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Quarterly Report on the Ferrocyanide Safety Program for the Period Ending September 30, 1994

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QUARTERLY REPORT ON THE FERROCYANIDE SAFETY PROGRAM FOR THE PERIOD ENDING SEPTEMBER 30, 1994

J. E. Meacham
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ABSTRACT

This is the fourteenth quarterly report on the progress of activities addressing the Ferrocyanide Safety Issue associated with Hanford Site high-level radioactive waste tanks. Progress in the Ferrocyanide Safety Program is reviewed, including work addressing the six parts of Defense Nuclear Facilities Safety Board Recommendation 90-7 (FR 1990). All work activities are described in the revised program plan (Borsheim et al. 1994), and this report follows the same format presented there. A summary of the key events occurring this quarter is presented in Section 1.2. More detailed discussions of progress are located in Sections 3.0 and 4.0.

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LIST OF TERMS

Btu/h	British Thermal Units per Hour
CASS	Computer Automated Surveillance System
CPAC	Center for Process Analytical Chemistry
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	Data Quality Objectives
EA	Environmental Assessment
ECN	Engineering Change Notice
EIS	Environmental Impact Statement
FAI	Fauske and Associates, Inc.
FTIR	Fourier Transform Infrared
FTIR-PAS	Fourier Transform Infrared-Photoacoustic Spectroscopy
FY	Fiscal Year
g-mole	Gram-Mole
GAO	U.S. General Accounting Office
IC	Ion Chromatography
IR	Infrared
ISB	Interim Safety Basis
kW	Kilowatt
LANL	Los Alamos National Laboratory
LOW	Liquid Observation Well
NIR	Near Infrared
PLS	Partial Least Squares
PNL	Pacific Northwest Laboratory
ppm	Parts Per Million
Rad/h	Rad Per Hour
RSST	Reactive Systems Screening Tool (small adiabatic calorimeter at FAI)
SA	Safety Assessment
SAR	Safety Analysis Report
SD	Supporting Document
SST	Single-Shell Tank
TC	Thermocouple
TMACS	Tank Monitor and Control System
USQ	Unreviewed Safety Question
vol%	Volume Percent
VSP	Vent Sizing Package (large adiabatic calorimeter at FAI)
wt%	Weight Percent

1.0 INTRODUCTION

1.1 PURPOSE

This quarterly report provides a status of the activities underway on the Ferrocyanide Safety Issue at the Hanford Site including actions in response to Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 90-7 (FR 1990). In March 1991, a DNFSB implementation plan (Cash 1991) responding to the six parts of Recommendation 90-7 was prepared and sent to the DNFSB. The implementation plan was updated in fiscal year (FY) 1993 (Borsheim et al. 1992). A revised Ferrocyanide Safety Program Plan addressing the total Ferrocyanide Safety Program, including the six parts of DNFSB Recommendation 90-7, was released in March 1994 (Borsheim et al. 1994). Activities in the revised program plan are underway or have been completed, and the status of each is described in Section 4.0 of this report.

1.2 QUARTERLY HIGHLIGHTS

- A new integrated characterization schedule was finalized this quarter (Stanton 1994). This new schedule shows core sampling and instrument tree installation to be completed for ferrocyanide tanks by July 1996 and September 1995, respectively.

- A report on criteria for upgraded temperature monitoring capabilities for ferrocyanide tanks was released this quarter (Fowler and Dukelow 1994). Comments received from the Washington State Department of Ecology were incorporated into the report.

- Heat load analyses and thermal characteristics were determined for tanks 241-BY-112, 241-C-108, -111, -112, 241-T-107, 241-TX-118, 241-TY-101, -103, and -104. A report of the results was released this quarter (McLaren 1994b). Heat load analyses have now been completed for all Ferrocyanide Watch List tanks. The maximum calculated heat load for the ferrocyanide tanks was below 4.2 kW.

- The dryout analysis report was completed and released this quarter (Epstein et al. 1994). This report examined possible dryout mechanisms including global evaporation, removal of liquid by leakage or pumping, boiling as a result of hot spots, and hot spot enhanced surface evaporation. The report concluded that dryout by any of these mechanisms is not credible.

- A report evaluating possible sources of flammable gases, including potential cyclic venting in ferrocyanide tanks, was released this quarter (Fowler and Graves 1994). The report concluded that continuous flammable gas monitoring in ferrocyanide tanks is not warranted.

- A rationale for not installing pressure monitors in ferrocyanide tanks was prepared and submitted to the U.S. Department of Energy (DOE) this quarter (Payne 1994). Low gas generation rates (Fowler and Graves 1994), and the low potential for exothermic ferrocyanide reactions (Postma et al. 1994) indicate that continuous pressure monitoring is not warranted. Pending DOE concurrence with not installing pressure monitoring in ferrocyanide tanks, no further work is planned in this area.

- A data interpretation report for the three cores taken from tank 241-T-107 was released this quarter (Sasaki and Valenzuela 1994). The most significant item noted is that none of the core samples or subsamples exhibited an exotherm. This is the first tank containing material from the U Plant scavenging flowsheet to be core sampled for the Ferrocyanide Safety Program.

- The ferrocyanide Data Quality Objectives (DQO) document (Meacham et al. 1994a) was updated and re-released this quarter as a Westinghouse Hanford Company Supporting Document (SD). Because the DQO report is a living document and may undergo several revisions, the SD format allows the Hanford analytical laboratories to quickly retrieve the most current version for their use.

- Fourier transform infrared-photoacoustic spectroscopic (FTIR-PAS) technology developed at the Ames Laboratory, Iowa State University, was transferred to Westinghouse Hanford Company this quarter. A report reviewing the progress on FTIR-PAS technology transfer and recommendations for future work was released this quarter (Rebagay et al. 1994).

- Testing of a prototype neutron probe for moisture monitoring concluded this quarter. A report documenting the design of the moisture monitoring probes and changes made in the existing surveillance vans were completed this quarter (Finfrock et al. 1994).

- Experiments measuring the rate of simulant drying at low relative humidity (30%) were concluded and the results published this quarter (King 1994). Results show that waste simulants will slowly dry at a rate proportional to the relative humidity difference between the sludge and the dome space.

- A three-month aging experiment conducted at pH 10 was completed this quarter. Results indicate that hydrolytic and radiolytic degradation of ferrocyanide still occurs, albeit at a much slower rate. A report summarizing FY 1994 progress was publicly released this quarter (Lilga et al. 1994).

- A report summarizing the influences of cesium, sodium, nickel, and ferrocyanide on the solubility of cesium was published this quarter (Rai et. al. 1994). Test results indicate that cesium does not exhibit retrograde solubility (i.e., decreasing solubility with increasing temperature).

- Studies continued this quarter to determine the capacity of ferrocyanide sludge to retain soluble cesium. A report summarizing the FY 1994 progress was released this quarter (Burgeson et al. 1994). Results obtained to date indicate that as the mole ratio of cesium to nickel ferrocyanide increases, the effectiveness of nickel ferrocyanide as an exchanger decreases.

- A report discussing FY 1994 microconvection modeling simulations was published this quarter (McGrail 1994). Modeling showed that it is possible for the internal heat generation to establish a bifurcated flow field within the tank. Convective mass transport along the flow streamlines in the flow field would help distribute radiocesium. Therefore, natural mass transport processes within the tank do not favor the formation of hot spots.

- A report summarizing ferrocyanide propagation tests conducted at Fauske and Associates, Inc. (FAI) was published this quarter (Fauske 1994). Results indicate that the minimum free water concentration required to prevent propagation of a stoichiometric mixture is 20 wt% for an initial temperature of 25 °C. For any mixture of ferrocyanide waste at 25 °C or less, a water content of 20 wt% would be sufficient to prevent a propagating reaction.

1.3 REPORT FORMAT

Progress of activities under each of the six parts of DNFSB Recommendation 90-7 are arranged in the same order as the program plan (Borsheim et al. 1994). The arrangement also follows the same order provided in Recommendation 90-7. To report on progress, each part of the recommendation is repeated in italics, followed by paragraphs explaining the scope of work on each part or subpart of the recommendation. Subheadings for each task activity report the following:

- Progress During Reporting Period
- Planned Work for Subsequent Months
- Problem Areas and Action Taken
- Milestone Status.

