for installation of TC trees in assumed leaker ferrocyanide tanks to DOE for review and comment. An acceptable installation method must be selected to meet this date. See also Section 4.1.5.1.

- **July 30, 1993:** Complete installation of additional TC trees in non-leaker ferrocyanide tanks (currently six tanks).

- **September 1, 1993:** Receive authorization from DOE, based upon revised SA and EA documentation, to install remaining TC trees in assumed leaker tanks.

- **September 30, 1994:** Complete installation of additional TC trees in assumed leaker ferrocyanide tanks (currently 14 tanks).

4.1.5.2 Multifunction Instrument Tree. A position had previously been developed that multifunction instrument trees (MIT) were required to monitor several parameters in waste tanks because a shortage of risers would not accommodate installation of several different instrument trees. Therefore, the MIT was to be designed with the capabilities to perform the following: (1) measuring temperatures at designated elevations within the waste and in the vapor space; (2) sampling vapor space gases at three elevations; and (3) monitoring vapor space gas pressure. In addition, there was some consideration that the MITs could be used in the future for deployment of in situ chemical sensors using fiber optic cables.

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 TC 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.

Alternative plans for the MIT functions have been examined. Validation of vapor space gas sampling by the Toxic Gas Program is in progress. First indications are that the sampling lines in the tank may have to be heated. Alternative designs, therefore, may have to be reviewed for gas sampling. With regard to another proposed MIT function to enable the use of chemical sensors, the need for deployment of chemical sensors is uncertain. If the need does arise, a separate riser would probably have to be used to carry the chemical sensor down into the waste using an auger or cone penetrometer. The design of the new TC tree does permit the replacement of individual TCs, if there is any question about the validity of data. In summary, alternative plans for use of the MIT have been developed, and the MIT is planned for service only in the flammable gas program at this time.

In all other respects, the TC tree will be equivalent to the MIT in providing long-term surveillance for ferrocyanide concerns. There will be significant cost savings in using TC trees for the second temperature indicating instrument (versus the MIT design), and the TC trees can be fabricated faster than the MITs. This will allow an accelerated knowledge of tank temperature characteristics.

4.1.5.3 Upgrades to Existing Tank Temperature Monitoring Instrumentation. This subtask began in response to Recommendation 90-3 and is a continuing activity. As part of this activity, the status and condition of presently installed TCs on the 24 ferrocyanide tanks were determined. Until new TC trees are installed, existing TCs are being used to provide temperature measurements in the ferrocyanide tanks.

A report has been issued summarizing the condition of TCs in all 24 ferrocyanide tanks (Bussell 1992). The exact condition of each existing TC has been determined by field resistance and voltage measurements across the junction and across each lead to ground. Two of the tanks (241-BY-111 and 241-BY-112) do not have functional TC trees, and the temperatures in these tanks are measured by a single dedicated TC located in each LOW. Temperatures in these two tanks as a function of elevation were determined as part of this subtask activity. A calibrated TC was held against the inside wall of the LOW by an inflatable bladder, thereby giving an accurate wall (waste) temperature.

The chief cause for TC failure appears to be corrosion of the iron lead, resulting in an open leg on the TC. A method was developed to restore some of the failed TCs to a functional condition by using the carbon steel body of the tree itself as a substitute for the iron lead. A total of 31 failed TCs have been returned to service using this technique.

The field work for evaluating existing TCs included the identification and restoration to service of a second installed TC tree in the 241-BY-105 tank. The TC readings from both trees are in good agreement and confirm the validity of the thermal modeling analyses for this tank (McLaren 1992c).

Work on correcting problems with the TCs and making repairs to marginal or failed TCs is now complete. In conjunction with the computer operated CTMS to eliminate operator-taken readings with portable instrumentation, these repairs have and will continue to improve the quality of temperature measurements and reduce the number of personnel required to take measurements by hand.

Progress on identified milestones is as follows:

- **March 31, 1992:** The original planned date for completing repair of the TCs was delayed due to other high-priority safety work and tank farm entry restrictions. This work was completed in September 1992.

4.1.5.4 **Hot Spot Thermal Modeling.** If radionuclides in a ferrocyanide tank are sufficiently concentrated in a local region, the radioactive decay heat in this "hot spot" might be sufficient to cause a ferrocyanide chemical reaction. If the ferrocyanide concentration is high enough and if water and other inert diluents do not adequately absorb/transfer the heat produced, a propagating reaction could possibly be initiated. Because there is typically only one TC tree in each 23 m (75 ft) diameter ferrocyanide tank*, uneven heat generation could exist in these tanks and not be detected.

This task models and analyzes available temperature data from the ferrocyanide tanks to (1) determine tank heat loads and (2) predict temperatures as a function of axial and radial distance within the tank. Sensitivity and parametric analyses are included to determine the conditions

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*Exceptions are tank 241-BY-105, which has two TC trees, and tanks 241-BY-111 and-112, which have only a single dedicated TC element in the LOW.

under which hot spots could become a serious safety concern. These analyses also aid in interpreting future data, assist in placement of new TC trees, and help to determine whether IR scanning of the tanks would be meaningful.

Two state-of-the-art, validated computer codes (HEATING7 and FATHOMS) are used in the modeling. These codes are verified against existing data and have two- and three-dimensional capabilities. Both steady-state and transient analyses are being performed.

An interim report on the analysis of SST 241-BY-104 was completed in September 1991 (McLaren 1991) using hot spots of various sizes. Most of the analysis involved a typical hot spot in the shape of a wedge approximately 1 m on each side. This analysis showed that, with an extremely conservative chemical heat generation curve, completely dried waste would require a radionuclide concentration 40 times greater in the hot spot than the average of the tank for the hot spot to reach a temperature of 177 °C (350 °F). This calculation assumed no moisture is present in the tank. Using present estimates of tank radionuclide concentrations, moisture levels, and temperatures, the model requires a radionuclide concentration in the hot spot of 150 times the tank average to reach 177 °C. The 177 °C temperature is very conservative based upon work at PNL (Hallen 1992) and at Fauske and Associates, Incorporated (FAI) (Cash and Fauske 1991). These investigations showed that the lowest exothermic reaction onset temperatures ranged from 220 °C (425 °F) to 240 °C (465 °F) for mixtures of cesium nickel ferrocyanide or sodium nickel ferrocyanide and nitrate/nitrite with 5 wt% ethylenediaminetetraacetic acid (EDTA). The EDTA acts as an added fuel and may help initiate the ferrocyanide-nitrate/nitrite reaction sooner.

The use of multiple TC trees as a method for ensuring detection of possible hot spots in a ferrocyanide waste tank is not feasible. Thermal modeling has shown that the thermal conductivity of the waste in these tanks is relatively low: 0.00433 w/cm-°C (0.25 Btu/hr-ft-°F). This value agrees well with measurements made in 1975 on actual SST wastes (McLaren 1991). Consequently, a TC tree can reliably measure temperatures only in a cylinder with a radius of about 3.1 m (10 ft). A pattern of 75 TC trees in a single tank would be required to ensure that the entire waste volume is included within the detection range of the TC trees. If any gaps exist in the coverage, the potential for undetected hot spots would still exist. The probability of locating a second TC tree in, or close to, a potential hot spot is small (McLaren 1991). However, the most recent analyses have indicated that the thermal conductivity of the waste could be as high as 0.0121 w/cm-°C (0.70 BTU/hr-ft-°F) (McLaren 1992c). This would decrease the number of TC trees needed to provide complete coverage, but the method would still be impractical to use because of the limited number and placement of risers in the tanks. To obtain the proper coverage would require drilling holes in the tank dome for new risers and inserting new TC trees. Without proper coverage, the method would not provide a definitive answer to the question of whether a hot spot exists.

A better way to monitor for abnormal temperatures in the ferrocyanide tanks may be infrared scanning. Based upon hot spot modeling completed to date, however, the temperature in the hot spot has to approach 220 °C (425 °F) before a significant increase in surface temperature above the hot spot would be detectable. A decision on the extent of infrared scanning efforts

for-worst-case ferrocyanide tanks will be made April 15, 1993, when a hot spot position paper is completed for DOE. The position paper will summarize the steady-state and transient thermal modeling completed to that point in time and provide conclusions on whether hot spots are credible in any of the ferrocyanide tanks.

The results of transient analyses of hot spot formation at the bottom of tank 241-BY-104* indicate that, should a hot spot take 1 year to stabilize, it would take an additional 4 months before a temperature change on the surface would indicate the presence of the formation (McLaren 1992a). Should the hot spot temperature be high enough to cause propagation, the surface temperature change would not give timely enough warning to prevent the propagation from occurring. It should be noted that the formation of a dangerous hot spot within 1 year from a nearly homogeneous condition is not considered credible. A hot spot, if credible, would most likely have formed as waste was added to the tank. As long as significant liquid is present, the hot spot would remain dormant, but it might start to heat up if excess liquid is pumped from the tank during waste transfers or interim stabilization.

A two-dimensional analysis of the gas space of tank 241-BY-104 was performed to determine the expected heat and water loss out the breather filter because of air infiltration into the isolated tank (McLaren 1992b). This analysis indicated that the expected heat removal (because of air infiltration) is less than 500 Btu/hr (146 W), with a maximum water loss of less than 3.8 L/day (1 gal/day). Other analyses (Grigsby et al. 1992) indicate that the water loss would be even less (approximately 0.57 L [0.15 gal]/day).

Analyses for six additional tanks were performed in FY 1992 to determine their heat generation rates and thermal characteristics. These tanks were 241-BY-105, 241-BY-106, 241-BY-108, 241-BY-110, 241-BY-111, and 241-C-109. Results (McLaren 1992c) show that the heat loadings for these tanks are considerably lower (up to 3 times lower, in most cases) than published earlier (Lewis and Alstad 1986).

This work was scheduled for completion by July 31, 1992, but was delayed to include additional work using thermal conductivities more representative of real ferrocyanide waste. Sensitivity analyses were completed using waste thermal conductivities ranging from 0.0029 to 0.012 w/cm-°C (0.17 to 0.70 Btu/hr-ft-°F).

An analysis of one of the six tanks noted above was performed to determine the effects of hot spot formation. This analysis included the maximum hot spot concentration for various conditions that would not exceed 220 °C (430 °F), and the transient response of the tank to this projected maximum hot spot with various formation rates. This temperature was selected because work in the laboratory with mixtures of ferrocyanide and nitrate/nitrite have shown that exothermic reactions can start at temperatures of

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*Tank 241-BY-104 may be one of the worst-case tanks for potential hot spot temperature monitoring because of its ferrocyanide inventory and large saltcake overburden. See Table 2-1. An additional TC tree has now been installed in this tank (Section 4.1.5.1).

220 °C (or greater) when an additional fuel (such as EDTA) is also present (Burger and Scheele 1991). It should be noted that the lowest exothermic onset temperature observed during tests with the ferrocyanide waste simulants was 245 °C (Fauske 1992d). (The simulants do not contain added fuel.)

Two hot spots were investigated in tank 241-BY-106. One was contained entirely in a thin layer on the bottom of the tank, and the other was a one meter cube placed on the bottom of the tank. The results of the first case showed that a concentration of 20% of the total heat in the tank into the hot spot was required to raise the temperature to 220 °C. This represents a concentration factor of 162 times the average heat load in the surrounding layer. The second hot spot required a concentration of 21% of the heat load of the tank into the hot spot to produce 220 °C.

The transient case utilized the cubical hot spot. The hot spot took 5 years to grow to 21% of the total heat load of the tank. The study was carried out for 10 years. The maximum temperature reached was 155 °C after 5.5 years, at which time the temperature started to decrease. This decrease was due to the decay of the radioactive heat source and the large thermal capacitance of the tank. The surface temperature above the hot spot increased 1 °C in 3 years, and reached a maximum increase of 3.4 °C at 9 years.

Progress on identified milestones is as follows:

- **July 31, 1992:** Determined the heat loads and thermal conductivities of the contents for tanks 241-BY-105, -106, -108, -110, -111, and 241-C-109. The upper and lower bounds of these parameters were calculated. The report on this work was delayed to September 30, 1992, to include additional work with thermal conductivities more representative of actual waste. A predecisional report was issued in September 1992.

- **September 30, 1992:** Performed a detailed thermal analysis of tank 241-BY-106 to determine the response of the tank contents to a hot spot of varying intensities. This analysis included both steady-state and transient analyses. A predecisional report was issued in September 1992.

The following future milestones have been established.

- **April 15, 1993:** Perform thermal modeling studies to (1) determine if there is enough likelihood for forming hot spots; (2) warrant infrared scans of ferrocyanide tanks; and (3) issue a position paper on whether hot spots of concern are credible.

- **June 25, 1993:** Complete thermal hydraulic analyses of four ferrocyanide tanks to determine heat loads and conductivities of the waste contents and issue a report that is approved for public release.

- **September 30, 1993:** Complete transient hot spot thermal modeling of a worst-case ferrocyanide tank, taking into account transpiration of moisture away from the hot spot, and document the results in a report approved for public release.

- **September 30, 1994:** Complete thermal analyses of ferrocyanide tanks that have had new TC trees installed in order to recalculate the heat loadings and thermal conductivities of the waste. The number of tanks analyzed will depend upon the number of TC trees installed in FY 1993 and FY 1994. Each tank will be analyzed as new data become available. Issue a report cleared for public release by September 30, 1994.

4.1.5.5 Additional Tank Monitoring Technologies.

4.1.5.5.1 Infrared Imaging System. The use of an IR scanner has been pursued as a potential means to detect hot spots within the tank waste. A formal design review of the IR scanner assembly and manufacturing drawings was completed by Westinghouse Hanford Engineering, Safety, Quality Assurance, and Tank Farm Operations. Resulting comments by this review committee were incorporated into the design before completion of the assembly. Manufacturing and delivery of parts and subassemblies necessary to lower the IR scanner into the tank were completed in February 1992. A scan was completed in April 1992 on non-watchlist tank 241-S-110, a tank similar to the ferrocyanide tanks in curie content of ^{137}Cs and ^{90}Sr, to demonstrate that surface temperature scans can reliably be interpreted without generating "false alarms." A predecisional report describing the results of the tank scanning was completed on May 29, 1992, for DOE. The report also provided an evaluation of the IR system for use in ferrocyanide tanks (Efferding 1992). It was concluded that the IR scanning system could not provide continuous temperature monitoring because of camera degradation from radiation. However, this scan, in conjunction with laboratory experiments and thermal modeling, has resulted in the determination that the IR scanning system can be used for the majority of the ferrocyanide tanks to detect surface temperature variations and to validate thermal modeling results.

A hot spot is defined as a localized region with a temperature that exceeds the temperature in the surrounding waste. A hot spot could result from an abnormally high concentration of radioactive, heat-generating materials (e.g., ^{137}Cs, ^{90}Sr, and other radionuclides) (see Section 4.1.5.4). A hot spot temperature of 220 °C (425 °F) or greater would be of concern because the onset of exothermic reactions has been observed at temperatures ranging from 220 °C (Burger and Scheele 1991) to 245 °C (Fauske 1992d).