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2.0 BACKGROUND

Various high-level radioactive wastes from defense operations have accumulated at the Hanford Site in underground storage tanks since the mid-1940s. During the 1950s, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short time period, and to minimize the need for constructing additional storage tanks, Hanford Site scientists developed a process to scavenge ^{137}Cs from 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 single-shell tanks (SSTs).

Ferrocyanide, in the presence of oxidizing material such as sodium nitrate and/or nitrite, can be made to react exothermically by heating it to high temperatures or by applying 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, but the lowest propagation temperature observed is approximately 250 °C. The reactive 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 ferrocyanide and nitrates and/or nitrites is likely to exist in some regions of the ferrocyanide tanks.

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

Although not considered a part of the safety analysis for 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* (DOE 1987) did include an environmental impact analysis of potential exothermic reactions involving ferrocyanide-nitrate mixtures. The EIS authors postulated an explosion during mechanical retrieval of saltcake or sludge from a ferrocyanide waste tank. The EIS authors concluded that this worst-case accident could create enough energy to release radioactive material to the atmosphere through ventilation openings, exposing persons offsite to a short-term radiation dose of approximately 200 millirem. A U.S. General Accounting Office (GAO) study (Peach 1990) postulated a greater worst-case accident, with independently calculated doses of one to two orders of magnitude greater than in the EIS. Coupling the ferrocyanide concerns with concerns about high organic concentrations and potential hydrogen accumulations in other Hanford Site high-level waste tanks, the DOE established the High-Level Radioactive Waste Tanks Task Force and Tanks Advisory

Panel in August 1990. These two groups were formed to ensure that all safety concerns with high-level waste 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 Westinghouse Hanford Company to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident.

The Ferrocyanide Safety Issue is a result of a combination of factors, beginning with the safety studies performed as precursors to using the ferrocyanide scavenging flowsheets. These studies did not address ultimate disposal of the ferrocyanide solids, and were not performed to the conservative standards used today. In addition, no rigorous inventory was kept of the ferrocyanide or other chemicals added to the tanks. Subsequent safety studies determining the risk of adding other chemicals were either not performed, or were performed to less conservative standards. Monitoring systems, such as temperature measurement instrumentation, were allowed to be disconnected and fall into disrepair because the potential hazard was not highlighted.

Although the EIS authors estimated the consequences from a hypothetical explosion, the GAO disagreed with the assumptions used for the dose consequence calculations. Work performed by Pacific Northwest Laboratory (PNL) in 1984-85 (Burger 1989) identified a potential safety problem, but no funding was provided until 1989 to study the Ferrocyanide Safety Issue. An additional issue was subsequently communicated about the assumed radioactive material source term (release fraction) resulting from a hypothetical explosion (Peach 1990).

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

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[1] An Unreviewed Safety Question, as defined by DOE Orders 5480.5 (DOE 1986) and 5480.21 (DOE 1991), is determined as follows. "A proposed change, test or experiment shall be deemed to involve a 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."

ferrocyanide [as the $Fe(CN)_6^{4-}$ anion]. These tanks were placed on a Ferrocyanide Watch List because of the USQ. Re-examination of the historical records (Borsheim and Simpson 1991) indicated that 6 of the 24 tanks do not contain the requisite 1,000 g-moles of ferrocyanide and should not have been included on the Watch List. Four of the 6 tanks were removed from the Watch List in June 1993 (Meacham et al. 1993) and removal of the other two tanks is pending (Borsheim et al. 1993).

The Ferrocyanide USQ was closed on March 1, 1994 by the DOE Assistant Secretary for Environmental Restoration and Waste Management (Sheridan 1994). Closure of the Ferrocyanide USQ was based on safety criteria proposed by Westinghouse Hanford Company and concurred on by outside reviewers and reviewers within DOE. This was the first USQ closure in the current Waste Tank Safety Program since the Watch List was created in 1990.

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3.0 FERROCYANIDE SAFETY DOCUMENTATION

The USQ process depends on an authorization basis that describes those aspects of the facility design basis and operational requirements relied on by DOE to authorize operation. The authorization basis is described in documents such as facility SARs and other safety analyses, hazard classification documents, technical safety requirements, DOE-issued safety evaluation reports, and facility-specific commitments, such as Safety Assessments (SAs) and the Interim Safety Basis (ISB). The potential hazards of a ferrocyanide-nitrate/nitrite reaction were discovered to represent an inadequacy in the then-existing authorization basis.

A strategy for closing the USQ and resolving the Safety Issue for the ferrocyanide waste tanks was developed by DOE and Westinghouse Hanford Company and presented to the DNFSB in August 1993 (Grumbly 1993). The strategy contains two key steps: (1) developing criteria for safety categories that rank the hazard for each tank, allowing closure of the USQ; and (2) confirmation and final placement of each tank into one of the categories based on core sampling and/or characterization of the tank contents. The Ferrocyanide USQ was closed on March 1, 1994 by the DOE Assistant Secretary for Environmental Restoration and Waste Management (Sheridan 1994).

Safety and Environmental Assessments. SAs are documents prepared to provide the technical basis to assess the safety of a proposed activity and to provide proper controls to maintain safety. The SA and the accompanying Environmental Assessment (EA) for that operation provide the basis for DOE authorization of the proposed activities. SAs have been approved for dome space sampling of all ferrocyanide tanks, waste surface sampling, push-mode and rotary-mode core sampling, thermocouple (TC)/instrument tree installation in sound and assumed leaker tanks, and removal of pumpable liquid (interim stabilization).

A generic EA covering all proposed operations in the tank farms has been approved, and a Finding of No Significant Impact was issued by DOE (Gerton 1994). Approval of the generic EA provides adequate National Environmental Policy Act coverage for the planned Ferrocyanide Safety Program activities and streamlines the approval process.

The authorization basis for intrusive tank operations was combined into one document, the ISB, which was approved in November 1993 (Wagoner 1993). Safety documentation concerning the ferrocyanide hazard was updated to reflect the approved ferrocyanide safety criteria and closure of the Ferrocyanide USQ. Updates to ISB Chapter 6, "Requirements," were provided in May 1994 via the controlled manual distribution of Engineering Change Notice (ECN) 168008. Updates to ISB Chapters 3, 4 and 5, including a revised topical report (Chapter 5, Section 5) were provided this quarter via the controlled manual distribution of ECN 606823.

Hazard Assessment. The effort to update the ferrocyanide hazards assessment document was redirected in June 1993 toward developing a technical basis document supporting resolution of the Ferrocyanide Safety Issue. An updated ferrocyanide hazards assessment, now referred to as a technical basis document, will not be started until adequate information is available for resolving the Ferrocyanide Safety Issue. Technical information from all Ferrocyanide Safety Program tasks will be incorporated into this document. This document may be necessary to support Safety Issue resolution in FY 1996 for the four Ferrocyanide Watch List tanks in C Farm.

Ferrocyanide Program Plan. An update of the Ferrocyanide Safety Program plan was initiated this quarter as a result of discussions with the DNFSB. These discussions emphasized the need for timely and formal notification to the DNFSB of changes in implementation of Recommendation 90-7. In the past, some changes in work scope and schedules from the original implementation plan (Cash 1991) were made without formal submittal by the Secretary of Energy and acceptance by the DNFSB. The new program plan outlines a protocol for future changes. Changes affecting the completion of milestones that closeout a DNFSB Recommendation will be submitted to the DNFSB via revision and resubmission of the Ferrocyanide Program Plan. Changes in milestones or schedules that are on the path to closure of a recommendation, but do not close out a DNFSB recommendation, will be addressed and assessed in the quarterly reports.

Dose Consequences. In September 1990, an Ad Hoc Task Force report recommended that studies be performed to provide information on: (1) the potential for a ferrocyanide-nitrate/nitrite explosion; (2) the conditions necessary in the tanks to initiate an explosion; and (3) the potential consequences of such an occurrence. The GAO advised the Secretary of Energy to implement these recommendations (Peach 1990). A closeout report addressing all three of the GAO recommendations was submitted to DOE last quarter (Meacham et al. 1994b). Pending DOE concurrence, no further work is planned in this area.

- **Milestone Status**

  - **January 31, 1994**: Westinghouse Hanford Company receives DOE approval to close the Ferrocyanide USQ (Safety Initiative 2s). The Ferrocyanide USQ was closed on March 1, 1994 (Sheridan 1994). A letter was sent on March 30, 1994 (Wisness 1994) informing the U.S. Environmental Protection Agency and the State of Washington Department of Ecology that Tri-Party Agreement milestone M-40-14 (closure of the Ferrocyanide USQ by March 31, 1994) was completed.

  - **June 24, 1994**: Westinghouse Hanford Company issues an ISB Level 1 report to DOE that provides the safety basis for safe operation of ferrocyanide tanks. An update to the ferrocyanide portions of the ISB was completed this quarter via ECN-606823.

- **January 31, 1996.** Westinghouse Hanford Company issues documentation supporting safety issue resolution for the four C Farm tanks, and recommends Ferrocyanide Safety Issue resolution for the C Farm tanks.

- **July 31, 1996.** Westinghouse Hanford Company receives DOE approval, Ferrocyanide Safety Issue resolved for C Farm tanks.

- **March 31, 1997.** Westinghouse Hanford Company issues documentation to support safety issue resolution for the remaining 14 tanks, and recommends Ferrocyanide Safety Issue resolution for all remaining tanks.

- **September 30, 1997.** Westinghouse Hanford Company receives DOE approval, Ferrocyanide Safety Issue resolved.

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4.0 DESCRIPTION OF ACTIVITIES

This section follows the format of the program plan (Borsheim et al. 1994) and describes all work associated with the Ferrocyanide Safety Program. Where applicable, each task activity is described relative to the DNFSB Recommendation (90-7.1 through 90-7.6). The specific part of the recommendation is given, followed by a summary of activities underway to respond (if not already closed out).

4.1 ENHANCED TEMPERATURE MEASUREMENT

"Immediate steps should be taken to add instrumentation as necessary to the SSTs 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 Instrument Trees

Work in several areas has developed a broader knowledge base and has warranted several changes in the approach to implementing this recommendation. Originally, it was planned to add several temperature measurement instruments to each tank. This plan has been modified to ensure that at least one instrument tree with replaceable temperature-sensing elements is in each ferrocyanide tank. Additionally, at least two operational temperature-sensing elements should be in the waste to ensure a true temperature measurement, and one or more in the dome space.

The new data that have warranted this action include: (1) many of the TC elements in the existing trees have been returned to service, and measured temperatures are as expected; (2) thermal modeling to date (McLaren 1994a, 1994b) and an enhanced understanding of waste properties that shows formation of hot spots in ferrocyanide tanks is not credible (Dickinson et al. 1993, Epstein et al. 1994); and (3) new estimates of tank heat content based on tank temperatures show lower values than previous estimates (Crowe et al. 1993, McLaren 1994a, 1994b).

When completed, the results will be two instrument trees in all but three ferrocyanide tanks (241-BY-106, -111 and -112). Tanks 241-BY-105 and -106 already contain instrument trees with replaceable temperature sensing elements. Tanks 241-BY-111 and -112 had no operable instrument tree, and the waste temperatures were measured via a dedicated TC element installed in each tank's liquid observation well (LOW). New instrument trees with replaceable temperature-sensing elements have now been installed in these two tanks. The existing instrument trees in the tanks will be monitored in addition to newly installed trees. The older trees are expected eventually to fail in a manner such that they cannot be repaired, and they will not be replaced.

- **Progress During Reporting Period.** Five instrument trees, each with a heated vapor sampling tube, have been fabricated for insertion into assumed leaker ferrocyanide tanks. All equipment and safety documentation supporting insertion of the trees has been completed. Installation of instrument trees in the remaining assumed leaker tanks has been delayed because of concern about riser availability for core sampling. Once an instrument tree is inserted into a riser, that riser is no longer available for core sampling. Therefore, instrument tree installation will occur after a tank is core sampled, or after verification that sufficient risers are available for characterization efforts after the instrument tree has been installed. A new integrated characterization schedule was finalized in September 1994 (Stanton 1994). This new schedule allows for instrument tree installation by September 1995.

  A report on criteria for upgraded temperature monitoring capabilities for ferrocyanide tanks was released this quarter (Fowler and Dukelow 1994). Comments received from the Washington State Department of Ecology were incorporated into the report. This completes Tri-Party Agreement milestone M-40-02A.

- **Planned Work for Subsequent Months.** Instrument trees will be installed into the remaining assumed leaker tanks, most after characterization of the affected tank is complete. Two additional instrument trees will be fabricated.

  A riser survey is currently being conducted for core sampling and instrument tree installation.

- **Problem Areas and Action Taken.** Installation of instrument trees has been delayed pending decisions on availability of risers for characterization and instrument tree installation. A riser survey is being conducted to determine the number of risers available for characterization and instrument tree installation.

- **Milestone Status.**

  - **September 30, 1994**: Westinghouse Hanford Company develops criteria for upgraded temperature monitoring capabilities in ferrocyanide tanks (Tri-Party Agreement milestone M-40-02A). The report was released on schedule this quarter (Fowler and Dukelow 1994).

- **April 30, 1995.** Westinghouse Hanford Company installs two of seven new instrument trees into assumed leaker ferrocyanide tanks (Tri-Party Agreement milestone M-40-02B).

- **September 30, 1995.** Westinghouse Hanford Company completes installation of remaining five instrument trees in assumed leaker ferrocyanide tanks. Existing temperature-sensing elements in the remaining two ferrocyanide tanks (241-BY-105 and -106) will be replaced as necessary (Tri-Party Agreement milestone M-40-02).

4.1.2 Upgrades to Existing Temperature Monitoring Instrumentation

This task determined the operability and accuracy of previously installed TC elements in the original 24 Ferrocyanide Watch List tanks. The original and newly installed instrument trees provide temperature measurements for the ferrocyanide tanks.

Field measurements were taken in 1991 on each TC element in the then-existing trees to determine the resistance and voltage across the junction and across each lead to ground. The exact condition of each TC element was determined by resistance and voltage measurements (Bussell 1992). This work was completed in FY 1991 with a total of 265 TC elements being evaluated. Work in FY 1992 focused on repair and recovery of 92 TC elements that were found to be failed or marginal in performance. This task was completed in FY 1992.

- **Progress During Reporting Period.** No progress was required or planned.
- **Planned Work for Subsequent Months.** None.
- **Problem Areas and Actions Taken.** None.
- **Milestone Status.** This task is complete.

4.1.3 Hot Spot Thermal Modeling

Radioactive materials decaying in Hanford Site waste tanks generate heat. A concern, raised when the ferrocyanide tanks first became a safety issue, has been whether an exothermic excursion and local propagation could occur within the ferrocyanide waste if a sufficient concentration of ferrocyanide and a high enough temperature were present. This task models and analyzes the available temperature data from the ferrocyanide tanks in order to determine the heat load and temperatures as a function of depth and radial location. Sensitivity and parametric analyses are included to determine the magnitude of hot spots that would have to exist within the waste to reach propagation temperatures.

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

- **Progress During the Reporting Period.** Heat load analyses and thermal characteristics were completed for tanks 241-BY-112, 241-C-108, -111, -112, 241-T-107, 241-TX-118, 241-TY-101, -103, and -104. A report of the results released this quarter (McLaren 1994b). The report compiles thermal analyses of Ferrocyanide Watch List tanks. The updated thermal model reported in McLaren (1993) and McLaren (1994a) was used for the analyses. Upper and lower limits for the estimated heat loads are presented in the report. The maximum heat load of any ferrocyanide tank is below 4.2 kW. This report closes out the heat load analyses task for the ferrocyanide tanks.

  The dryout analysis report was completed and released this quarter (Epstein et al. 1994). This report addresses whether the ferrocyanide sludge could dry sufficiently to be chemically reactive, either globally or locally. Possible dryout mechanisms considered are global evaporation, removal of liquid by leakage or pumping, boiling as a result of hot spots, and enhanced surface evaporation from hot spots. The report concludes that dryout by any of these mechanisms is not credible.

- **Planned Work for Subsequent Months.** None.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **May 31, 1994.** Complete additional analyses and issue an update of the report *Ferrocyanide Safety Program: Credibility of Drying out Ferrocyanide Waste by Hot Spots* (Dickinson et al. 1993), approved for public release. This effort was extended to include discussion of additional dryout mechanisms and the results of experiments that provide the bases for the discussions. A comprehensive report on ferrocyanide waste dryout was published this quarter (Epstein et al. 1994).