It has been determined that the IR scanning system has the capability to detect and present surface temperature contours that will identify a possible hot spot of significance under the surface of the waste (Mailhot 1992). The detection limits are sensitive enough that a hot spot of concern (220 °C [425 °F]) will create a detectable surface temperature pattern that can be identified and analyzed. If a hot spot is determined to be credible, even the ferrocyanide tanks with larger amounts of waste with low thermal conductivity can be scanned for hot spot indications with a high degree of confidence. The system will not allow an exact hot spot size and temperature determination, but it does provide the necessary information to model the worst-case hot spot causing the temperature pattern detected.

Data acquired by the infrared scans are turned into temperature maps of the waste surface, using one of the various commercial software codes available. From the shape of the isotherms and the change of the contours,

the possible existence of a hot spot can be inferred. Should the existence of a hot spot be suspected, an analysis of the scan data will be made to determine worst-case hot spot sizes and placement. The analysis will utilize computer models to determine the maximum hot spot that could create the temperature contours that are seen. This maximum hot spot will then be evaluated to determine if it is approaching a thermal runaway condition. If the hot spot does not approach a thermal propagating condition, it may be concluded that no immediate cause for concern exists. If desired, future scans could be completed and compared to determine if thermal conditions within the tank are remaining stable.

It should be noted that the information of interest is a comparison of temperatures with each other, not the actual temperatures themselves. An elevated surface temperature, by itself, is no cause for alarm if the surface temperature is uniform. What is being sought is a map showing a "bulls-eye" shape (e.g., an area with a temperature greater than approximately 1 °C (2 °F) above the surrounding areas). If a hot spot is suspected, the error band of the measured temperatures will be applied so as to provide the most conservative result (McLaren 1991, 1992a).

Modeling studies that have been completed (McLaren 1991, 1992a, 1992c), and those in progress will be used to determine whether there is enough likelihood of the formation of hot spots to warrant scans of the ferrocyanide tanks. The thermal modeling work will be summarized in a hot spot position paper to be completed by April 15, 1993. This paper will provide a basis for whether hot spots are credible in any of the ferrocyanide tanks. A recommendation on whether infrared scans of selected ferrocyanide tanks should be conducted will also be made to DOE by this date.

The lowest exothermic onset reaction temperature observed was 220 °C (425 °F) (Burger and Scheele 1991). This temperature was observed with a pure stoichiometric mixture (i.e., cesium nickel ferrocyanide and sodium nitrate/nitrite with 5 mole% EDTA added and no diluents) (Hallen 1992b). Results of tank waste simulant studies to date all exhibit higher reaction temperatures. Prior modeling studies used a lower temperature (177 °C [351 °F]) and still concluded a hot spot was improbable. Additional studies using the higher temperatures should show that high concentrations of heat are even more unlikely, thereby indicating that IR scanning is not warranted. Even if hot spots are not a concern, it is possible that the IR technique might be used for providing increased knowledge of the temperature homogeneity of the tanks. This could be used to augment TC tree data and to guide placement of TC trees.

The following future milestone has been established.

- **January 29, 1993:** Incorporate comments received on report of infrared monitoring of non-watchlist tank 241-S-110 and issue the revised report, approved for public release.

- **April 15, 1993:** Depending upon the conclusions of the hot spot position paper (Section 4.1.5.4), make a recommendation on whether infrared scans should be performed in selected ferrocyanide tanks.

4.1.5.5.2 Estimation of Moisture Content. The moisture content in each tank, particularly of waste near the surface, may be a critical surveillance parameter for monitoring waste stability. If results from waste characterization and waste simulant studies indicate a potentially reactive inventory of ferrocyanide is present in a tank, control of moisture and temperature could still be used to ensure safe storage of the waste. Therefore, a means to monitor moisture content on a routine basis will need to be developed and deployed. Estimation of the water in the tank waste is required because water is an important diluent. This water increases the thermal conductivity of the waste and requires a relatively large quantity of heat of vaporization to be supplied by an external source before the temperature of the waste could be elevated high enough to initiate a propagating reaction.

As a part of the in-tank surveillance program in the early 1980's, neutron probe scans were implemented for measurement of interstitial liquid levels and to provide an estimate of interstitial liquid moisture content. The existing system uses the LOWs to gain access to tank contents. Accurate measurement of moisture was precluded by limitations of the available calibration facility. There is some additional uncertainty involved in moisture measurements from the LOW, in that (1) the neutron probe can "see" moisture in the waste only in a radius of approximately 15 cm (6 in.) around the LOW; and (2) the LOWs were sluiced into place with hot water. While the water would be expected to migrate out into any drier region, the moisture content immediately surrounding the LOW may not be typical of the in-tank waste. Detailed Monte Carlo calculations began in 1991 and have been completed to analyze and identify the relationship between the BF_3 neutron detector readings with respect to several variables, including the waste's moisture content, signal processing, tank material, detector modeling, and automated processing of the tank gamma scans.

A workshop of technical contributors with experience in neutron moisture measurement methods, as well as a variety of other approaches, was conducted in February 1992. The technical merits of all identified approaches to moisture measurement were examined at the workshop. The relative merit of optimizing the existing neutron probe and the potential benefits of designing a new probe were considered at the workshop (as well as other moisture measurement approaches). Design features of a calibration facility were also discussed. Individual participants rated the various methods, and the results of these assessments were compiled and included in the meeting minutes. The most promising measurement approaches were listed. The workshop participants indicated that enhancement of the neutron probe sensor was one of the most promising techniques; therefore, additional work is being done is this area. Modifications for the existing neutron probe have been fabricated and are being tested to determine if the probe sensitivity to moisture can be enhanced.

Progress on identified milestones is as follows:

- **July 31, 1992:** Completed fabrication of four neutron source extenders.

- **August 29, 1992:** Completed preliminary neutron probe scans of a non-watchlist tank using the modified neutron probe.

- **September 30, 1992:** Issue a letter report describing the current status of the study of using the in-tank neutron probe for moisture measurements. This task was completed on schedule.

The following future milestones have been established:

- **March 29, 1993:** Identify and prepare special simulant-filled drums for neutron probe moisture standards.

- **June 25, 1993:** Complete limited calibration using special simulant-filled drums as neutron probe moisture standards.

- **September 27, 1993:** Complete additional ferrocyanide in-tank neutron probe scans with varied source-to-detector spacings and additional laboratory measurements of special moisture standards; issue a proof-of-principle report that is approved for public release on in-tank neutron probe moisture monitoring.

4.2 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.2 (CONTINUOUS TEMPERATURE MONITORING)

"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."

4.2.1 Background

All of the Hanford SSTs were originally equipped with TC trees for temperature measurement. By 1989, many of the TCs were inoperable, and the "good" TCs were being manually read by operators, generally on a 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 1989. The additional readings, coupled with the temperature upgrade program (see Section 4.1.5.3), 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 to provide continuous, direct temperature readouts and alarms to a continuously manned station was started. As a first phase, strip chart recorders were placed on two of the higher temperature ferrocyanide tanks (241-BY-106, -110) in March 1991.

4.2.2 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. When tanks are removed from the watchlist and/or when the USQ resolution

safety studies allow, the temperature monitoring requirements may be relaxed. See Section 4.6.5.1 for the action plan for response to an increasing ferrocyanide tank temperature.

4.2.3 Baseline Assumptions

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

4.2.4 Method to Close Recommendation 90-7.2

The connection of TCs in the radioactive waste (both existing and from new TC trees) to the continuous temperature monitoring system will provide the necessary temperature monitoring. (See also Section 4.1.5.1 for provisions for new TC trees.)

4.2.5 Action Plan

The objective of this task is to have continuous and more accurate temperature monitoring, data logging (recording), and alarms on all 24 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 24 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 TC readings of an individual tank.) It is agreed that 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. The use of 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.

4.2.5.1 Continuous Temperature Monitoring System (CTMS). The purpose of the CTMS is two-fold. One purpose is to provide timely notification of a temperature increase that could indicate a change in tank stability. The second purpose is to provide a reliable database that can be analyzed for trends and provide support and confirmation of thermal modeling. The manual measurements are subject to wide variations in indicated temperature because of portable instrument malfunctions, operator error, and local readout problems (i.e., the poor condition of the aboveground TC switches and wiring).

The intent of the program is to connect existing and new TC trees to the CTMS. The timing of the connections may be grouped; thus, a group of TC probes may be installed in tanks, and then connected to the CTMS after installation is complete. All data are collected automatically at the continuously manned CASS Operator Control Station in the 2750E Building (200 East Area). The monitoring system is independent of the CASS and 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 has alarms for change in level of all in-tank temperature points. On occurrence, alarms 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 is identified by point and time of occurrence. Operator acknowledgement of the alarm silences the audible annunciator. Currently, abnormal readings are treated in accordance with the *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991b; see Section 4.6.5.1).

Signal conditioning and multiplexing is 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 effects, and thermal gradients are thereby reduced.

The CTMS is operational for tanks 241-BY-101, -103, -104, -105, -106, -107, -108, -110, -111, and -112; all temperatures in these tanks are being read continuously. This system consists of TC trees in all tanks except 241-BY-111 and 241-BY-112, which have a TC element in the LOW. Tank 241-BY-105 has two TC trees.

The data collected to date for these tanks indicate that the temperatures are stable. Typically, they vary by only about ±1 °C over several days. No significant changes have been observed over the total period of operation of the CTMS (6 to 9 months). The data are presented graphically to the operator showing axial and radial positions relative to the tank. In addition, all temperatures are logged to disk every 15 minutes. Data from this logged file can be plotted versus time on the operator display.

The system has been expanded to include three ferrocyanide tanks in the 241-TY Tank Farm, and one in the 241-TX Tank Farm; these four tanks were connected before the end of April 1992. This is a change from the previous plan to connect four tanks in 241-C Tank Farm. The change was prompted by existing restrictions on work in 241-C Tank Farm because of the occasional presence of noxious gas. The new TC trees being installed in the BY Farm will also be connected to the CTMS; however, C Farm CTMS monitoring will not be operational until FY 1993, along with the T and BX Farms.

Progress on identified milestones is as follows.

- **September 26, 1991**: Completed installation of the CTMS for five tanks in the 241-BY Tank Farm.

- **December 30, 1991**: Completed installation of the CTMS for the five remaining ferrocyanide tanks in the 241-BY Tank Farm.

- **April 30, 1992:** Completed installation of continuous monitoring of three tanks in the 241-TY Tank Farm and one tank in the 241-TX Tank Farm on April 29, 1992, (a change from the previous milestone for the 241-C Tank Farm).

The following future milestones have been established.

- **July 30, 1993:** Complete installation of continuous monitoring for the four ferrocyanide tanks in 241-C Farm.
- **August 30, 1993:** Complete installation of continuous monitoring for the two ferrocyanide tanks in 241-T Farm.
- **September 30, 1993:** Complete the design and installation of continuous monitoring for the four ferrocyanide tanks in the 241-BX Farm.
- **September 30, 1993:** Connect the new TC trees installed during FY 1993 to the CTMS.
- **September 30, 1994:** Connect the new TC trees installed during FY 1994 to the CTMS.

4.3 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.3 (COVER GAS MONITORING)

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

4.3.1 Background

All 24 ferrocyanide tanks, like most SSTs, are passively ventilated to the atmosphere via a HEPA breather filter. 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 from the low fission product contents. Sampling of the ferrocyanide tanks to date has shown only trace amounts of hydrogen (<0.1 vol%) or 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 or barely detectable (~ 5 ppb) levels. The normal practice before working 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 monitor and Draeger tubes) as directed by the Industrial Hygiene organization. Supplied breathing air is initially used if a tank riser is opened. A cryogenic trap sampling system that collects condensible gases for subsequent laboratory analysis was used on several

tanks; however, this is not a validated method. Currently, all work on any ferrocyanide tank requires that workers use supplied breathing air. As more gas samples are taken from these tanks, this restriction will be reexamined and may be reduced or eliminated.

4.3.2 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, thermocouple tree installation). To date, there is no indication that continuous monitoring for compositional changes is needed.

4.3.3 Baseline Assumptions

- Flammable gases are assumed to be present until proven otherwise.
- Noxious gases are assumed to be present until proven otherwise.
- Sample analyses data will be evaluated and, if appropriate, the number of sampling points within a tank may be reduced.
- 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, however.

4.3.4 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. Sample data analyses will address the question of how fast the gas composition within a given tank may change.

4.3.5 Action Plan

The intent of this task is to provide intermittent gas sampling for the 24 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 a number of the ferrocyanide tanks have been sampled and the data analyzed for gas content, concentration, and distribution. An evaluation will be completed by March 30, 1994, to determine which gases may need to be continuously monitored and whether a prototype monitor should be

installed in certain tanks. To date, there is no evidence that continuous monitoring is necessary for any gases.

The schedule for flammable gas sampling has slipped because of (1) competing high priority safety-related work in the tank farms (241-SY-101 tank and noxious vapors from 241-C-103) and (2) other high priority tank farm work. The subtask to provide permanent gas monitoring equipment is on hold until additional tank vapor space sampling demonstrates a need. Some tank vapor space gas modeling was performed in FY 1991 and 1992.

4.3.5.1 Flammable Gas Monitoring. An effort is now underway to conduct flammable gas monitoring and analyses in the 24 ferrocyanide tanks. Tanks 241-BY-104, 241-C-112, 241-C-109, and 241-BY-110 were sampled in FY 1992. Because the safety issue associated with ferrocyanide tanks is a USQ, this activity requires the DOE-EM Headquarters Program Secretarial Office approval to perform sampling activities within the tanks. Safety and environmental assessments were written and approved by DOE for vapor sampling all ferrocyanide tanks. Appropriate readiness review activities are conducted and DOE approvals obtained before initiation of the sampling.

Tank vapor gas samples were taken through two different risers and at three elevations for the first two ferrocyanide tanks. The lowest elevation sample was at about 30 cm (1 ft) above the waste surface, with one sample in the middle and one near the top of the vapor space. Evaluations are performed for each tank to determine the distribution of gas within the vapor space. The number of lateral sample locations has been reduced, and the number of vertical samples will be reduced if the evaluation determines there is no advantage to taking the increased number of samples.

Initially, flammable gas sampling of the ferrocyanide tanks was integrated with additional types of sampling to identify and characterize potential toxic or noxious gases. This sampling utilized cryogenic traps, at -90 °C (-130 °F), to collect condensible gases for later analysis by a gas chromatograph/mass spectrometer. The sampling system also includes a gas chromatograph in the field that is calibrated to quantify low concentrations of hydrogen. The cryogenic sampling system was developed to characterize vapors in/from all of the underground waste tanks, not just ferrocyanide tanks. As noted later, the cryotrapping system is not presently being used.

Gas sampling of ferrocyanide tank 241-BY-104 was completed in October 1991, and field readings for the tank did not show any significant flammable concentrations. Cryogenic trap and flow-through bulb samples were analyzed and low concentrations of normal paraffin hydrocarbons, acetone, and 1-butanol were found. Ammonia was also found, using Draeger tubes, with concentrations of up to 275 ppm (0.03 vol% - 200 mg/m^3), which is significantly above the threshold limit value of 25 ppm (18 mg/m^3). This has no impact on ferrocyanide safety except to require appropriate respiratory protection for work around the tank for personnel health. The lower flammability limit for ammonia is 16 vol%. In addition, vapor space sampling of the 241-C-112 tank was completed on March 19, 1992. Field readings showed no detectable flammable or toxic gases. For sampling of the remaining tanks, an expedited method for completing readiness reviews was developed to reduce the review cycle. The 241-C-109 tank vapor space was sampled on August 26, 1992, after

completing the streamlined review procedure. Field readings for this tank also showed no detectable flammable or toxic gases.