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

  - **September 30, 1994.** Complete thermal hydraulic analyses of heat loads for all remaining ferrocyanide tanks and issue a report available to the public. This report was issued on schedule (McLaren 1994b).

4.1.4 Infrared Scanning System

Infrared (IR) scanning systems are commercially available from numerous vendors. These systems are sensitive to changes of ±0.3 °C or less under ideal conditions, and offer promise for mapping surface temperature profiles in the ferrocyanide tanks. Thermal modeling performed on ferrocyanide tank 241-BY-104 suggested that if hot spots with temperatures of concern are possible, surface temperature differences might be great enough to be detected by infrared mapping.

A position paper on the credibility of hot spots and the need for further IR scanning was issued in April 1993 (Dickinson et al. 1993). Further analyses have been performed to assess potential dryout of the ferrocyanide waste (Epstein et al. 1994). These reports examined potential mechanisms for forming hot spots. Analyses indicate that hot spots are not credible in ferrocyanide tanks. Based on these analyses, Westinghouse Hanford Company recommended that no further planning be pursued for IR scans for the purpose of detecting hot spots.

- **Progress During the Reporting Period.** A report on infrared scanning of tank 241-S-110 was published this quarter (Efferding et al. 1994).

- **Planned Work for Subsequent Months.** None.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **December 31, 1994.** Westinghouse Hanford Company publishes document on infrared scans of tank 241-S-110. A report on infrared scanning of tank 241-S-110 was published this quarter (Efferding et al. 1994).

4.2 CONTINUOUS TEMPERATURE MONITORING

"The temperature sensors referred to above [Recommendation 90-7.1] should have continuous recorded readouts and alarms that would signal at a permanently manned location any abnormally high temperatures and any failed temperature instrumentation."

This task provides continuous monitoring of presently installed (and operable) temperature-sensing elements for the ferrocyanide tanks. New instrument trees will be connected to the system as they are installed into each tank, resulting in continuous monitoring of temperature in the ferrocyanide tanks. All data are collected automatically at the continuously manned Computer Automated Surveillance System (CASS) Operator Control Station. 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, which became operational in September 1991, has the capacity to assign alarms for a change in the value of any temperature point. Alarms, if they occur, trigger an audible annunciator and are logged immediately to hard copy. An alarm summary display provides a list of the most recent alarms in order of occurrence. Each alarm can be identified by point and time of occurrence. Operator acknowledgement of the alarm will silence the audible annunciator. Signal conditioning and multiplexing are performed locally at each tank. This eliminates the need to transmit low-level signals to the tank farm boundary and reduces cable runs. Electronic noise, extension wire corrosion, and thermal gradients are also reduced.

- **Progress During Reporting Period.** Ferrocyanide tanks with temperature-sensing have been connected to the Tank Monitor and Control System (TMACS) for temperature monitoring, with the exception of tanks 241-BY-107 and 241-TX-118. Temperatures are being monitored on a continuous basis.

- **Planned Work For Subsequent Months.** Connection of new instrument trees to TMACS will be made as soon as practical after the trees are installed. Two instrument trees now installed remain to be connected to TMACS.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **September 30, 1994.** Westinghouse Hanford Company completes installation of TMACS for the four ferrocyanide tanks in C Farm, one tank in T Farm, and two tanks in BX Farm. Ferrocyanide tanks removed from the Watch List (241-BX-110, 241-BY-101, and 241-T-101), or pending removal from the Ferrocyanide Watch List (241-BX-102 and -106), will be connected in FY 1995. This milestone was completed during the quarter ending June 30, 1994.

  - **September 30, 1995.** Westinghouse Hanford Company completes installation of the TMACS for all ferrocyanide tanks. The completion of the TMACS installations is also a Tri-Party Agreement milestone (M-40-02).

4.3 COVER GAS MODELING

"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 Interim Flammable Gas Monitoring

The effort to conduct flammable and toxic gas monitoring and analyses in the ferrocyanide tanks is continuing. Most of this effort was transferred to the Tank Vapor Issue Resolution

Program, which is coordinating interim gas monitoring of the ferrocyanide tanks, as well as those tanks involved with the tank vapor program. Tank dome spaces are measured for flammability using a commercial combustible gas monitor (calibrated with pentane gas), and are monitored for potential toxic gases using an organic vapor monitor and Dräger[2] tubes as required by the safety assessment and work procedures for a particular activity. Development and validation of alternative technologies for dome space characterization are in progress using SUMMA[3] canisters and specific absorption (Dräger™) tubes. The initial dome space sampling was done in several tank locations (i.e., from two widely separated risers) and at three elevations in the dome space. Review of the sample data indicated that sampling from one riser and one elevation was adequate.

- **Progress During Reporting Period.** No instrument trees were installed and no core samples were taken from ferrocyanide tanks this quarter. However, three ferrocyanide tanks were vapor sampled (241-TY-101, -103, and -104). Results from the analyses of these three tanks will be available early next quarter. Table A-2 in Appendix A reviews results from the gas analyses completed through the end of this quarter.

- **Planned Work For Subsequent Months.** Flammable gas sampling and selected noxious gas monitoring will continue, as required, to support planned core sampling, instrument tree installation, and the Tank Vapor Program.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status**

  - **September 30, 1994.** Westinghouse Hanford Company completes dome space sampling of remaining ferrocyanide tanks, as required, to support various field activities. Dome space sampling, as required for field activities, was completed on schedule.

  - **September 30, 1995.** Westinghouse Hanford Company completes dome space sampling of remaining ferrocyanide tanks. This milestone addresses the November 1995 Tri-Party Agreement milestone M-40-03.

4.3.2 Continuous Gas Monitoring

Options for installing a gas monitoring capability on new instrument trees were reviewed and a heated vapor sampling tube was added to the design of the remaining instrument trees to be installed in ferrocyanide tanks. These modifications will allow dome space sampling on a

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[2]Trademark of Drägerwerk Aktiengesellschaft, Inc., Lubeck, Germany.

[3]Trademark of Molectrics, Inc., Cleveland, Ohio.

continuous or intermittent basis. The first instrument tree incorporating the new design was installed in tank 241-BY-107 in April 1994. The need for continuous gas monitoring was addressed in a study that also assessed the potential for cyclic venting and the possibility of accumulating flammable gases (Fowler and Graves 1994).

The possibility that localized concentrations or stratification of gases exist in the tanks has been evaluated. A modeling study to determine airflow patterns in the dome space of tank 241-C-109 was conducted to evaluate the amount of mixing and the local gas concentrations that could occur. The study revealed that the gases in the tank are well mixed and follow Graham's law for gaseous diffusion; therefore, an analysis of a second tank was considered unnecessary because of the well-mixed environment calculated for 241-C-109 (Wood 1993).

- **Progress During Reporting Period.** A report evaluating possible sources of flammable gases, including potential cyclic venting, was released this quarter (Fowler and Graves 1994). The report concluded that continuous flammable gas monitoring in ferrocyanide tanks is not warranted based on: (1) the low concentration of flammable gases found to date; (2) anticipated low ferrocyanide concentrations because of waste aging; (3) analytical results from tanks 241-C-109 and -112 showing that the fuel concentration in the tanks is not as high as postulated by flowsheet values and operating records; and (4) calculations of hydrogen generation using realistic generation values and passive ventilation assumptions.

- **Planned Work For Subsequent Months.** Pending DOE concurrence with the findings in the Fowler and Graves (1994) report, no further work is planned in this area.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.**

  - **March 31, 1994**: Westinghouse Hanford Company completes an evaluation report to determine which gases, if any, need to be continuously monitored in selected ferrocyanide tanks. The report was publicly released this quarter (Fowler and Graves 1994).

  - **September 30, 1995**: Westinghouse Hanford Company develops and designs continuous monitoring equipment, if required.

  - **September 30, 1997**: Westinghouse Hanford Company installs continuous gas monitoring equipment in six tanks, if required.

4.3.3 Tank Pressure Monitoring

Public Law 101-510, Section 3137 (also known as the Wyden Amendment) requires that "... *the Secretary of Energy shall identify which single-shell tanks [Watch List]... may have a serious potential for release of high-level waste due to uncontrolled increases of ... pressure. After completing such identification, the Secretary shall determine whether continuous monitoring is being carried out to detect a release or excessive ... pressure at each tank so identified. If such monitoring is not being carried out, as soon as practicable the Secretary shall install such monitoring....*"

The ferrocyanide tanks were initially identified as having "a serious potential for release" and were placed on the Watch List; however, pressure monitoring capability does not presently exist for the tanks. Several years would be required for pressure monitoring instrumentation to be installed and connected to a continuously manned location, because of the capital project time cycle. Sufficient knowledge about the safety of the Ferrocyanide Watch List tanks exists at this time such that the USQ has been closed (see Section 4.0). Because of waste aging, it is very likely that all of the ferrocyanide tanks now contain less than the 8 wt% sodium nickel ferrocyanide specified in the fuel criterion for the SAFE category (see also Postma et al. 1994). Characterization (core sampling and data interpretation) is anticipated to place all of the tanks into the SAFE category, because of the low fuel value remaining. Placement of the tanks into the SAFE category means the tanks are candidates for removal from the Ferrocyanide Watch List. This would eliminate the need for continuous pressure monitoring for offgases from a ferrocyanide reaction.

- **Progress During Reporting Period.** A summary of the rationale for not installing pressure monitors in ferrocyanide tanks was prepared and submitted to DOE this quarter (Payne 1994). Low gas generation rates (Fowler and Graves 1994), and the low potential for exothermic ferrocyanide reactions (Postma et al. 1994) indicate that continuous pressure monitoring is not warranted.

- **Planned Work For Subsequent Months.** No further work is planned in this area, pending DOE concurrence with the Westinghouse Hanford Company recommendation not to install pressure monitoring instrumentation in ferrocyanide tanks.

- **Milestone Status.**

  - **July 29, 1994.** Westinghouse Hanford Company completes studies to determine whether continuous pressure monitoring is required for some or all ferrocyanide tanks. A summary of the rationale for not installing pressure monitoring was completed on schedule (Payne 1994).

  - **September 30, 1995.** If required, Westinghouse Hanford Company completes design and prepares for installation of the first phase of pressure monitoring instrumentation.

- **September 30, 1996.** If required, Westinghouse Hanford Company installs pressure monitoring instrumentation and readout capability on all applicable ferrocyanide tanks.

4.4 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."

Characterization of the waste in the ferrocyanide tanks is necessary to: (1) guide further chemical reaction studies with the ferrocyanide waste simulants; (2) determine actual waste chemical and physical properties; (3) determine how the ferrocyanide waste can be safely stored in situ, and classify the tanks by safety category accordingly, until retrieval and disposal actions are completed; and (4) apply the study results to the final remediation of the waste. This information is necessary to resolve the Ferrocyanide Safety Issue.

The important reactive materials present in the ferrocyanide tanks are fuel (ferrocyanides, sulfides, and reduced carbon species such as organic complexants), oxidants (nitrates and nitrites), and inerts or diluents (including phosphates, aluminates, sulfates, carbonates, oxides, and hydroxides). The location of fission products such as ^{137}Cs and ^{90}Sr is important because these products are heat sources and potential source terms in postulated radiological releases from a hypothetical ferrocyanide reaction. The water content of the waste is very important because water's high heat capacity and vaporization heat make it an effective inerting material. Water can prevent a sustained combustion or a propagating reaction; wet ferrocyanide material would require drying before it could react or propagate.

4.4.1 Core Sampling and Analyses

Core Sampling. Both rotary-mode and push-mode core sampling capabilities will be used to obtain core samples from the Watch List tanks. Tanks without saltcake and with relatively soft waste solids can be core sampled by the push-mode method. If a hard saltcake layer is present, rotary-mode core sampling will be used. The first ferrocyanide tank scheduled for rotary-mode core sampling is 241-BY-106.

Each core consists of several 48-cm segments (or portions thereof) depending on the depth of the waste in the tank. The sludge layer in these cores will be divided into four 12-cm subsegments for each 48-cm segment. If the tank contains a saltcake layer, the saltcake segments will be divided into only two subsegments. Process flowsheet knowledge, tank historical data, and results obtained from tests with ferrocyanide sludge simulants are used to supplement the analytical results from core sampling.

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

- **Progress During Reporting Period.** As reported last quarter, push-mode core sampling of tanks 241-C-108 and -111 yielded poor sample recovery (less than 25 vol%). However, visual inspection of the waste recovered indicated that the waste in these tanks is viscous, and retains its shape after extrusion. Because of the difficulty in obtaining adequate push-mode core recovery, these tanks have been scheduled for auger sampling. Samples will be obtained through subsequent 12-cm auger samplings (equivalent to quarter segments). The waste appears viscous enough not to slump into the auger hole during successive samplings.

  The data interpretation report for the three cores taken from tank 241-T-107 was released this quarter (Sasaki and Valenzuela 1994). The most significant item noted is that none of the core samples or subsamples exhibited an exotherm. This is the first tank containing material from the U Plant scavenging flowsheet to be core sampled for the Ferrocyanide Safety Program.

  The ferrocyanide DQO document (Meacham et al. 1994a) was updated and re-released this quarter as a Westinghouse Hanford Company SD. Because the DQO report is a living document and may receive several revisions, the SD format allows the Hanford analytical laboratories to quickly retrieve the most current version for their use.

  A new integrated characterization schedule was finalized this quarter (Stanton 1994). This schedule represents the best estimate of what is achievable. Auger samples from tanks 241-C-108 and -111 will be taken by December 1994. All remaining ferrocyanide tanks are scheduled for sampling by July 30, 1996.

- **Planned Work For Subsequent Months.** Tanks 241-C-108 and -111 will be auger sampled. Readiness preparations for the rotary-mode core sampling truck have taken longer than anticipated and sampling has been rescheduled for October 1994.

- **Problem Areas and Actions Taken.** Push-mode sampling of ferrocyanide tanks 241-C-108 and -111 resulted in poor core recovery. As a result, these tanks will be auger sampled next quarter.

- **Milestone Status.**
  - **February 28, 1994**: Westinghouse Hanford Company completes interpretation of ferrocyanide tank 241-T-107 analytical data and issues a report cleared for public release. This milestone was deferred to August 5, 1994, because of difficulty in interpreting the limited data from core samples with low recovery. A report was completed and issued in August 1994 (Sasaki and Valenzuela 1994).
  - **October 31, 1994**. Westinghouse Hanford Company secures rotary-core samples from ferrocyanide tank 241-BY-106.
  - **June 30, 1995**. Westinghouse Hanford Company obtains core and/or auger samples from four ferrocyanide tanks.
  - **September 30, 1995**. Westinghouse Hanford Company completes data interpretation reports, available for public release, for four ferrocyanide tanks. The data interpretation reports for tanks 241-C-108 and 241-C-111, in addition to the existing data reports on tanks 241-C-109 and 241-C-112 (Simpson et al. 1993a, 1993b), will help provide the technical basis for recommending that the Ferrocyanide Safety Issue be resolved for the four C Farm tanks.
  - **June 30, 1996**. Westinghouse Hanford Company obtains core samples for an additional five ferrocyanide tanks.
  - **September 30, 1996**. Westinghouse Hanford Company completes data interpretation reports, available for public release, for five ferrocyanide tanks.
  - **March 31, 1997**. Westinghouse Hanford Company obtains core samples from the remaining ferrocyanide tanks.
  - **June 30, 1997**. Westinghouse Hanford Company completes data interpretation reports, available for public release, for the remaining ferrocyanide tanks.

Fourier Transform Infrared Spectroscopy Analyses. Fourier Transform Infrared (FTIR) spectroscopy is rapidly becoming the method of choice for demanding applications such as in situ and remote characterization of highly toxic and hazardous materials. Recent developments in FTIR-based fiber optic spectroscopy have provided a new methodology to chemically characterize ferrocyanide-bearing waste. Chemometrics and microprocessors that allow storage and rapid analyses of data have contributed significantly to the development of state-of-the-art fiber optic probes.

- **Progress During Reporting Period.** The FTIR-PAS technology developed at the Ames Laboratory, Iowa State University, was transferred to Westinghouse Hanford Company this quarter. Instrumentation, similar to the Ames Laboratory instrumentation (FTIR-PAS spectrometer and photoacoustic cell), was installed in the 222S Laboratory. The FTIR-PAS system is capable of sample examination from the far infrared to the ultraviolet regions of the light spectrum. A report reviewing the progress in this task and recommendations for future work was released this quarter (Rebagay et al. 1994).