Requirements for a permanent monitoring capability will be determined after all of the ferrocyanide tanks have been sampled, now projected for March 1994. The analyses of the initial samples will be used to determine the need for a permanent, online gas monitoring capability, and to determine which tanks, if any, will require the installation of permanent monitoring equipment. However, if the results of the sampling at any point indicate the necessity for online monitoring, installation will be pursued as a priority task. If the ferrocyanide chemical reaction studies identify a reaction product gas associated with incipient exothermic ferrocyanide-nitrate/nitrite reactions, the feasibility of monitoring the tank vapor spaces for that gas(es) will also be examined.

Delays in the gas sampling schedule have resulted from a longer than planned review period for the safety and operational readiness documents, which was extended because of the need to review the impact of low pH waste potentially present in the tanks. Schedule delays were also caused by the requirement that work around and in the ferrocyanide tanks must be performed with respiratory air supplied for workers.

The analysis of cryogenic gas samples has been discontinued, pending validation of this or an alternative method. In the meantime, the sampling apparatus can still be used with industry standard analytical methods (e.g., Draeger tubes, combustible gas analyzer, a volatile organic monitor, online gas chromatograph, etc.) to analyze for flammable and potentially toxic gases.

Progress on identified milestones is as follows:

- **September 30, 1992**: Completed vapor space sampling of four ferrocyanide tanks (241-BY-104, -C-112, -C-109, and -BY-110).

The following future milestones have been established.

- **September 30, 1993**: Complete vapor space sampling of eight additional ferrocyanide tanks to support push-mode core sampling and TC tree installation. Issue periodic evaluation reports of gas sampling data.

- **March 31, 1994**: Complete an evaluation report to determine which gases, if any, need to be continuously monitored on selected ferrocyanide tanks.

- **September 30, 1994**: Complete vapor space sampling of remaining ferrocyanide tanks as required to support various field activities and issue a final report that is approved for public release.

4.3.5.2 Vapor Space Gas Modeling. The possibility that localized concentrations or stratification of gases exist in the tanks continues to be evaluated. Some gases may have the potential to be explosive or otherwise hazardous, should their concentrations become large enough and be mixed properly with air. This concern is being addressed through a concerted

sampling effort. A modeling effort that was completed in FY 1992 had determined the airflow patterns in the tank vapor space of 241-C-109 to evaluate the amount of mixing and local gas concentrations that occur. The results of this analysis will be used to evaluate the hazards and risks involved in sampling and other intrusive activities within the tank. This work will aid in developing a methodology for performing vapor space analysis for all ferrocyanide tanks.

The study determined how rapidly the composition of the vapor space gases change with time and can be used to predict what the steady-state equilibrium values should be for gases of interest. Because the 24 ferrocyanide tanks are all passively ventilated, the vapor space gas composition is strongly dependent upon the air in-leakage, gas generation rates, waste temperature, convective mixing, and heat transfer out of the tank.

Two state-of-the-art, validated computer codes (HEATING7 and GOTHIC) are being used in the modeling. These codes are validated using existing data and employ two-dimensional capabilities. The workscope for this task was established during the first quarter of FY 1992, and work has been initiated.

An analysis of tank 241-C-109 vapor space was performed to (1) determine the airflow patterns within the tank and (2) determine the potential for local concentrations within the vapor space. An analysis of a second tank was planned to confirm results of the first tank, but this is not considered necessary because of the well-mixed environment calculated for the first tank. The results of this study have shown that the gases in the tank are well mixed and follow Graham's law for gaseous diffusion.

Progress on identified milestones is as follows:

- **April 30, 1992**: A detailed vapor space analysis of ferrocyanide tank 241-C-109 was completed; a predecisional report was to have been issued by July 30, 1992. Although the analysis was completed, preparation and issuance of the report was deferred because of limited FY 1992 resources.

The following future milestone has been established.

- **February 8, 1993**: Complete analysis of airflow patterns in Tank 241-C-109 and issue a report approved for public release.

- **August 30, 1993**: Complete an analysis of airflow patterns of a second ferrocyanide tank, if warranted, with greater differential temperatures within the tank; issue a report that is approved for public release. [There is currently no funding identified for this activity].

4.4 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.4 (FERROCYANIDE WASTE CHARACTERIZATION)

"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."

4.4.1 Background

The ferrocyanide sludges were deposited in the SSTs in the mid-1950's. Sampling and analysis of the sludges since that time have been very limited. The 241-TY Tank Farm (which contains T Plant flowsheet sludges) was core sampled in 1985; thus, some data on these tanks (including total cyanide analyses on two archived sample composites) are available. An extensive core sampling program for the ferrocyanide tanks has been initiated, with two tanks (241-C-112 and 241-C-109) sampled by the end of FY 1992. Two surface (saltcake) samples from the 241-BY-104 tank were also secured.

The 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 fact that: (1) only a limited number of entry risers are available; (2) Hanford Site analytical facilities (hot cells and labs) to handle these highly radioactive samples have a limited capacity; and (3) the full suite of analyses for a typical full depth core sample costs approximately $700,000 (about $300,000 of this are incremental costs for ferrocyanide analyses).

4.4.2 Evaluation of Issue

It is agreed that sampling and characterization of the ferrocyanide tanks to adequately resolve the safety issues are required. The current schedule for ferrocyanide tank sampling obtains samples from all 24 ferrocyanide tanks by the end of FY 1997. It appears impractical, and it is anticipated to be unnecessary, to take more than two to three core samples per tank, and in some cases, only one sample. Process flowsheet knowledge and work with ferrocyanide sludge simulants are being used to supplement the core samples. Core sample analytical data from several tanks (at least two to three) from the In Farm and U Plant flowsheets and at least one tank containing T Plant flowsheet waste will require evaluation to determine the variability of the waste and confirm or refute the adequacy of this approach.

4.4.3 Baseline Assumptions

- Limited core sampling (two to three cores/tank) will show that, even allowing for waste variability within the tank, the moisture safety criterion below is met.

- Some waste forms are reactive and capable of propagating reactions above some onset temperature (currently estimated from simulants to be >245 °C), unless shown otherwise.

- Even if reactive, stored wastes cannot reach this onset temperature from their storage temperature (<57 °C), unless the moisture content of the waste drops below some critical concentration, currently estimated to be <20 wt%. Studies of moisture transport in ferrocyanide tanks have concluded that the waste will retain a moisture content of 40 wt% or more, even if the tanks leak or are saltwell pumped (Grigsby et al. 1992).

- The most reactive ferrocyanide sludges are those from the In Farm flowsheet; these are stored in the four 241-C Farm ferrocyanide tanks. T-Plant ferrocyanide sludge is expected to exhibit chemical and physical behavior similar to U-Plant flowsheet sludge because their compositions are comparable.

- Sampling and analyzing for ferrocyanide-related concerns concurrently with standard SST core sample analyses are the most efficient use of resources. This allows for meeting Environmental Restoration and Remediation Action (ERRA) commitments while still securing data for safety issue resolution.

- Waste simulants and modeling assumptions are conservative estimates appropriate for use in resolving the USQ.

4.4.4 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, the ferrocyanide tank sampling plan can be finalized.

4.4.5 Action Plan

Characterization of the chemical and physical properties of tank contents is necessary to (1) determine the chemical reactivity of the waste; (2) guide chemical reaction studies; (3) provide a basis for estimating the likelihood and consequences of any postulated uncontrolled ferrocyanide reaction; and (4) allow application of the study results to resolution of the USQ and for final remediation of these tanks. 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, analysis of auger surface samples of the 241-BY-104 tank, and analysis of gamma scan data from tanks containing LOWs. Additionally, Raman scattering spectroscopy is being developed for analyzing

waste for ferrocyanide/ferricyanide and other species. Note that tank characterization work is also underway using flowsheet simulants (see Section 4.5).

Initial core sampling efforts have focused on the 241-C Farm ferrocyanide tanks rather than the 241-BY Farm (as planned in the original implementation plan) because flowsheet analysis and simulant testing indicate these In-Farm scavenged wastes are likely to be more reactive than the other ferrocyanide wastes. Other changes from the original plan include limiting auger surface sampling and eliminating penetrometer testing (see Section 4.4.5.2). A task on Ferrocyanide Waste Tank Hazard Assessment (4.4.5.5) has been added to address the recommendation of the AEP and provide an activity that assembles all data on the ferrocyanide tanks into comprehensive periodic hazards assessment reports (Grigsby et al. 1992). A new section (4.4.5.6) on Safety Assessments for Ferrocyanide Tank Activities is also included.

4.4.5.1 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., phosphates, water, sulfates, carbonates, oxides, and hydroxides). The location of fission products, such as ^{137}Cs and ^{90}Sr, is important because they 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 very important because of the high heat capacity and heat of vaporization of water; water also is an effective inerting material and prevents sustained combustion. Wet ferrocyanide material expected to have precipitated in the tanks with 50 wt% or greater water should 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. Other materials (e.g., nickel, sulfides, copper, lead, and rare earths) may be important as potential catalysts, but have not been identified as such in a preliminary PNL screening (see Section 4.5.5.4).

The waste characterization plan for the Hanford Site SSTs (Winters et al. 1990) calls for obtaining two full-length cores from each SST by 1998, as part of the ERRA program. The number and location of cores that can be taken from the SSTs is limited by the number of available risers on the tanks. The ferrocyanide tanks were not a high priority for sampling in Revision 1 of the characterization plan (Winters et al. 1990) because the saltcake layer in several of these tanks was expected to make core sampling difficult. The priority for sampling ferrocyanide tanks has now been changed (Hill et al. 1991) to reflect the need to determine the reactive properties of the contents. This change in priority will not affect ERRA commitments because core segments obtained from the ferrocyanide tanks are part of the same commitment. Ferrocyanide tank cores will undergo all analyses to satisfy ERRA requirements, with emphasis on those analyses required to resolve safety issues. Three ferrocyanide tanks (241-C-112, 241-C-109, and 241-T-107) suitable for push-mode core sampling were placed on the list of SSTs to be core sampled in FY 1992 (two were completed, and 241-T-107 is now scheduled for December 31, 1992).

Until it can be demonstrated that rotary-mode core sampling will not produce excessive temperatures in the waste, the push-mode technique is the only approved Hanford Site method for waste tank core sampling. Tanks without saltcake and with relatively soft waste solids can be core sampled by the push-mode method. Core segments will be removed from these tanks first. If a hard saltcake layer is present, rotary-mode core sampling (presently under development) will undoubtedly be required.

Cores are normally full-depth, taken in 48.3 cm (19 in.) segments starting above the top of the expected solids level and working down to the tank bottom. The sample analysis test plan specifies how the segments will be handled for analysis; that is, how subsegments are prepared 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 analysis scenario described for ferrocyanide tanks (Hill et al. 1991) called for dividing each segment into two 24.1-cm (9.5-in.) subsegments and performing analyses on each homogenized subsegment. Studies conducted by the Waste Tank Safety Programs office indicated the possible existence of ferrocyanide scavenged waste in layers approximately 7.6 cm (3 in.) to 10.2 cm (4 in.) in thickness. Therefore, the test plan was modified to reduce the analysis horizon to more thoroughly characterize thinner layers that may contain concentrated ferrocyanide waste. Complete and comprehensive characterization of the three cores from tank 241-C-112 was determined to be more technically defensible and economically preferred to partial analysis of three ferrocyanide SSTs. Quarter-segment length samples from tank 241-C-109 and tank 241-T-107 will also be analyzed. A revised test plan for the three ferrocyanide SSTs was prepared to provide the level of detail necessary for the Office of Sample Management to revise the statement of work (Hill 1991).

Three full-depth cores, consisting of two segments each, were obtained from tank 241-C-112 in March 1992. It was found that one of the cores contained an empty segment, and there was low recovery in the other segment. Steps have been taken to improve core recovery. These methods have been more successful in the most recent core sampling activities. The analytical results of 241-C-112 were received in October and November 1992 from the 325 PNL Analytical Laboratory. A decision on resampling tank 241-C-112 to obtain a third core will be made after the results of other 241-C Farm tank core samples are evaluated. Three one-segment cores from tank 241-C-109 were taken September 2-7, 1992. Dates for analyses of the other tank core samples are being established. Generally, 6 months are required to provide a validated analytical results package from the date of core delivery to the laboratory.

Five additional ferrocyanide tanks are now scheduled for sampling in FY 1993. These include 241-T-107, -C-111, -C-108, -T-101, and -BX-102 using the push-mode technique. Additional ferrocyanide tanks are not scheduled in FY 1993 because of the need to sample other watchlist tanks and the limitation of analytical throughput capability. The order in which the remainder of the tanks are sampled may depend upon results of analyses of cores obtained previously and waste simulant studies. The schedule for the remainder of the ferrocyanide tanks assumes that most of the total core sampling efforts are

devoted to the watchlist tanks. The assumption for the ferrocyanide tanks is that the first 241-C Farm tanks to be sampled will have three cores taken and quarter segment analyses done. Samples taken in saltcake tanks will have only one or two cores taken initially, with analyses on the saltcake segments done only on whole segment. Samples of sludge layers will have analyses done on half segments, unless visual evidence of layering suggests a greater division of segments is warranted. In other words, more analyses will be done on samples for tanks or layers that potentially contain more, or larger concentrations of, ferrocyanide. There has been an attempt to reduce the amount of initial analyses to enable the acceleration of analyses of all ferrocyanide tanks. In addition, it may be possible to eliminate some sampling based on new flowsheet studies and obtain samples from certain tanks as a confirmation of process knowledge. When all appropriate tanks have been sampled, it may be necessary to resample some tanks depending upon the analytical results obtained.

Core sampling and auger sampling activities have not proceeded as rapidly as originally scheduled, primarily due to (1) the length of time required to assess safety and environmental hazards and implement controls to minimize risk (e.g., SAs and Operational Readiness Reviews) and (2) limited laboratory facilities to receive, prepare, and analyze the samples. Methods to alleviate these delays are being pursued.

The length of time required to obtain surface and core samples of ferrocyanide tanks was tied to the preparation and approval of safety and environmental documentation and to the tank data that must be obtained to support the assessments. The environmental assessment documents for obtaining auger surface samples and push-mode core samples were combined and approved because of their similarity and to reduce the documents that would require top-level review. This EA covers all 24 ferrocyanide tanks except tank 241-TX-118, which is believed to also contain high organic concentrations. Readiness review approval was received from DOE, and surface auger samples from tank 241-BY-104 were taken in June 1992. It is anticipated that the analysis of the surface samples from tank 241-BY-104 will indicate that surface sampling for other tanks will not be necessary before core sampling. The information obtained from these surface samples will provide information for the safety assessment, plans, and approvals for core sampling using the rotary-mode core drill.