- **Planned Work For Subsequent Months.** Develop ferrocyanide analytical software and complete a hot cell demonstration with actual ferrocyanide waste.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.**

  - **July 30, 1994**: Westinghouse Hanford Company provides an interim letter report on the status of FTIR system performance in analyzing simulants and actual waste material. This task was completed on schedule.

  - **September 30, 1994**: Westinghouse Hanford Company issues a publicly available progress report on FY 1994 FTIR work with recommendations on future work. A report was issued on schedule (Rebagay et al. 1994).

  - **September 30, 1995**: Westinghouse Hanford Company issues a final report on FTIR technology development and demonstration.

  - **September 30, 1996**: Westinghouse Hanford Company deploys an in situ FTIR system, if warranted.

4.4.2 Estimation of Moisture Content

Methods for determining moisture concentrations in ferrocyanide waste tanks are being developed using data analysis and available surveillance systems. Two in situ moisture monitoring technologies are currently being investigated by the Ferrocyanide Safety Program: neutron diffusion and near infrared (NIR) spectroscopy. Additional moisture monitoring technologies, such as copper foil activation, phase change thermal measurements, electrical conductivity, and time domain reflectometry, are being evaluated by other programs.

Neutron Diffusion. Well-logging techniques, coupled with computer modeling, were developed and applied to an existing neutron probe to determine information about moisture levels, material interfaces, and other waste characteristics in the ferrocyanide tanks. Based upon this experience, a new, improved neutron diffusion-based moisture measurement detector system has been developed. This improved system would primarily be used to determine the axial moisture concentration profile within the ferrocyanide tanks.

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

Two methods are generally used in the measurement of moisture concentration around wells using neutron diffusion. The first method, the moisture gauge, has a short source-to-detector spacing (near field) on the order of 0 to 6 cm. The response of a moisture gauge is characterized by an increase in detector response with increasing moisture concentration of the surrounding medium. The second method, the neutron log, often has two detectors with longer source-to-detector spacings: 20 to 50 cm (far field). The detectors in a neutron log arrangement exhibit a decreased response to increased moisture concentrations. The detector placed at the shorter spacing is used to correct the response of the longer-spaced detector for borehole effects.

The tank moisture measurements are taken from within LOWs. The LOWs are installed, sealed pipes that extend from the riser top through the tank waste to near the tank bottom. The LOWs allow axial information about the surrounding waste materials to be obtained using certain detectors.

- **Progress During Reporting Period.** Using the knowledge gained from computer modeling, in situ measurements, and experimental calibration data with the current in-tank neutron probe (Watson 1993), prototype moisture measurement neutron probes have been designed and developed. This system consists of three neutron probes: a near-field thermal neutron probe, a far-field thermal neutron probe, and a far-field epithermal neutron probe. The near-field thermal probe exhibits both improved moisture sensitivity and vertical spacial resolution over the existing in-tank liquid level neutron probe. The far-field thermal probe provides additional information about the geometry and moisture content of the waste surrounding the LOW. The far-field epithermal probe is needed to provide moisture measurements that are unaffected by the thermal neutron absorber content of the LOW or surrounding waste. A cleared report documenting the design of the moisture monitoring probes and the changes made to the existing surveillance vans was completed this quarter (Finfrock et al. 1994).

  Developmental testing was required to assemble the neutron probe moisture concentration monitoring system. These tests included component level tests designed to assure that the preamplifier, high voltage supply, and detector were operating satisfactorily, both individually and as a unit. The tests were designed to demonstrate that the system should be functional in the expected waste tank environment. The results of these tests show that the system is fully operational. The system has not yet undergone a complete moisture calibration because of the unavailability of acceptable waste moisture simulants. Full moisture calibration tests of the system will be finished after the preparation of appropriate ferrocyanide waste moisture simulants is completed.

- **Planned Work for Subsequent Months.** Final calibrations will be performed on the completed neutron probe prototypes. Moisture concentration waste simulants will be prepared containing about 15, 20, and 25 wt% water. Computer modeling will be performed to compare calculated predictions with the measurements. These same computer models will then be adapted to perform tank waste modeling. Results of the tank waste modeling will assist with interpretations of the tank scans. This task will correlate all scan data with modeling results to produce best estimate moisture profiles of tank waste.

- **Problem Areas and Action Taken.** Simulant preparation has been delayed because of a problem with the first container. The waste moisture simulant barrel reacted with the barrel wall, causing a leak. The simulant was not salvageable. An identical simulant mixture is being prepared in a barrel containing an inert polyethylene liner to prevent the simulant from reacting with the container.

- **Milestone Status.**

  - **September 30, 1994:** Westinghouse Hanford Company fabricates a documented working prototype moisture monitoring neutron probe system. This milestone was completed on schedule (Finfrock et al. 1994).

  - **September 30, 1995:** Westinghouse Hanford Company completes installation and deployment of the first phase of the neutron moisture monitoring system and initiates monitoring.

  - **September 30, 1996:** Westinghouse Hanford Company completes installation and deployment of the neutron moisture monitoring system for routine monitoring in ferrocyanide tanks.

Near Infrared Spectroscopy. Infrared spectroscopy of samples containing water is normally dominated by strong absorption from the water molecules. The absorption is strong enough that near-infrared light backscattered from a surface can be used to determine the water content. In a Phase I feasibility study, the University of Washington Center for Process Analytical Chemistry (CPAC) examined the moisture sensitivity of three optical regions: visible (450 to 1,000 nanometers), near-infrared (1.0 to 2.5 microns) and mid-infrared (2.5 to 25 microns).

For waste tank applications, two methods of implementing the NIR optical absorption are being investigated: a spectroscopy system with remote fiber optic probe, and a spectroscopy system with "open-path" optics (optical camera) concepts. Both of these implementation concepts make use of optical reflectance and spectral processing to extract moisture data. This work showed that the NIR region exhibited a very strong absorption that could be instrumented with conventional fiber optics, detectors and other optical components for sensing moisture content.

The Phase 2 CPAC work showed that for a tank-scale demonstration of the remote, non-contact camera concept, adequate sensitivity exists to consider a non-contact camera type moisture sensing system. This work also showed that particle size and chemical changes in the waste increase the measurement error, but it is still possible to obtain moisture readings within a ± 5 wt% accuracy envelope using the reflectance spectrum. These interferences caused a slight increase in the moisture prediction error, but did not present a technical roadblock for this optical measurement concept. This atmospheric absorption would not be a factor in a fiber optic implementation concept.

The remote fiber optic probe system has several Hanford Site applications, including as a hot cell screening tool and as an end-effector for the Light Duty Utility Arm or Cone Penetrometer system for in situ waste tank use. A second concept being investigated is the "open-path" concept where a sensitive NIR detector and powerful NIR source would be combined with a scanner system to provide moisture content of a tank's waste surface. Moisture data would be obtained as a function of surface position much the same way that temperature contours are obtained using thermal cameras.

- **Progress During Reporting Period.** NIR calibration spectra were obtained this quarter using four simulants (representative of 241-BY-104 saltcake, 241-SY-101, and T Plant Top and Bottom sludges). The moisture content of the test simulants ranged from 0 to 50 wt%. Moisture validation for each sample was completed using a standard thermogravimetric method. These simulants were chosen for this calibration because each represents a different type tank material. For example, the 241-BY-104 is a saltcake material, with moisture ranging up to about 24 wt%. The T-Plant simulants are representative of slurry types of materials and could hold over 50 wt% moisture.

  The spectra were truncated to a spectral range of 1,250 to 1,500 nanometers and Partial Least Squares (PLS) fit models calculated for the ensemble of simulants with their different moisture contents. Results indicated that moisture can be determined to ± 5 wt% for all of the simulants over a 0 to 60 wt% range. PLS models built for each specific simulant demonstrated an even better prediction error (± 2 to 3 wt%) with only a five-factor PLS model.

  Some software errors and system hardware failures were experienced while obtaining the calibration spectra. Because of delays caused by the software and hardware problems, a decision was made not to transfer the NIR system to the hot cell this quarter. Only cold calibration tests with tank simulants were completed this quarter. The next step in development of the NIR technology is to demonstrate moisture sensing with actual waste tank materials. This will be done by starting with the PLS models developed for simulant materials and adding the actual tank spectral data to new PLS models.