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. Los Alamos National Laboratory (LANL) high explosive drilling experts reviewed Westinghouse Hanford's drilling approach and concurred. Preliminary drill bit testing on KAMAG* material in early 1991 caused the drill bit to overheat and exceed over-temperature limits, resulting in the re-engineering of the rotary drilling approach. Instrumentation specialists have been contacted and are under contract for development of drill bit temperature monitoring concepts. No viable concept has been found to date to provide direct reading of the rotary bit temperature. Therefore, a safety envelope is being established by laboratory testing with simulants under conditions controlled by operational

*KAMAG is a trademark of Western AG Minerals Company.

procedures. Core sampling of ferrocyanide tanks that contain saltcake will be deferred until the rotary-mode core sample truck is available for field use. The schedule for its deployment is being established, currently expected to be October 1993.

Progress on identified milestones is as follows:

- **August 31, 1992:** Take three full-depth core samples from tank 241-C-109. These samples were taken on September 4-7, 1992.

The following future milestones have been established.

- **December 31, 1992:** Secure two full-depth core samples from tank 241-T-107.

- **September 30, 1993:** Obtain two full-length push-mode cores from four additional ferrocyanide tanks in FY 1993; the following order for sampling the tanks is planned: 241-C-111, -C-108, -T-101, and -BX-102.

- **September 30, 1993:** Secure core samples from four more ferrocyanide tanks. (Tanks 241-C-111, -108, -T-101, -BX-102)

- **September 30, 1994:** Secure core samples from four ferrocyanide tanks. (Tanks 241-BY-104, -110, -107, -105)

- **September 30, 1995:** Core sample four ferrocyanide tanks. (Tanks 241-BY-103, -112, -TY-103, -BY-106)

- **September 30, 1996:** Core sample four ferrocyanide tanks. (Tanks 241-BY-101, -TY-101, -104, -BY-110)

- **September 30, 1997:** Core sample the remaining five ferrocyanide tanks. (Tanks 241-BX-106, -111, -BY-111, -TX-118, -BY-108)

4.4.5.2 **Penetrometer Tests.** At the time the original implementation plan was prepared, there was concern that saltcake in the ferrocyanide tanks might contain sufficient organic carbon and/or ferrocyanide to support a chemical reaction, if ignited. This is the same concern that prevailed before crust sampling in tank 241-SY-101 (i.e., hydrogen burn initiation in the vapor space and/or core drill heating of the crust to cause burning). Because of the USQ associated with the ferrocyanide tanks, the potential combustibility of the saltcake from either a flammable gas burn or ignition during core drilling has to be addressed before core samples can be obtained from the tanks. The potential for a flammable gas burn in each tank is being determined by vapor space sampling of each ferrocyanide tank before more intrusive operations are permitted (Section 4.3.2). Auger samples were obtained from one ferrocyanide tank, 241-BY-104, in June 1992 and will be evaluated to determine the need for further auger samples from other tanks. The analytical results are expected to be complete by November 30, 1992.

Originally, there was also a need to determine the hardness and penetration resistance (shear strength) of the saltcake to ascertain how difficult it would be to obtain a core sample using the rotary-mode core

drill. This information could then be input for preparing and testing waste simulants in the laboratory. Data on actual saltcake properties were also to be used for the SA, the EA, and operational procedures required for rotary core drilling.

The method originally chosen to obtain the hardness and penetration resistance data on saltcake was a combination of the penetrometer and the auger sampler. However, testing of these two techniques in the development laboratory during their design and development and a review by two independent reviewers resulted in the conclusion that a penetrometer test would yield only an order of magnitude approximation of the saltcake shear strength. Basically, the same information plus other chemical and physical properties can be obtained by using only the auger sampler and performing appropriate tests in the analytical laboratory.

The decision not to proceed with the penetrometer tests will delete the penetrometer milestone. If the samples obtained using the auger sampler in tank 241-BY-104 do not provide all the information needed about the chemical and physical properties of the saltcake, this decision will be revisited.

4.4.5.3 Gamma Monitoring. Other monitoring completed on some of the ferrocyanide tanks at the Hanford Site includes gamma and neutron probe scans. These techniques can only be applied to the 12 ferrocyanide tanks that have LOWs. A LOW is a closed-end, nonmetallic (sometimes fiberglass) tube approximately 10 cm (4 in.) in diameter that enters the tank through a riser and extends to near the tank bottom. LOWs were originally installed in tanks to monitor the interstitial liquid level as a means to follow saltwell pumping operations. The LOWs also provide some enhanced leak detection in tanks that do not contain supernatant liquid. In some cases, the LOWs are also being used for measuring the waste temperature by placing a dedicated TC into the well (i.e., tanks 241-BY-111, -112).

The need to accurately measure cesium concentrations arises from a concern that high concentrations of cesium, as $Cs_2NiFe(CN)_6$, could locally heat the waste. In addition, cesium was deposited in many tanks as part of the waste concentration activities that put evaporator bottoms liquor on top of ferrocyanide sludges.

With existing monitoring techniques, gamma scans show gross radiation levels within a tank as a function of elevation. A new state-of-the-art gamma detector, cadmium telluride, was used to allow characterization of certain isotopes within the waste as a function of elevation. In addition, new signal processing and analyses of gamma and neutron scans were applied to obtain useful information previously not available, such as percent moisture content as a function of elevation (Section 4.1.5.5.2). Gamma and neutron count rates were recorded at 3-cm (0.1-ft) intervals to provide a nearly continuous scan along the height of the tank. In the past, the gross scans were used primarily for tank liquid-level measurement and to identify potentially leaking tanks.

The cesium inventories and distributions as measured from the LOWs were recorded for the 12 tanks. This provided a second assessment of the ^{137}Cs and associated heat load currently in these ferrocyanide tanks, with some concern for bias because of the LOW installation method. Evaluations of three LOW

installations (i.e., only those installations for which water usage datasheets were located) in 200 East Area tanks show that 83 L (22 gal) to 1,100 L (290 gal) of water were used to install these LOWs. Additional studies or measurements may be required to resolve whether the sludge was disturbed enough to invalidate the results. The cesium measured averaged 71% of the estimate, based on the Track Radionuclide Components (TRAC) data (Postma et al., 1992). If the core sample analyses agree, the results will help to validate both sets of data.

Calibration of the cadmium telluride detector for ^{154}Eu allowed determination of ^{154}Eu and concentrations as a function of waste elevation from the collimated scan made in tank 241-BY-106. The scan of 241-BY-106 also showed a detectable concentration of ^{60}Co. Europium can be used as a tracer to identify the location of transuranics (TRU) in the waste, and thus support safety analyses and aerosol accident analyses. A spectral gamma scan of tank 241-BY-106 shows a maximum concentration of transuranics at or near the bottom of the tank, as would be expected for such higher density materials. This is similar to the ^{154}Eu scan obtained previously for tank 241-BY-104.

No further work is planned in this area unless other studies require it.

4.4.5.4 Raman Scattering. The objective of this work is to develop an optical spectroscopy method for qualitative and quantitative measurements of ferrocyanide, ferricyanide, and free cyanide species in the concentration levels and morphology existing in each of the 24 ferrocyanide tanks. Raman spectroscopy can also be used to measure other species present, such as nitrate, nitrite, phosphate, aluminate, etc. These techniques could allow looking at changes in chemical composition, both in a hot cell or in situ, using fiber optic probes. Since Raman scattering spectroscopy has such a wide range of potential application, the initial exploratory work is being funded by the DOE Office of Technology Development.

Contract negotiations were completed early in FY 1992 with Florida State University (FSU) to investigate applications of Raman spectroscopy for identifying and quantifying constituent species in tank waste. The FSU investigations include the application of the technique to solid, liquid, and slurry phases of the different species. Screening studies are being conducted to identify possible sources of interferences and limitations of Raman scattering by the presence of organic and inorganic decomposition products in the waste matrix.

Westinghouse Hanford worked with FSU to establish a test matrix that FSU can complete by December 1992. This work will provide the basis for applying Raman spectroscopy instrumentation initially in hot cells (as a waste tank sample screening tool), and ultimately for in-situ waste tank materials characterization. It can also serve as a possible process control function for the grout, pretreatment, and Hanford Waste Vitrification Plant processes. The FSU contract will result in data that will support the direct measurement of various analyte concentrations in tank samples. Future work will focus on the deployment of a fiber optic sensor in hot cells or in the Hanford Site tanks as part of the Tank Characterization Task sponsored by the Underground Storage Tank-Integrated Demonstration program (EM-55). Complementary work on

Raman scattering, also being followed by the Ferrocyanide Safety Program, is being funded at Lawrence Livermore National Laboratory by the DOE Office of Technology Development (EM-50).

For FY 1992, FSU focused efforts on the ferrocyanide/ferricyanide species reactivity, delivery of spectral and speciation data to Westinghouse Hanford and delivery of speciation software to quantify these species by September 30, 1992. Westinghouse Hanford Analytical Laboratories are working with FSU investigators to set up a Raman system in a Hanford Site hot cell by December 1992.

During the first half of FY 1993, FSU will be investigating Raman spectroscopy capabilities for the balance of waste tank materials, including organics. FSU will evaluate interferences from alkali, nitrates/nitrites, phosphates, and sulfate ions. The contract with FSU may be extended depending upon these results and availability of funding from the Office of Technology Development.

The initial data indicates that Raman technology will be useful for a number of applications, including homogeneity and speciation applications. Comparison with other methods and applicability in high radiation fields must be determined.

Expected completion dates for the FSU work area are as follows:

- **May 1, 1992**: Receive initial experimental data from FSU on tests using In-Farm and U-Plant simulants provided by Westinghouse Hanford. Data from FSU on these simulants was received on schedule.

- **September 30, 1992**: Receive predecisional final report including data, data collection, and validation methods for ferrocyanide and ferricyanide. This report was issued by FSU on October 26, 1992.

Progress on identified milestones is as follows:

- **December 31, 1992**: Receive final report from FSU on data and validation methods for the remainder of the ferrocyanide waste simulant constituents, e.g., nitrates, nitrites, phosphates, and sulfates.

- **January 15, 1993**: Decide whether FSU contract should be extended to complete additional work.

NOTE: These dates are not shown in the Section 5 schedules because the work is separately funded.

4.4.5.5 Ferrocyanide Waste Tank Hazards Assessment and Resolution of the USQ. The scope of the ferrocyanide hazards assessment task is to provide an assessment and periodic updates of the ferrocyanide waste tank safety concerns and provide the basis for resolution of the USQ. These assessments are based upon information as it becomes available from all parts of the Ferrocyanide Safety Program. Contributions are included from FAI, LANL, PNL, Westinghouse Hanford, and other sources.

A predecisional interim report assessing the ferrocyanide waste tank hazards was issued on December 3, 1991, for review and comment by DOE and TAP staff members. Comments were incorporated into a new revision, which was issued for public availability in July 1992 (Grigsby et al. 1992). The assessment is a snapshot in time of the current understanding of the ferrocyanide safety issue at the time the report was written. It presents an integrated evaluation and interpretation of historical data and recently-acquired information as of that date. This task provides for updating the report as additional information becomes available from ongoing work.

The next phase of the hazards assessment includes development of a refined hazards identification. The specific conditions necessary for the uncontrolled release of material from a ferrocyanide waste tank by a slow burn will be identified. These potentially hazardous conditions will then be investigated through testing, experiments, and analytical modeling in a focused and prioritized fashion.

As part of this tank activity, the AEP was commissioned to look at possible accident scenarios with emphasis on how aerosols might be generated and released to the environment if a ferrocyanide reaction were to occur. The panel met in March 1992 and recommended that small-scale aerosol tests be conducted. The consensus of the panel members (based on current information from historical data and laboratory tests available at that time) was that any ferrocyanide reaction, if one does occur in the bulk of the tank waste, would result in only a slow burn. The slow burn would be expected to plug and rupture the passive HEPA breather filter on the tank and cause a slow release of aerosols to the environment. The AEP recommended that small-scale tests be conducted to measure the rate of aerosol generation [release of total mass, including cesium, strontium, and a TRU stand-in] and particle size distributions from ferrocyanide compositions of interest. The panel also recommended that, if results of additional studies currently being conducted discredit this slow burn perception, large-scale tests and overburden participation in aerosol behavior would have to be evaluated. (See Section 4.5.5.1)

In accordance with the recommendations of the panel, aerosol releases to the atmosphere will be estimated by: (1) measurements of aerosol generation from small-scale burns, followed by (2) calculation of subsequent coagulation and removal in the tank head space using an established aerosol code. The MAEROS code (Gelbard 1982) was selected to perform these aerosol calculations. The CONTAIN code (Murata et al. 1989), which includes MAEROS within it, will be used to determine the thermal-hydraulic conditions required for input to the aerosol calculations.

As a companion to this work, dose consequence recalculations are also planned using the source term(s) defined by the aerosol tests. These dose calculations must await results of the small-scale burn tests. The offsite dose calculation would be based on a near-term (one year) exposure using accepted computer codes approved for these calculations.

The aerosol test and subsequent dose consequence recalculations were scheduled for FY 1993. Small-scale aerosol facilities are available for conducting these tests in FY 1993 at PNL or Sandia National Laboratories. FY 1993 program funding for these tests has not been identified as of December 1992.

Westinghouse Hanford is currently evaluating the possibility of a reduced aerosol testing program that would require a smaller budget to accomplish. To aid in this decision the ferrocyanide waste simulants being tested at FAI will be analyzed to determine how much cesium is lost during the slow burn propagation tests. The In Farm simulant had cesium added to the flowsheet for this purpose. Additionally, an aerosol sampler and collection foils will be added to the FAI calorimeter for selected tests in order to gather data that may be useful in providing a source term for modeling aerosol release and subsequent onsite and offsite dose consequences in the highly unlikely event that a burn of ferrocyanide were to occur (worst-case bounding accident).

Since inception of the Ferrocyanide Safety Program at the Hanford Site, the end objective of the program has been to resolve the safety issue. To accomplish that goal, the USQ must be resolved and appropriate safety documentation that provides an adequate safety envelope must be issued and approved. A new activity was started at the beginning of FY 1993 to (1) devise a strategy that would be acceptable to DOE and oversight panels for resolving the USQ; and (2) to follow with a detailed USQ resolution plan. Two DOE Orders are applicable for this objective: DOE Order 5480.21 (DOE 1991b), *Unreviewed Safety Questions*, and DOE Order 5481.23 (DOE 1992), *Nuclear Safety Analysis Reports*.

Progress on identified milestones is as follows:

- **November 27, 1991**: A predecisional position paper on the current understanding of the safety of ferrocyanide tanks at the Hanford Site was issued. This document will be updated periodically to present an overview of the state of knowledge of the ferrocyanide safety issue. The document was issued as a cleared report in July 1992 (Postma et al. 1992).

- **December 3, 1991**: The first interim report on ferrocyanide waste tank hazards assessment was issued. The document was issued as a cleared report in July 1992 (Grigsby et al. 1992).

- **March 30, 1992**: A letter report issuing recommendations of the AEP for performing small-scale aerosol tests was completed.

- **June 1, 1992**: The aerosol model report on selection of an appropriate model for predicting releases to the atmosphere was issued.

- **October 19, 1992**: Submit draft strategy letter to DOE on proposed approach for resolution of the ferrocyanide USQ. The strategy letter was issued to DOE on October 28, 1992.