CPAC issued an interim report on their Phase 3 studies showing the impact of atmospheric moisture on moisture determination from NIR spectra. Tank dome space water vapor will be a strong interference in the implementation of the NIR system as a non-contact camera sensor. The impact of water vapor can be compensated for by explicitly including the water vapor spectral response in the NIR spectra used to generate the PLS calibration model. PLS models constructed with NIR spectra, where water vapor absorption was included as an interferant, predicted moisture from NIR spectra with root mean square error fits in the range of 0.729 to 0.743 wt% moisture. The models worked equally well with or without the water vapor interferant present in the sensed NIR spectra.

Interim results of the University of Idaho contract to examine probe and material interactions indicate that the optical backscattering in tank waste materials is not limited to micron levels, but that depths are on the order of 10 to 100 microns, depending on moisture content. This confirms earlier findings where sample size had to be adjusted to obtain accurate NIR spectra with wet simulant materials.

- **Planned Work for Subsequent Months.** Hot cell testing on actual waste materials will be conducted with the NIR system. Results will be used to adjust the PLS calibration models. Based on these test results, a decision will be made on the status of the NIR and its potential use for hot cell analyses of actual waste tank materials.

- **Problem Areas and Action Taken.** None.

- **Milestone Status.**

  - **March 31, 1994:** CPAC completes Phase 2 surface monitoring interference study/scale-up report. This milestone is complete and a report was publicly released this quarter (Reich and Veltkamp 1994).

  - **December 30, 1994:** CPAC completes Phase 3 surface monitoring work and provides a report.

  - **September 30, 1995:** Westinghouse Hanford Company completes the surface moisture measuring development work and the in-tank demonstration test.

- **September 30, 1996:** Westinghouse Hanford Company initiates installation of surface moisture monitoring equipment if the demonstration test is successful and the need is warranted.

- **September 30, 1997:** Westinghouse Hanford Company completes installation of the surface moisture monitoring system, if warranted.

4.4.3 Preparation and Characterization of Ferrocyanide Waste Simulants

Ferrocyanide waste precipitates are being prepared and analyzed to determine the composition, physical properties, and chemical reaction properties of simulants that represent ferrocyanide waste stored in SSTs. The analytical results from these simulants, along with analyses of actual tank waste samples, waste tank monitoring, and waste modeling, provide information to characterize with a great deal of assurance safety concerns relating to the sludge in each of the ferrocyanide tanks.

Five waste simulants (without radioactive species) are being used to represent the variety of waste produced in the mid-1950s and stored in SSTs. Ferrocyanide waste produced at the Hanford U Plant is represented by U Plant 1 and U Plant 2 test mixtures. The U Plant 1 waste simulant represents 41 of 59 batches and the U Plant 2 simulant represents 9 of 59 batches of U Plant waste. The average U Plant batch volume was about 2,300,000 L. The other nine batches of U Plant waste are expected to have a ferrocyanide concentration between that of U Plant 1 and U Plant 2. A test mixture representing these batches will not be prepared and tested.

The In Farm flowsheet waste (in four C Farm tanks) is represented by In Farm 1 and In Farm 2 test mixtures. The In Farm 1 test mixture is representative of one batch (expected to have the greatest ferrocyanide concentration) of the 29 In Farm batches processed in the 1950s. In Farm 2 is representative of 11 intermediate ferrocyanide concentration batches of the 29 In Farm batches. An average-sized In Farm batch was approximately 1,500,000 L. It should also be noted that 6 of these 29 scavenging batches did not contain any ferrocyanide, but sodium sulfide was added to enhance precipitation of ^{60}Co.

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

Three main adjustments from the actual processes used in the 1950s were made in the laboratory scavenging preparation method to provide waste simulants representative of ferrocyanide sludges. These changes are as follows: (1) the solution concentrations were adjusted to include nitrite at a 1:3 molar ratio of nitrite/nitrate, to account for nitrite buildup over time in the waste by radiolysis of nitrate; (2) the waste simulants prepared for characterization do not contain radioactive isotopes present in actual waste, because of the difficulty in working with radioactive materials; and (3) the settled waste simulants from the laboratory scavenging process were typically centrifuged at a force of ~2,500 gravities to mimic an equivalent 30-year settling period.

The moisture content of ferrocyanide sludge is very critical in preventing exothermic ferrocyanide/nitrate-nitrite reactions. Studies are underway to evaluate the moisture retention properties of ferrocyanide simulants as they relate to possible waste tank leaks, tank stabilization by pumping, and possible evaporation from exposed surfaces.

- **Progress During Reporting Period.** Relative humidity experiments were concluded and a report published this quarter (King 1994). Results show that waste simulants will slowly dry at a rate proportional to the relative humidity difference between the sludge and the dome space. If the relative humidity in the dome space dropped below the equilibrium value with wet sludge, then the sludge could slowly dry (globally). In a ferrocyanide tank situation, drying is limited by surface area and air exchange with the outside atmosphere. Substantial drying could not occur in a reasonable time frame (Epstein et al. 1994).

  The rate of evaporative moisture loss from saltcake (241-BY-104), U Plant, and In Farm simulants were measured during the experiments. The simulants were exposed to 30% relative humidity at 25 °C for over 4,000 hours. The samples were weighed periodically and the moisture evaporation estimated from the weight loss. Results indicated that the simulants retain substantial moisture even under these drying conditions. The saltcake and In Farm sludge simulants retained greater than 7 and 5 wt% moisture, respectively. Some of the weight loss during the U Plant test was attributed to decomposition reactions. Therefore, results from the U Plant test were indeterminate.

  Drying depends on the rate of heat conduction to the moisture evaporating surface, and on the amount of heat available to supply latent heat for vaporization of water. On the other hand, drying rate is limited by how rapidly moisture can flow to the surface, as a consequence of hydraulic gradients acting within the sludge. Permeability of the sludge medium also determines how rapidly moisture can replenish a drying surface.

  A report evaluating the three simulant drying methods was publicly released this quarter (Bredt and Scheele 1994). The three drying methods were: 60 °C for 24 hours under a 51-cm vacuum, 105 °C for 24 hours, and 120 °C for 18 hours. Samples of In Farm simulant were dried using the three methods and the bound water was measured by thermogravimetric analyses. The bound water content for the three drying methods was 8.7, 9.7, and 7.6 wt%, respectively.

- **Planned Work for Subsequent Months.** Modeling of the drainage properties of the simulants will continue. Experiments will be conducted to measure consolidation as a function of water evaporation. The quantitative information

from the drying experiments will be used in developing a model in FY 1995 for evaluating the moisture retention in a tank profile. Ultimately, the objective is to estimate how fast and how much water could evaporate from ferrocyanide sludge if exposed to a relative humidity deficit.

- **Problem Areas and Actions Taken.** None.

- **Milestone Status.**

  - **March 31, 1994:** PNL issues a publicly available report on the evaluation of the three waste simulant drying methods. This milestone was delayed because some of the moisture analyses had to be repeated. This milestone was completed this quarter (Bredt and Scheele 1994).

  - **May 31, 1994:** Westinghouse Hanford Company issues a report, available to the public, on the chemical and physical properties of the T Plant ferrocyanide waste simulant. A report on testing of T Plant material was released ahead of schedule (Fauske and Jeppson 1994).

  - **September 30, 1994:** Westinghouse Hanford Company completes drainage tests on ferrocyanide waste simulants and issues a publicly available report on modeling and moisture retention of ferrocyanide sludge. This effort was combined with the hot spot task (Section 4.1.3) to produce a comprehensive report on ferrocyanide sludge dryout (Epstein et al. 1994). This milestone was completed on schedule.

  - **September 30, 1994:** Westinghouse Hanford Company issues a publicly available report on the effects of relative humidity on moisture retention in ferrocyanide waste. A report was released this quarter, on schedule (King 1994).

  - **September 30, 1995:** Westinghouse Hanford Company issues a publicly available report evaluating water loss as a function of relative humidity.

4.5 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."

Chemical reaction studies on ferrocyanide waste simulants are being conducted by Westinghouse Hanford Company, Fauske and Associates, Inc. (FAI), PNL, and Los Alamos National Laboratory (LANL). Westinghouse Hanford Company and PNL have produced flowsheet simulant materials for testing and characterization. FAI is conducting adiabatic calorimetry and propagation tests on these same flowsheet materials. The test program at LANL was completed in FY 1993.