The following future milestones have been established.

- **January 29, 1993:** Submit a predecisional USQ resolution plan to DOE providing details on the approach for resolving the ferrocyanide USQ.

- **May 31, 1993:** Complete the first update of the ferrocyanide hazards assessment document (Grigsby et al. 1992) that is approved for public release.

- **May 31, 1993:** Complete small-scale aerosol tests and complete final aerosol report. This work is currently not funded in the ferrocyanide program budget approved for FY 1993.

- **September 30, 1993:** Complete a final report, approved for public release, on dose consequence recalculations. Included with the report will be an update of progress towards resolving the ferrocyanide USQ.

- **July 31, 1994:** Issue second update of ferrocyanide hazards assessment document that is approved for public release.

4.4.5.6 Safety Assessments for Ferrocyanide Tank Activities. The DOE order on USQs establishes the process for USQ identification and resolution (DOE 1991b). The steps in the USQ process include the following.

- Identify a situation that may be a potential USQ.

- Take action to place the facility in a safe condition while a safety evaluation is being prepared, so as to determine if an actual USQ exists.

- If an USQ is identified, establish the interim operating conditions for safe operation of the facility while a safety analysis is being performed.

- Perform a safety analysis to resolve the USQ by establishing a new safety envelope relative to the USQ issue.

- Incorporate into the existing SAR or authorization basis any changes that are needed as a result of the safety evaluation, safety analyses, or other action taken.

The USQ process depends on an authorization basis that describes those aspects of the facility design basis and operational requirements relied upon by DOE to authorize operation. The authorization basis is described in documents such as the facility SAR and other safety analyses, Hazard Classification Documents, Technical Safety Requirements, DOE-issued safety evaluation reports, and facility-specific commitments (such as the SAs).

The potential hazards of a ferrocyanide-nitrate/nitrite reaction were discovered to represent an inadequacy in the authorization basis. Therefore, a USQ was declared for the ferrocyanide safety issue, and activities in the waste tanks that could increase the likelihood of an accident involving the ferrocyanide-nitrate/nitrite reaction were restricted (Deaton 1990). Until the USQ is resolved, proposed activities that may impact the safety of the ferrocyanide tanks (intrusive activities) must be assessed for potential safety and environmental consequences. Further, these proposed activities must be authorized by DOE.

Safety Assessments are the 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 the accompanying EA, provides the basis for DOE authorization of the proposed activities.

Since inception of the Ferrocyanide Safety Program, safety assessment documents have been completed for vapor space sampling of all 24 tanks, waste surface sampling, push-mode core sampling, and TC tree installation in sound (non-leaker) tanks. Work on the limited Safety Analysis Report (SAR) for rotary-mode core sampling has started.

Preparation of an SA for removal of remaining pumpable liquid using a saltwell screen (interim stabilization) of remaining ferrocyanide tanks was initiated in February 1992 in support of the effort to stabilize all SSTs by 1996. Eight ferrocyanide tanks remain to be pumped (see Table 2-1; tank 241-BX-110 will also be further jet pumped). This SA also addresses saltwell pumping of a ferrocyanide tank if there are indications of a leak. Progress on this SA was interrupted to prepare documentation for stabilization of non-watchlist tanks. Work resumed on the ferrocyanide tank stabilization SA in May. The document, along with an EA, was submitted to DOE on September 30, 1992.

In the past, issues have arisen regarding the scope to be addressed in SAs, the level of detail, and the consistency between SAs and EAs. These issues are being satisfactorily resolved by using guidelines issued by DOE. The entire review and approval process needs to be streamlined for cost effectiveness. To this end, criteria to determine whether proposed activities require a safety assessment are being developed to avoid the cost and delay of unnecessary documentation.

Progress on identified milestones is as follows:

- **April 15, 1992:** Issue the initial SA and EA for TC instrument tree installation in sound ferrocyanide tanks. These documents were first issued on schedule, but required revision to reflect the Westinghouse Hanford decision to install TC trees initially in only sound (nonleaker) tanks. Authorization based upon these documents was approved by DOE in September 1992.

- **May 29, 1992:** Issue SA for saltwell pumping (stabilization) of ferrocyanide tanks. This milestone was delayed to September 30, 1992, because of the DOE request to prepare safety documentation for non-watchlist tanks. A companion EA document will be submitted with

the SA, along with the stabilization recommendations listed below. This work was completed September 30, 1992.

- **June 30, 1992:** Submit recommendations to DOE on stabilization of ferrocyanide tanks. This milestone is delayed to September 30, 1992, because the SA was not completed on the original schedule. This work was completed September 30, 1992.

The following future milestones have been established.

- **February 1, 1993:** Receive authorization from DOE, based upon revised SA and EA documentation, to proceed with pumping of leaking ferrocyanide tank 241-T-101.

- **March 30, 1993:** Submit safety and environmental documentation for installation of TC trees in assumed leaker ferrocyanide tanks to DOE for review and comment. An acceptable installation method must be developed to meet this date. See also Section 4.1.5.1.

- **May 7, 1993:** Issue limited SAR and EA documentation to DOE for rotary mode core sampling of ferrocyanide tanks for approval.

- **September 1, 1993:** Receive authorization from DOE, based upon SA and EA documentation, to install remaining TC trees in assumed leaker tanks.

4.5 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.5 (CHEMICAL REACTION STUDIES)

"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."

4.5.1 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 concludes 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). Core sampling and analyses of waste from the 24 ferrocyanide tanks are being pursued in a safe manner and on a high-priority basis. (Refer to Section 4.4, DNFSB Recommendation 90-7.4.)

The schedule for determining of 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 [$Cs_2NiFe(CN)_6$], but since 1990 they have been focused mainly on disodium mononickel ferrocyanide [$Na_2NiFe(CN)_6$] (because that is believed to be the major ferrocyanide precipitate), actual waste tank samples, and 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 mass of ferrocyanide to react. Studies have also been initiated to determine the temperatures at which reactions begin in relation to gas release, heat release, and propagation 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 1950's, and actual waste samples as they become available from the tanks. These waste studies, along with modeling studies and tank waste temperature and moisture monitoring, support the preparation of safety documentation for core sampling and tank farm operations. The information will also be used to resolve the overall ferrocyanide USQ.

4.5.2 Evaluation of Issue

At present, there are 18 Hanford Site waste storage tanks (Borsheim and Simpson 1991) that are likely to contain at least 1,000 g-moles (465 lb) of ferrocyanide, at unknown concentrations, mixed with sodium nitrate and sodium nitrite oxidant. Some 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, can propagate at temperatures as low as 220 - 240 °C (430 - 465 °F) to release heat and aerosols. 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 expected in the waste; 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 70%) of the ferrocyanide sludges stored in the Hanford Site waste storage tanks was produced by the U Plant flowsheet process. Simulated sludges produced from this flowsheet have been shown not to propagate even when dried and heated above 400 °C. Propagation testing of 70 g of the more concentrated dried U-Plant simulant (U-Plant 2, bottom fraction) with external heating to approximately 270 °C showed sufficient reaction to raise the sample temperature to 620 °C (Fauske 1992d). The potential for aerosol generation with this material needs further evaluation.

About 10% 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 2500 g for an equivalent 30 gravity-years settling time) did not propagate when the moisture content was 15 wt% or greater. Centrifuged In-Farm sludge simulant has a water content of about 50 wt%. Dry (0 wt% water) In-Farm sludge exhibits propagation rates up to 10 cm/min when external heat is applied, and can produce temperatures up to 1200 °C. This shows the importance of measuring the water content of the actual tank waste, to ensure that there is sufficient water present to prevent propagation from occurring in the In-Farm sludges. The T-Plant simulant has not been tested, but is expected to be at a much lower ferrocyanide concentration than the In-Farm sludge, and comprises about 20% of the stored ferrocyanide waste. The T-Plant simulant is scheduled to be tested later in FY 1993. As stated in Section 4.4.3, the T-Plant simulant is expected to behave similar to U-Plant simulant.

Compositions of actual waste must be determined at present storage conditions and compared to simulant behaviors to provide a firm basis for waste modeling. Effects of catalysts, initiators, other fuels, and diluents on the behavior of present waste must be evaluated.

4.5.3 Baseline Assumptions

- The waste in each tank must be 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, tank monitoring, historical and simulant studies, and modeling.
- One of the following conditions must be established to attain passive safety (see Kazimi et al. 1992).
  - Cyanide concentrations must be below a determined value - yet to be established
  - When cyanide is present at greater than the above value, then to achieve controlled safety a minimum water content must be established (Kazimi et al. 1992).

4.5.4 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 of the range of ferrocyanide waste concentrations in the Hanford Site tanks and develop criteria for safe storage. Ferrocyanide sludges in the tanks were produced by three different flowsheets, resulting in variations in chemical composition of sludges produced. The extent of sludge mixing and changes due to the addition of waste in later years on top of ferrocyanide sludges is being determined. The present form and quantity of

ferrocyanide in the tanks will be determined. The moisture content of the sludge is an important parameter for reactivity of the ferrocyanide and will need to be measured and monitored. The simulant having the greatest ferrocyanide concentration (In-Farm 1), also containing excess oxidant, has been shown not to react when exposed to an intense ignition source as long as the moisture content is greater than 15 wt%. When completely dry this simulant has been shown not to detonate, but does propagate at a rate of 5-10 cm/min. It is unlikely that waste exists in the tanks with a moisture content of less than 15 wt%. In-Farm sludge centrifuged at 2500 g for an equivalent 30 gravity-years (30 g-y) settling time has a moisture content of about 50 wt%.

Effects of catalysts, initiators, other fuel, diluents, and present waste forms will be determined, along with their effects on waste behavior. Safety analyses will be conducted with pertinent information, and continued safe storage monitoring and control methods will be implemented, or else a remediation process will be identified and implemented.

4.5.5 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, to determine potential reactivity.
2. Identify changes to the waste forms that may have occurred because of radiation exposure over time, 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 (e.g., high pH waste from decladding operations and evaporator bottoms were added to many of the ferrocyanide tanks). 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).
5. Perform safety evaluations and recommend courses of action. (See Section 4.4.5.5.)

Information for these studies is gathered from historical data, laboratory studies on ferrocyanide simulants produced by the three flowsheets 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 temperature, moisture, cesium, and gas monitoring, support the preparation of safety documentation for core sampling and tank farm operations. These studies will also be used to resolve the overall ferrocyanide USQ.

4.5.5.1 Chemical Reaction Studies. Chemical reaction studies on ferrocyanide waste simulants are being conducted by Westinghouse Hanford, PNL, LANL, Washington State University, and FAI. Westinghouse Hanford and PNL have produced flowsheet simulant materials for testing and characterization. PNL is performing studies to determine the present form of cyanide species in the waste after 35+ years of aging in the tanks. PNL work includes reaction mechanisms, kinetics, and effects of waste mixture compositions, including those that may act as catalysts and initiators or as diluents.

PNL is also administering the subcontract with LANL. In FY 1992 LANL conducted chemical reaction sensitivity tests on ferrocyanide waste simulants to identify what stimuli (emphasizing non-thermal) may cause a reaction to occur. FAI is conducting adiabatic calorimetry and propagation tests on these same replicated flowsheet materials. The FAI scope of work in FY 1993 has been expanded to include selected aerosol studies.

Five types (U-Plant 1, U-Plant 2, In-Farm 1, In-Farm 2, and T-Plant) of ferrocyanide simulants (excluding uranium diluent, radioactive species, degradation products, or organic impurities) have been or are being produced in the Westinghouse Hanford Chemical Engineering Laboratory and at PNL to provide representative ferrocyanide sludges for testing and characterization. These simulants represent waste with the greatest ferrocyanide concentrations produced at the Hanford Site by three general flowsheets: U Plant*, In Farm**, and T Plant***. In addition, PNL is preparing iron ferrocyanide that could have formed during the U Plant scavenging campaigns.

Estimated compositions of four Westinghouse Hanford-prepared simulated waste sludges were calculated from measured volumes of centrifuged ferrocyanide sludge, measured water content, and calculated insoluble materials. The T-Plant sludge will be prepared later in FY 1993.

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*The U-Plant flowsheet ferrocyanide sludge resulted from scavenging the uranium recovery waste produced in the Hanford Site U Plant. The sludge produced by using the flowsheet contains a substantial quantity of other solids in addition to the ferrocyanide precipitate. This material was transferred to seventeen tanks in the 241-BY, 241-BX, 241-T, and 241-TX Tank Farms.

**Uranium recovery in U-Plant of high-level tank waste began before the ferrocyanide scavenging process was developed. Later, the neutralized supernatant from the uranium recovery waste was transferred from storage in SSTs to a vault containing stainless steel tanks where the pH was adjusted and the ferrocyanide scavenging process was applied. This In Farm flowsheet sludge contained a smaller percentage of total solids and, thus, a higher concentration of ferrocyanide than the U Plant flowsheet. The In-Farm ferrocyanide-bearing wastes were transferred to four tanks in the 241-C Tank Farm.

***The T-Plant flowsheet ferrocyanide-bearing sludge resulted from scavenging first cycle wastes from the T Plant bismuth phosphate extraction process. Only about 10 percent of the fission products were present in that waste stream. Thus, the T-Plant ferrocyanide sludge is expected to be somewhat richer than the U-Plant sludge, but is more dilute that the In-Farm ferrocyanide waste, and contains less fission product heat generation. This waste was transferred to three tanks in 241-TY Farm.

Westinghouse Hanford and PNL are characterizing the simulated wastes during and after preparation to determine the chemical reactivity, explosivity, physical behavior during settling, and the physical and chemical properties of the synthetic wastes representative of the freshly prepared scavenging wastes. The prepared wastes are usually centrifuged to simulate settling for up to 30 g-y and subsequently are characterized to determine their reactivity and explosivity. Two solids layers result when using the U-Plant and In-Farm flowsheets. The Westinghouse Hanford prepared simulants are being used in calorimetry testing by FAI.

Other planned activities in FY 1993 include aging studies at PNL to determine the effect of pH, radiolysis, and alkaline hydrolysis on the ferrocyanide waste originally added to the tanks. U-Plant and In-Farm waste simulants are being used for the aging studies. In the event that other cyanide species are identified in the aging studies, their behavior in a waste matrix may be determined.

Adiabatic calorimeter tests performed by FAI on dried U-Plant 1 and U-Plant 2 simulants indicates that a propagating reaction cannot occur with these materials, even when dried. The U-Plant 1 material represents the bulk (41 of 59 total batches) of the U Plant produced sludge and U-Plant 2 represents 9 of the 59 batches. However, the dry (0 wt% water) U-Plant 2 bottom fraction (U-Plant simulant most concentrated in ferrocyanide) did self heat up to 620 °C in tests utilizing about 70 g while providing external heating to 270 °C. The potential for aerosol generation from this material is being further evaluated.

The difference between the two flowsheets is that U-Plant 1 specified ferrocyanide treatment to a concentration of 0.0025 *M*, and U-Plant 2 specified treatment to a ferrocyanide concentration of 0.005 *M*. The remaining 9 batches were treated to a ferrocyanide concentration of 0.005 *M* using a flowsheet that produced additional inert solids (calcium phosphate) in the sludge, resulting in a material with reduced ferrocyanide concentrations. It was noted in the U-Plant 1 tests that there was a slight exothermic reaction near 280 °C (535 °F). The energy released, however, was not typical of explosive materials and is insufficient to dry the waste out and cause the surrounding material to react (Fauske 1991a).

Adiabatic calorimetry tests have also been conducted on mixtures of washed, dried, and pulverized vendor-procured sodium nickel ferrocyanide and nitrate/nitrite mixtures to determine their kinetic properties as a function of temperature without diluents present. The results indicated that no propagation would be expected for near-dry mixtures up to 10 wt% sodium nickel ferrocyanide (dry basis). At concentrations of 20 to 40 wt% sodium nickel ferrocyanide (dry basis), the material indicated properties that would result in propagation at temperatures as low as 240 °C (465 °F) (Fauske 1991b). Adiabatic calorimeter tests conducted on U-Plant 2 simulants show some exothermic activity at about 200 °C and substantial exothermic activity at around 265 - 270 °C, indicating Arrhenius-type behavior and self heating to 500 °C (Fauske 1992a).

Calorimetry testing conducted by FAI on two dried (0 wt% water) In-Farm simulants (In-Farm 1 and 2) indicate propagating tendencies and potential for aerosol production (Fauske 1992b; Fauske 1992c). The In-Farm simulants have

ferrocyanide concentrations near 26 wt% (dry basis), but also have nonparticipatory solid diluents and about 50 wt% water present even after centrifugation at 2,500 g. Propagation tests conducted at FAI on the In-Farm 1 bottom fraction (greatest ferrocyanide concentration) material (50 wt% water) show that the simulant would not propagate even when subjected to a strong ignition source. The propagation rate for dry (0 wt% water) In-Farm 1 bottom fraction material was measured at 5-10 cm/min, and a maximum temperature of 1200 °C was produced (Fauske 1992d). A heat release of 1270 kJ per mole of ferrocyanide was measured. No detonations occurred, and the bulk of the solid reaction products remained in the test cylinder.

Westinghouse Hanford and PNL use various test methods, such as differential scanning calorimetry (DSC), scanning thermogravimetry (STG), and the PNL time-to-explosion (TTX) tests to determine chemical reactivity and explosivity. To determine chemical compositions and the chemical nature of the precipitates, standard chemical analytical techniques (e.g., inductively coupled argon plasma/atomic emission spectroscopy, ion chromatography [IC], total cyanide analysis, and infrared spectroscopy (IR) are used. The latter was added to the standard suite of analyses performed because of the successes demonstrated in the analytical methods development activities by PNL and Westinghouse Hanford.

Studies at PNL using temperature programmed pyrolysis coupled with gas mass spectroscopy have shown that dried In-Farm simulants prepared by PNL begin to react at temperatures as low as 90 °C. However, the DSC analyses show no aggregate exothermicity at these low temperatures. Analysis of the DSC results is difficult and confounded with simultaneous vaporization of water, even with nearly dry samples. Significant exothermic behavior does not begin until a temperature above 200 °C is reached. Other studies using the PNL small-scale TTX test on simulated wastes show explosive behavior down to 300 °C for In-Farm simulants. U-Plant 1 waste did not explode after 30 minutes at 400 °C.

LANL provides expert technical guidance in the area of explosive material testing. Sensitivity tests were conducted in FY 1992 by LANL on the Westinghouse Hanford prepared ferrocyanide simulants and mixtures of the washed vendor-supplied sodium nickel ferrocyanide and nitrate/nitrite oxidants. Impact, friction, spark, differential thermal analysis, vacuum thermal stability, Henkin, and accelerating rate calorimetry measurements on these representative materials were completed. None of the simulants were found to be sensitive or reactive to the suite of tests under the severe conditions tested. A predecisional report was completed for DOE.

Progress on identified milestones is as follows.

- **November 27, 1991:** Completed calorimetry and propagation tests and issued report (Fauske 1991) on U-Plant 1 simulant, $Cs_2NiFe(CN)_6$ - nitrate/nitrite materials, and vendor-prepared $Na_2NiFe(CN)_6$ - nitrate/nitrite materials.

- **July 31, 1992:** Completed screening propagation test matrix and report at FAI (Fauske 1992d) on the most reactive simulant material (In-Farm 1).

- **September 30, 1992:** Complete DSC, STG, and TTX tests at PNL on Westinghouse Hanford-prepared waste simulants. This work has been completed and a report is being prepared.

The following future milestones have been established.

- **September 30, 1992:** Complete LANL sensitivity tests on three flowsheet simulants and an In-Farm 1 mixture of washed and dried vendor-supplied sodium nickel ferrocyanide and nitrate/nitrite. The LANL test program was completed and a predecisional report was issued to DOE by September 30, 1992.
- **December 31, 1992:** Define parametric and aerosol sampling tests to be conducted at FAI using In-Farm and U-Plant flowsheet ferrocyanide waste simulants.
- **February 15, 1993:** Complete production of T-Plant ferrocyanide waste simulant and ship samples to PNL, FAI, and Westinghouse Hanford for characterization.
- **July 31, 1993:** Complete parametric and selected aerosol tests on the most reactive (In-Farm) flowsheet simulant at FAI and issue a test report that is approved for public release.
- **September 30, 1993:** Complete characterization tests of T-Plant ferrocyanide waste simulants at PNL, FAI, and Westinghouse Hanford. Incorporate results in the second update of the hazards assessment document (scheduled for July 1994).

4.5.5.2 **Chemical Form of Cyanide in Waste.** The chemical form of the cyanide in the waste could have an impact on the reaction sensitivity and mechanism of the cyanide-oxidant reaction. Efforts are underway to determine the present forms of ferrocyanide or, possibly, free cyanide (CN^-) in the waste. Determinations are being made on the ferrocyanide forms originally precipitated, those possibly produced by radiolysis, and those produced by long-term exposure to a highly alkaline environment. Included as part of the PNL program is an effort to develop analytical methods for cyanide species analyses.

Analysis of ferrocyanide waste simulants from flowsheet preparations show that disodium mononickel ferrocyanide [$Na_2NiFe(CN)_6$] is the dominant precipitate, and has between 3 and 6 waters of hydration. The two In-Farm simulants and the U-Plant 2 simulant tend to separate into two layers during centrifugation at approximately 2,500 g for an equivalent time amounting to 30 g-y. The In-Farm simulants contain approximately 50 wt% water in both the top and bottom fractions after centrifugation, while the U-Plant 2 simulant top and bottom fractions each contain about 65 wt% water.

Propagation temperatures for the two layers of the In-Farm simulants differed slightly. Propagation started at approximately 250 °C (480 °F) for the In-Farm 1 bottom layer, and at approximately 280 °C (530 °F) for the In-Farm 1 top layer. In-Farm 2 simulants show propagation temperatures of 245 °C (470 °F) and 255 °C (490 °F), respectively, for the bottom and top layers. As noted, the bottom layers are more reactive, probably because a

higher ferrocyanide concentration is present in these layers. Chemical characterization of these simulants is still in progress. Dry U-Plant 2 simulants (both top and bottom layers) did not propagate.

Aging studies showing that disodium mononickel ferrocyanide [$Na_2NiFe(CN)_6$] becomes soluble and hydrolyzes in agitated solutions at pH 12 to 14 have been performed by PNL. The results of the studies show that $Na_2NiFe(CN)_6$ reacts with NaOH to form insoluble $Ni(OH)_2$ and soluble $Na_4Fe(CN)_6$. These results were determined from dissolution experiments of $Na_2NiFe(CN)_6$ samples in solutions that were initially 1.0 *M* NaOH (pH 14), 0.1 *M* NaOH (pH 13), and 0.01 *M* NaOH (pH 12) for 144 hours. The dissolution reaction occurs rapidly. This is based upon results of atomic absorption experiments monitoring soluble iron species in the reaction supernates.

In these studies, essentially, all of the $Na_2NiFe(CN)_6$ is solubilized within the first hour after mixing in the 1.0 *M* NaOH solutions. $Na_2NiFe(CN)_6$ is solubilized slower in the 0.1 *M* NaOH solution, but even at this hydroxide concentration it is completely solubilized. At 0.01 *M* NaOH the OH^- anion is exhausted after about 6 minutes and no further reaction occurs. The presence of sodium cations (0.1 *M* NaOH and 0.01 *M* NaOH solutions adjusted to 1.0 *M* [Na^+]) suppress the rate of dissolution of $Na_2NiFe(CN)_6$. These data are also supported by atomic absorption measurements of soluble iron. The rate of dissolution of $Na_2NiFe(CN)_6$ in 0.01 *M* NaOH solutions is increased when SST simulant salts are added to the reaction mixtures. The SST simulant salts are added to provide solutions which contain 0.1 *M* [Na^+]. The pH of the solutions were adjusted to 13 with NaOH. These results indicate that nickel ferrocyanide solids placed in underground storage tanks with high pH (13 or greater) waste placed on top could have become soluble to some extent. Some dissolved ferrocyanide may have been transferred to other tanks during saltwell pumping or other waste transfers. The extent of this effect depends upon the degree of mixing or diffusion of the high pH solutions with the nickel ferrocyanide sludges placed in the tanks at an earlier time. Cyanide analyses of all solid and liquid waste samples obtained from waste tanks are being made to determine the extent of this effect. Cyanide hydrolysis produces NH_3, and a greater degree of hydrolysis occurs in the more basic solution. The extent of hydrolysis in these studies was very small but over time (35 years), the effect could be significant and result in substantial degradation of the ferrocyanide species. The largest yield was on the order of 0.02 percent (i.e., the fraction of cyanide groups converted to NH_3 was 0.0002) for the 96-hour experiment at room temperature. Ion exchange chromatography analysis was used to measure free [CN^-] in reaction solutions, thus corroborating the low levels of cyanide hydrolysis. Future work will involve gamma pit exposure experiments to determine the impact of ionizing radiation on the dissolution characteristics of vendor-supplied $Na_2NiFe(CN)_6$ in the aqueous SST simulated salts.

Westinghouse Hanford and PNL have shown that Fourier Transform IR (FTIR) spectroscopy is a promising quantitative method for the detection of ferrocyanides in flowsheet simulant material. FSU is using Raman spectroscopy to determine cyanide species in flowsheet preparations (see Section 4.4.5). They will also recommend a method to allow Raman spectroscopy to be used in Hanford Site hot cells, laboratory hoods, and possibly in situ for tank waste analysis.

Work at PNL to support speciation methods has shown that FTIR, Raman, and X-ray diffraction (XRD) are capable of identifying the various cyanide species, and has demonstrated a quantitation limit of 0.1 wt% for $Na_2NiFe(CN)_6$ in solid simulated waste mixtures. Analytical methods were also developed at PNL based upon aqueous solution FTIR and IC techniques for the quantitative detection of ferrocyanide, ferricyanide, and free cyanide in simulated wastes. Excellent agreement was observed for the quantitative detection of cyanide species using solution FTIR and IC methods performed on six ferrocyanide simulants (top and bottom layers of U-Plant 2, In-Farm 1, and In-Farm 2). Initial quantitation limits for the FTIR and IC solution methods are approximately 0.1 wt% ferrocyanide in the original sample. With current technology, these solution methods can be deployed for use on ferrocyanide tank samples within a laboratory hood environment.

Continued work at PNL on speciation methods will emphasize development of solution FTIR and IC techniques. These methods need to be verified using waste simulants containing known or suspected interferences. Later in FY 1993, these solution methods will be demonstrated on actual ferrocyanide tank samples. Subsequent work will also address development of methods (such as FTIR) for direct analysis of the waste solids.

In order to produce contaminant-free ferrocyanide compounds (as determined by ICP, XRD, and IC), based on scavenging flowsheet preparations, washing techniques were developed. During the washing process, colloids were formed that contained the ferrocyanides; therefore, chemical and physical methods to break up these colloids were developed. Washing of the ferrocyanide waste simulants might be used as a remediation method for these tanks, but the washing methods would require additional steps to break the colloids. This might be accomplished by washing three times with 0.01 NaOH, followed by settling and decanting after the first two washes, and centrifuging and decanting after the third wash.

Progress on identified milestones is as follows.

- **September 30, 1992:** Issue PNL predecisional report on effects of aging of ferrocyanide wastes. This report was issued on schedule.

- **November 27, 1992:** Issue the final cleared report on FY 1992 Aging Studies conducted at PNL. This report, PNL-8387 (Lilga et al. 1992), was issued on November 25, 1992.

The following future milestones have been established.

- **January 29, 1993:** Issue a report, approved for public release, on the chemical and physical characteristics of five ferrocyanide simulants.

- **September 30,1993:** Issue a final draft PNL report on the effects of aging on ferrocyanide waste to Westinghouse Hanford for review and clearance.

- **September 30,1993:** Issue a final PNL report of FY 1993 ferrocyanide microconvection modeling activities at PNL; approve for public release.

- **September 30,1993:** Issue a final PNL report on ferrocyanide speciation method development and deployment of a system in PNL hot cells or laboratory hoods, approved for public release.

4.5.5.3 Reaction Mechanisms and Kinetics. The manner and rate at which cyanide-nitrate/nitrite containing compounds react (i.e., mechanism and kinetics) are being determined by measuring the energy released and by identifying solid and gaseous reaction products as functions of temperature, time, and pressure. This work is being conducted by Westinghouse Hanford, PNL, and FAI.

DSC, adiabatic calorimetry, and simultaneous thermal analysis-quadruple mass spectroscopy in an inert atmosphere are used to quantify gas species and the heat released as a function of time and temperature. Propagation tests are also being conducted under conditions of constant venting and under confined geometry where the pressure increases as the reaction progresses. These measurements are being made on flowsheet ferrocyanide simulants and will be made for other cyanide species identified as relevant from the cyanide speciation studies.

Identification of reaction products can be used to verify the expected reactions based upon measured gas and heat release. The results from these studies are used to develop theoretical reaction models for predicting rates of reactions, energy produced, gas generation rates, reaction temperatures, and reaction products. Identified reaction product gases will also be considered for monitoring to detect incipient propagating reactions. (See Section 4.3.5.1.)

Progress on identified milestones is as follows.

- **July 31, 1992:** Issue Westinghouse Hanford predecisional report on gas and heat releases from In-Farm 1, In-Farm 2, and U-Plant 2 simulant sludges during heating to 500 °C. This has been completed (Fauske 1992d). The report, approved for public release, was issued October 27, 1992.

- **September 30, 1992:** Complete kinetic experiments at PNL on reaction between sodium nickel ferrocyanide and nitrate. This work was completed on schedule. A report is being prepared.

The following future milestone has been established.

- **June 30, 1993:** Issue final PNL report, approved for public release, on results of ferrocyanide kinetic studies.

4.5.5.4 Effects of Catalysts and Initiators. Investigations have been conducted by PNL on the effects of sodium EDTA, nickel hydroxide, chromium (III) hydroxide, and ferric hydroxide on the TTX behavior for reaction mixtures of (1) washed sodium nickel ferrocyanide and equimolar sodium nitrate/nitrite and (2) sodium nickel ferricyanide and equimolar sodium nitrate/nitrite. The results of the statistical analysis of the ferrocyanide reactions were reported (Scheele et al. 1992).

Preliminary results of these studies indicate minimal effects from any of the catalysts or initiators at the levels tested. The minimum explosion temperature observed in these tests was about 290 °C (555 °F). The minimum observed temperature for onset of exothermic activity was 240 °C (465 °F) using DSC. Previous work with cesium nickel ferrocyanide showed a reduction in the explosion temperature in the PNL TTX test for EDTA and the hydroxides of iron and nickel.

The TTX testing of the ferrocyanide-nitrate/nitrite system showed that, at 0.03 mole of catalyst or initiator per mole of ferrocyanide, only EDTA or some mixtures containing EDTA statistically reduced the time to explosion at temperatures greater than 380 °C. In general the TTX, when one of these potential catalysts or initiators was present, was less than when absent, but the reduction was small and not statistically significant. These results suggest little catalytic effect of these materials until high temperatures (>350 °C) are reached.

A second screening study to determine the effect of these same potential catalysts and initiators on the explosivity of a mixture of sodium nickel ferricyanide [$NaNiFe(CN)_6$] and equimolar sodium nitrate and nitrite was performed. Sodium nickel ferricyanide is a potential aging product for the sodium nickel ferrocyanide precipitated during the scavenging campaigns. The data from these tests are now being analyzed; a report will be issued in April 1993. DSCs and STGs of the ferricyanide show similar observed onset temperatures, as well as a simpler reaction path compared to the analogous ferrocyanide, which shows a multistep reaction mechanism with equimolar sodium nitrate and nitrite.

As a result of the catalyst and initiator screening study (Scheele et al. 1992) with ferrocyanide (which identified EDTA as a potential catalyst/initiator), along with preliminary studies showing a rapid reaction of NiS (which could be present in In-Farm waste forms with nitrate and nitrite), PNL will start a second series of experiments to further investigate the catalytic effects of EDTA and NiS on the reaction between sodium nickel ferrocyanide and equimolar nitrate and nitrite. A similar study is scheduled for the compounds that statistically reduce the explosion time for mixtures of sodium nickel ferricyanide, nitrate, and nitrite.

Nickel sulfide, only added to the tanks as part of the In-Farm 1 flowsheet, is a concern because nickel sulfide rapidly oxidizes to sulfate or sulfite in the presence of nitrate/nitrite, when heated to high temperatures. The heat released from this reaction is small compared to the potential ferrocyanide reactions, but the reaction occurs at a lower temperature and is being evaluated as a potential initiator.

Progress on identified milestones is as follows:

- **May 1992:** A PNL report (Scheele et al. 1992), approved for public release, on catalyst and initiator screening studies was issued.

The following future milestone has been established.

- **April 30, 1992:** Issue a final PNL report on catalyst, initiator, and diluent studies that is approved for public release.

4.5.5.5 Effects of Diluents. Ferrocyanide sludges in the tank waste appear to be mixed intimately with water, water soluble, and solid nonparticipatory diluents in addition to the nitrate/nitrite oxidant. These nonparticipatory diluents increase the mass that must be heated, and in the case of water, a relatively large quantity of heat of vaporization must be supplied by a separate source before a temperature can be reached to initiate a propagating reaction. The nonparticipatory diluents, other than water, include iron hydroxide, sodium phosphate, sodium sulfate, sodium aluminate, and calcium or strontium phosphate. The heat of fusion for sodium nitrate/nitrite must also be supplied before the reaction could propagate.

Slight exothermic sodium nickel ferrocyanide reactions with nitrate/nitrite were shown in the dry U-Plant 1 and U-Plant 2 simulant materials by the FAI adiabatic calorimetry tests to occur near 280 °C (536 °F). The two dry In-Farm simulants, however, both propagate in the calorimetry test (See Section 4.5.5.1). The most reactive simulant (bottom layer, In-Farm 1) starts to propagate at about 245 °C (475 °F). These tests were done with completely dried simulants, a condition that is unlikely to occur within the tank because of the high percentage of water (approximately 50 wt% for the In-Farm sludge simulant) and the high heat of vaporization, as discussed above.

Thermodynamic calculations on the effects of diluents indicate that it would require 3 g of water, 24 g of sodium nitrate, or 61 g of sodium aluminate to prevent the temperature of a 60 °C mixture of 1 g of sodium nickel ferrocyanide and stoichiometric sodium nitrate from exceeding 200 °C.

Tests have begun to evaluate the explosive concentration ranges of mixtures of sodium nickel ferrocyanide and sodium nitrate and nitrite with potential diluents using the PNL TTX test. The initial activities have focused on the amount of the oxidant mixture, equimolar sodium nitrate, and nitrite as the diluent. These mixtures have been found to be reactive within 30 minutes for oxidant to ferrocyanide stoichiometric ratios of 0.5 to 1 at 320 °C and 0.1 to 2.4 at 400 °C. Future studies will investigate the presence of sodium aluminate and calcium phosphate as potential diluents.

The following future milestone has been established.

- **April 30, 1993:** Issue a final PNL report on catalyst, initiator, and diluent studies that is approved for public release.

4.6 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.6 (RESPONSE PLANNING)

"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."

4.6.1 Background

Since this recommendation was issued by the DNFSB, Westinghouse Hanford 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 those tanks with the potential for an exothermic reaction. The ferrocyanide tanks have heat loadings less than 11.7 kW (40,000 Btu/h), and dissipate their heat via natural circulation (i.e., convection and radiation to the tank headspace and conduction to the surrounding earth). Temperatures in 14 of these tanks are monitored continuously, while the remaining 10 tanks are monitored weekly. The highest temperature observed in any of the tanks is less than 57 °C (135 °F). This is well below the minimum exothermic reaction temperature of approximately 220 °C (430 °F) observed in the laboratory (Burger and Scheele 1990) 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 believed to be ≥40 wt%, based upon (1) ferrocyanide tank samples taken prior to 1986; (2) moisture analysis results from tank 241-C-112 samples taken in March 1992; and (3) recent flowsheet simulant investigations, which show at least 50 wt% moisture for simulants centrifuged at 2500 g. However, no moisture surveillance system is currently installed for monitoring the tanks. See Section 4.1.5.5.2 for work in progress to estimate the tank waste moisture content.

4.6.2 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.

4.6.3 Baseline Assumptions

- Control of ferrocyanide waste temperature and moisture content will prevent propagating reactions.
- Temperature excursions are possible until proven otherwise.
- Moisture loss from a ferrocyanide tank is possible until demonstrated not to be a problem.
- Thermal response of these large tanks is quite slow.

4.6.4 Method to Close Recommendation 90-7.6

The DOE considers this recommendation to be closed with the proviso that the abnormal conditions response plan and emergency plan are updated and revised as required to incorporate any additional controls determined to be appropriate by the ongoing ferrocyanide safety issue investigations.

4.6.5 Action Plan

An action plan to respond to developing abnormal conditions in ferrocyanide tanks and an emergency plan to respond to a release from a ferrocyanide tank have been issued (as described below). The Westinghouse Hanford Emergency Plan specifies the frequency of emergency exercises.

4.6.5.1 Action Plan for Response to Abnormal Conditions. The *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991a, revised in December 1991) was initially prepared in response to this part of the DNFSB recommendation. 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, and includes the following:

- Adjustments or modifications to tank ventilation systems, including the addition of active ventilation (i.e., portable exhausters).
- Possible addition of a refrigerated cooling system into the tank or as a part of the ventilation system. System requirements have not yet been defined.
- Addition of water (even to a leaking tank) in minimum quantities to prevent temperature increases and restore temperature control. Water shall not be added unless dry cooling methods are ineffective at keeping the waste temperature below 93 °C (200 °F).
- To date, no control equipment to permit quick response to temperature limit deviations has been provided. Past experience and modeling results indicate that the thermal response of the 75-ft-diameter waste tanks is very slow.

Studies of moisture transport in ferrocyanide tanks have concluded that waste will retain a moisture content of 40 wt% or more, even if the tanks leak or are saltwell pumped (Grigsby et al. 1992). The theoretical concentration range of potential reactants, inert components, and water in ferrocyanide waste for a set of conservative conditional parameters have been compared to an estimated range of ferrocyanide tank waste compositions.

Results indicate that ferrocyanide sludge generated by the U Plant flowsheet scavenging processes would be nonreactive if the sludge contained more than approximately 20 wt% water. It has been suggested that each ferrocyanide tank be re-examined to verify that evaporation does not remove significant quantities of water. This effort was started as part of the hot spot thermal modeling task activity (see Section 4.1.5.4).

The action plan was revised and issued as WHC-EP-0407, Rev. 1 (Cash and Thurman 1991b) in December 1991. This revision includes updates for monitoring criteria, responses to abnormal levels of flammable and toxic gases, and reporting requirements. Requirements governing the frequency of ferrocyanide tank vapor monitoring may be added to the action plan at a later date if planned vapor space sampling identifies significant gas concentrations that would justify routine or constant surveillance. Once sufficient data are available from the vapor sampling program to form a sound technical basis, these requirements will be established and implemented as appropriate.

Additional studies by FAI (Fauske 1992d) show that U-Plant 1 and U-Plant 2 simulants will not propagate even when completely dry. The FAI tests were performed in an adiabatic calorimeter from room temperature to over 400 °C.

A letter report was issued in December 1991 in response to the following question posed by DNFSB: "What would Westinghouse Hanford do if there were a leak from a ferrocyanide tank?" Immediate actions mentioned in the response included the following:

- Assign initiating responsibilities
- Prepare and submit appropriate safety documentation
- Implement the readiness review process
- Install equipment external to the tank.

Upon receiving DOE approval to pump, the transfer lines would be leak checked, final pumping equipment would be installed, and pumping would continue until established criteria were met for interim stabilization. See Section 4.4.5.6 for safety documentation plans on ferrocyanide tank stabilization.

Progress on identified milestones is as follows.

- **December 3, 1991:** A letter report on response actions for a leaking ferrocyanide tank was issued.

- **December 30, 1991:** A revised action plan (WHC-EP-0407, Rev. 1) to incorporate flammable and toxic gas monitoring criteria (Cash and Thurman 1991b) was issued.

- **August 31, 1992:** Issue SA and EA documentation for saltwell pumping to DOE for review. These documents were submitted to DOE on September 30, 1992, along with stabilization recommendations.

- **September 30, 1992:** Issue recommendation to DOE on the feasibility and safety of stabilizing SST ferrocyanide tanks. This recommendation also addresses actions to be taken if a tank shows evidence of a leak. This recommendation was submitted on schedule.

4.6.5.2 Response to a Release from a Ferrocyanide Tank. If an airborne radioactive release from a ferrocyanide tank were to occur, it would be detected by one or more radiation monitoring systems in each tank farm and at other locations within the 200 East and 200 West areas. 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 event involving an underground radioactive waste tank is a unique event with potentially serious consequences both onsite and offsite. Westinghouse Hanford and DOE have analyzed the potential impacts of an event involving one of these tanks and have taken additional steps so that emergency personnel will be able to take mitigating actions in a timely fashion. These analyses resulted in development of the *Tank Farm Emergency Response Stabilization Plan* in March 1991 (WHC 1991). The 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 plan addresses responses in four distinct and defined steps that cover the range of consequences. The stabilization plan provides quick, preplanned actions that can be used to stabilize an emergency event at an underground radioactive waste tank.

A field exercise was conducted on December 18, 1991, that tested the Westinghouse Hanford and the DOE, Richland Field Office (RL) emergency management systems as well as the tank farm emergency response organizations (Emergency Control Centers and Emergency Management Center). This exercise tested portions of the waste tank emergency plans and procedures for response to an evaporator-crystallizer emergency. A critique of the December 1991 exercise was issued on January 31, 1991.

Westinghouse Hanford and RL Emergency Preparedness developed a table-top exercise for the DOE Emergency Operations Center. The scenario was a tank farm event involving a waste tank emergency. This exercise was completed on June 23, 1992.

Approval of the emergency event classification criteria is necessary before RL and DOE approval of event recognition and classification procedures for any Hanford Site facility. Concurrence was obtained from RL Defense Programs and Environmental Management emergency personnel. Training was completed for the new procedures, which are considered to be in effect as of June 1, 1992.

A radiological field team drill and a Westinghouse Hanford Emergency Management exercise (including the Emergency Control Centers and Emergency Management Center) were completed on schedule. Additionally, protective actions associated with Columbia River closure have been completed, and county/state emergency management exercises were completed on schedule.

Section 4.0 of the WHC Emergency Plan requires the following emergency drills and/or activities to be conducted at 200 Area tank farm facilities to maintain compliance with WHC and DOE Emergency Preparedness requirements.

Type of emergency/activity	Required frequency
Fire	Once per year
Evacuation	Once per year
Take cover	Once per year
Contamination spread (radioactive)	Once per year
Loss of utilities (if the loss would result in an emergency situation)	Once per year
Hazardous materials spill/release	Once per year
Bomb threat (as applicable)	Once per year
Participate in an exercise with the northern area emergency control center	Once every 2 years

Progress on identified milestones is as follows.

- **December 1, 1991:** Completed draft of Tank Farm Emergency Event Recognition and Classifications Procedures.
- **January 31, 1991:** Completed validation exercises of emergency response organizations and a critique for tank farm emergency responders.
- **March 30, 1992:** Completed Tank Farm Emergency Event Recognition and Classification Procedures and transmitted comment copies to DOE.
- **May 29, 1992:** Formally issued Tank Farm Emergency Event Recognition and Classification Procedures to DOE. The procedures are in effect at the Hanford Site as of June 1, 1992.
- **June 23, 1992:** Completed the DOE Emergency Operations Center table top exercise on a waste tank emergency.
- **June 30, 1992:** Completed Tank Farm Emergency Event Recognition and Classification Procedure validation exercises. The validation exercise was completed on May 18, 1992. The critique was issued June 30, 1992. A letter to DOE documenting the validation exercise and officially transmitting the critique was issued August 1, 1992.

The above milestones complete all actions with respect to emergency planning, emergency event recognition, protective action recommendations, and emergency response procedures at this time. Further revisions to these documents will be accomplished as part of the normal emergency planning efforts. No further reporting on these issues is planned in this document or in the quarterly progress reports (WHC-EP-0474-X).

5.0 SCHEDULES

The schedules shown in Figure 5-1 reflect the level of effort required to respond to DNFSB recommendations. In preparing these schedules, it is assumed that the Westinghouse Hanford Waste Tank Safety Program will receive the requested level of funding for FY 1993 and 1994. If that funding is not made available, the schedule will need to be modified and extended as necessary.

Another possible challenge to these schedules is the availability of engineering and operations personnel for (1) preparing design, safety, and work control documentation; and (2) conducting field operations required for the ferrocyanide tanks. Safety issues associated with ferrocyanide tanks and other watchlist tanks command the highest priority at the Hanford Site.

The schedules will be statused in the DNFSB quarterly reports (WHC-EP-0474-X) to reflect progress of the individual tank activities. Projected or actual milestone completion dates will be indicated on the statused schedule.

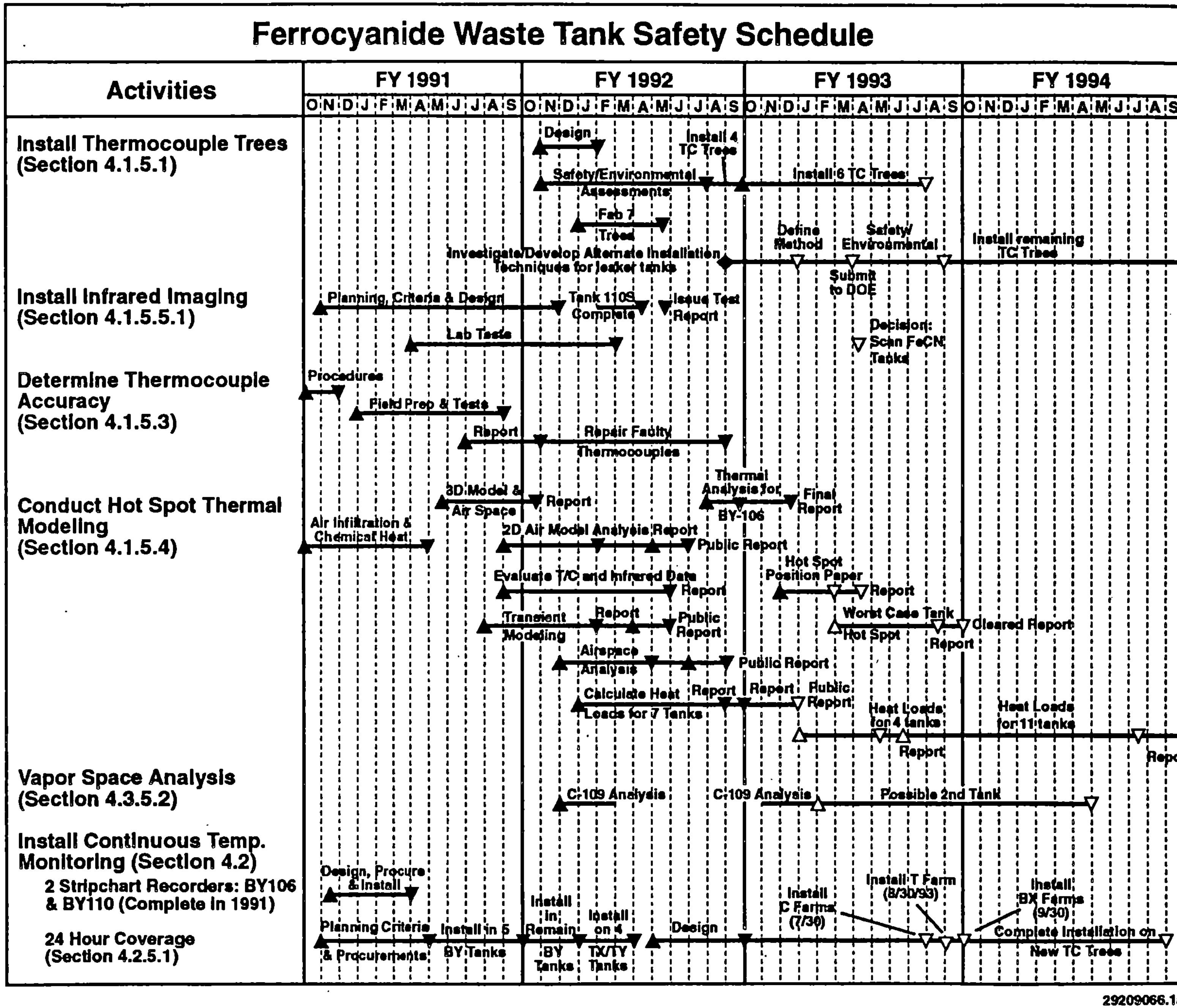
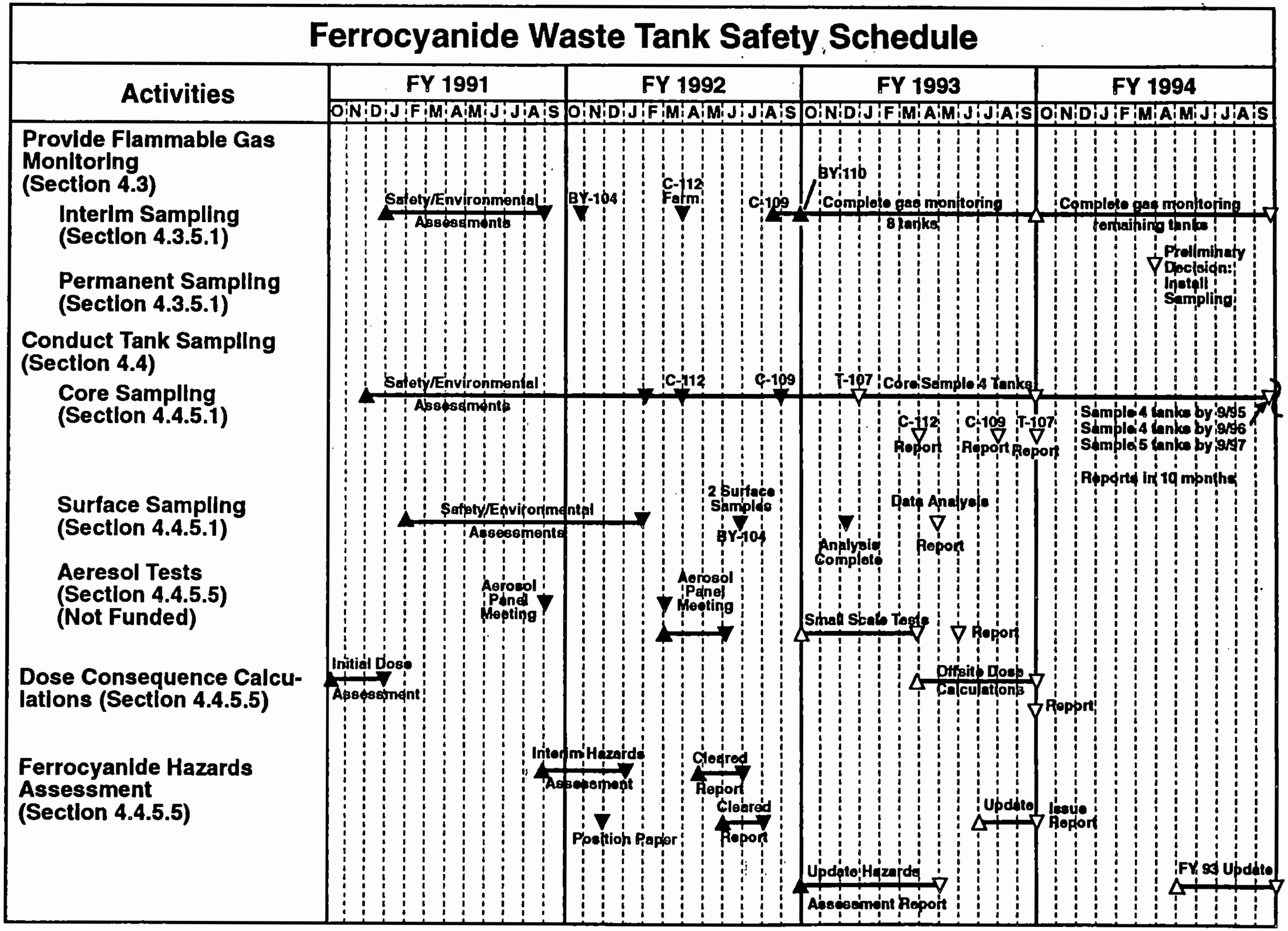


Figure 5-1. Schedule. (sheet 1 of 4)



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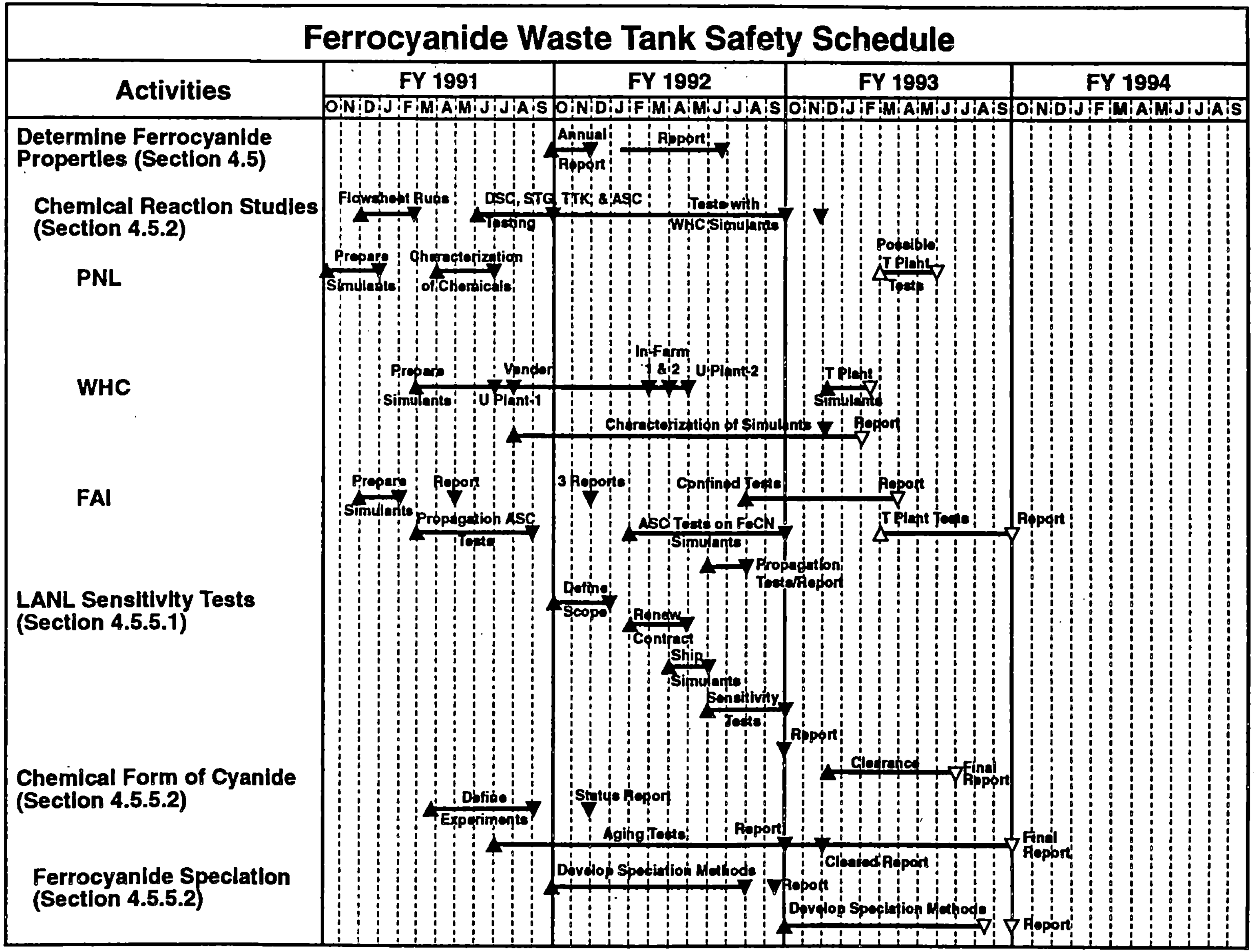

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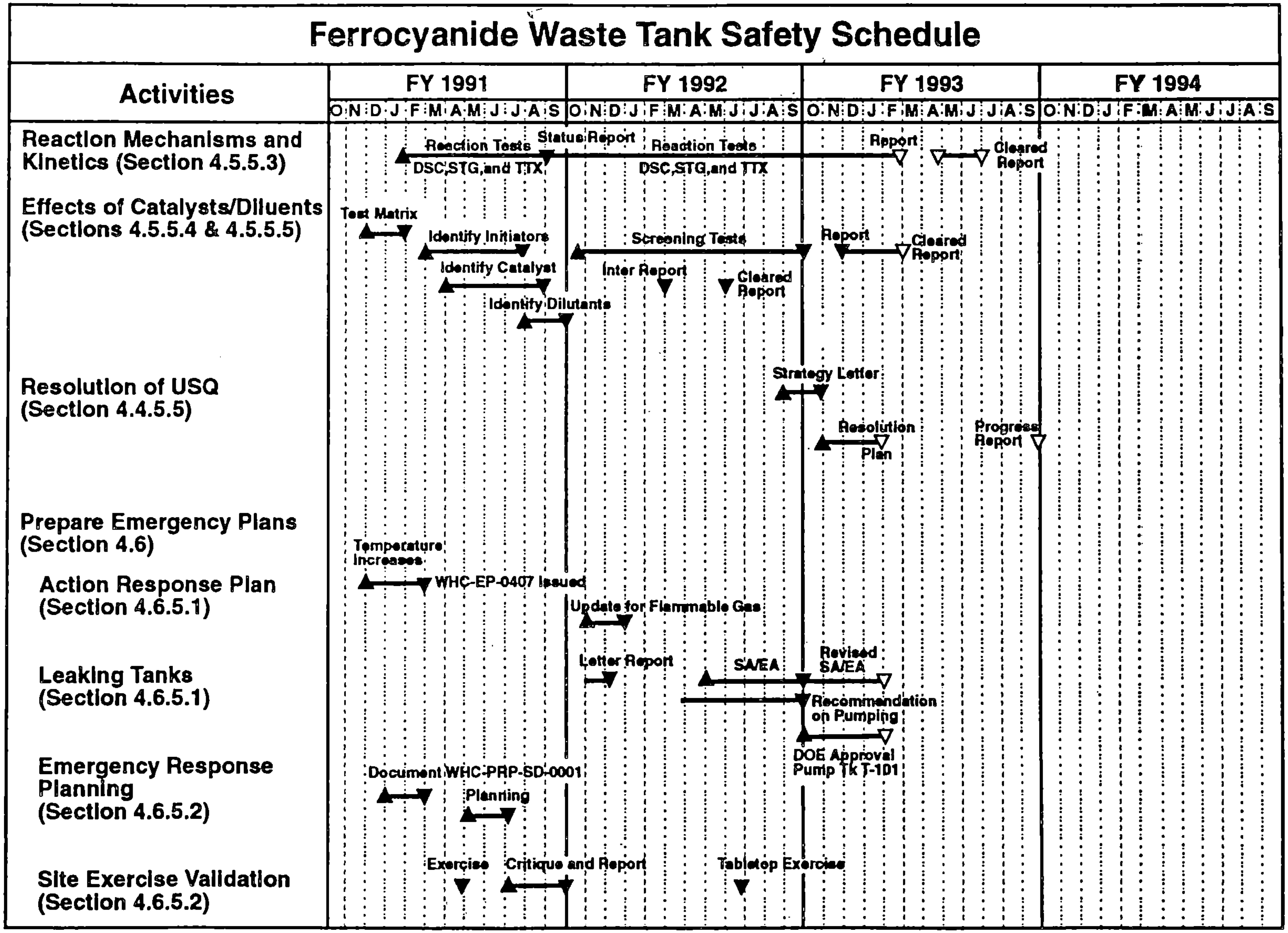

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Figure 5-1. Schedule. (sheet 4 of 4)

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