4.5.1 Chemical Reaction Studies at Pacific Northwest Laboratory

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

- **Progress During Reporting Period.**

  Aging Studies. A report summarizing FY 1994 progress was publicly released this quarter (Lilga et al. 1994). Experiments included determining the effect of ferrocyanide concentration on the hydrolysis behavior of In Farm 1B (IF-1B) ferrocyanide waste simulant in a gamma field. Samples containing half (0.25 g) and twice (1.0 g) the usual amount of IF-1B were added to eight vessels containing 25 mL of 2 molar sodium hydroxide solution. The vessels were purged with argon, sealed, and six were placed in the gamma pit and irradiated at 1×10^5 Rad/h gamma for three weeks at 90 °C. The remaining two vessels were not irradiated. Individual vessels were removed from the gamma field at various times, cooled, and sampled for ammonia in the gas and solution phases.

  Figure 4-1 compares ammonia concentration in solution for each experiment. Following an initial induction period, the data show that more ammonia is produced when more IF-1B is present, ammonia being a product of cyanide hydrolysis. A similar induction period was observed for all experiments until about 7 days of reaction, when the ammonia concentration began to increase rapidly. Ammonia concentration behaved as expected until day 12, when the solution containing the highest initial ferrocyanide concentration showed a rapid decrease in dissolved ammonia. The decrease was more rapid than could be accounted for by gamma radiolysis of ammonia. It is possible that ammonia binds to either iron or nickel, decreasing the amount detected.

  A hydrolysis experiment using IF-1B in the presence of an aluminum decladding waste simulant was completed during the quarter. The simulant was prepared to mimic the $BiPO_4$ flowsheet neutralized aluminum coating waste, and contained 1.6 molar $NaAlO_2$, 1.5 molar NaOH, 0.9 molar $NaNO_3$, and 1.2 molar $NaNO_2$. The $BiPO_4$ simulant (25 mL) was added to IF-1B (0.5 g), heated to 90 °C, and irradiated at 1 x 10^5 Rad/h. Figure 4-2 shows the ammonia production for this experiment in comparison with a previous hydrolysis experiment conducted in 2 molar NaOH under identical conditions. The initial stages of reaction are identical for both sets of conditions until about 11 days, when ammonia production in the decladding waste simulant experiment levels off. The rate of hydrolysis is apparently impeded by the presence of aluminum; however, this effect has not been confirmed.

In the gamma field, nitrate destruction and nitrite production follow zero-order kinetics yielding the rate constants shown in Table 4-1. The rate of nitrate destruction equals the rate of nitrite formation, suggesting conversion of nitrate to nitrite. The data also show a general trend of increasing rate constant with increasing dose rate, but Figure 4-3 shows that this relationship is not linear.

Table 4-1. Rate Constants for Nitrate Destruction and Nitrite Formation at Various Gamma Dose Rates.

Dose Rate (Rad/h)	Nitrite Formation rate (moles/liter·day)	Nitrate Destruction Rate (moles/liter·day)
1.07 x 10^5	4.5 x 10^{-3}	4.6 x 10^{-3}
4.25 x 10^4	2.9 x 10^{-3}	2.9 x 10^{-3}
8.91 x 10^3	7.8 x 10^{-4}	8.6 x 10^{-4}

A three-month IF-1B hydrolysis experiment at pH 10 was completed during the quarter to investigate the possible fate of ferrocyanide-containing tank waste that did not subsequently come in contact with highly caustic wastes. The experiment was conducted in a carbonate buffer at 60 °C with one vessel in a gamma field of 1 x 10^5 Rad/h and the other under identical conditions without irradiation. The irradiated solution contained 2.96 x 10^{-3} molar NH_3, while the non-irradiated control contained 3.08 x 10^{-4} molar NH_3, an order of magnitude less. Because ammonia is destroyed in the gamma field, the extent of hydrolysis will not be known until further analyses can be conducted.

Figure 4-1. Ferrocyanide Concentration Dependance of Ammonia Production by Hydrolysis in a Gamma Field (1×10^5 Rad/h) at 90 °C.

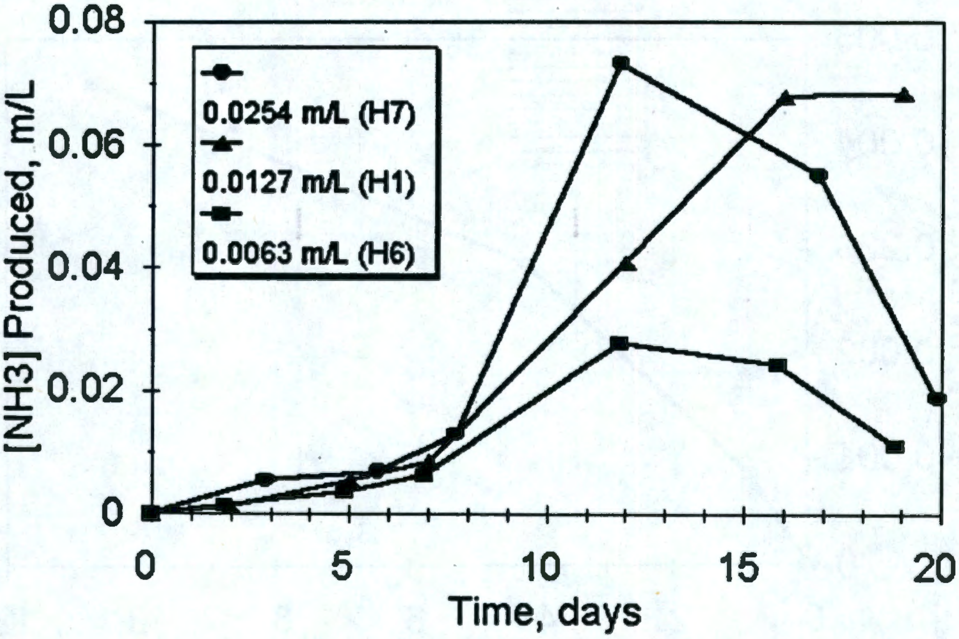


Figure 4-2. Comparison of Hydrolysis in 2 Molar Sodium Hydroxide and in an Aluminum Cladding Waste Simulant.

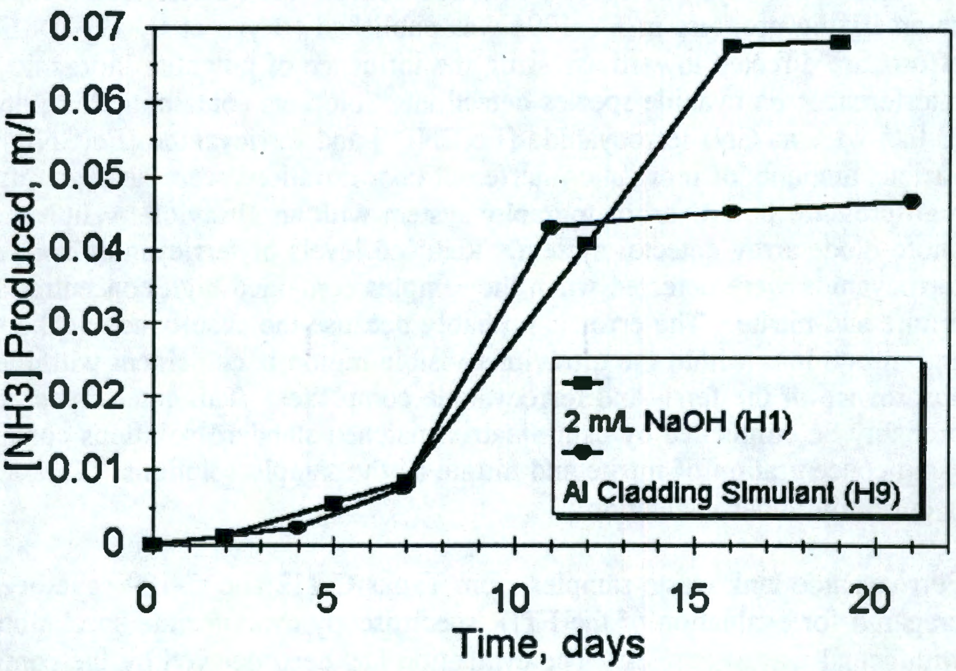
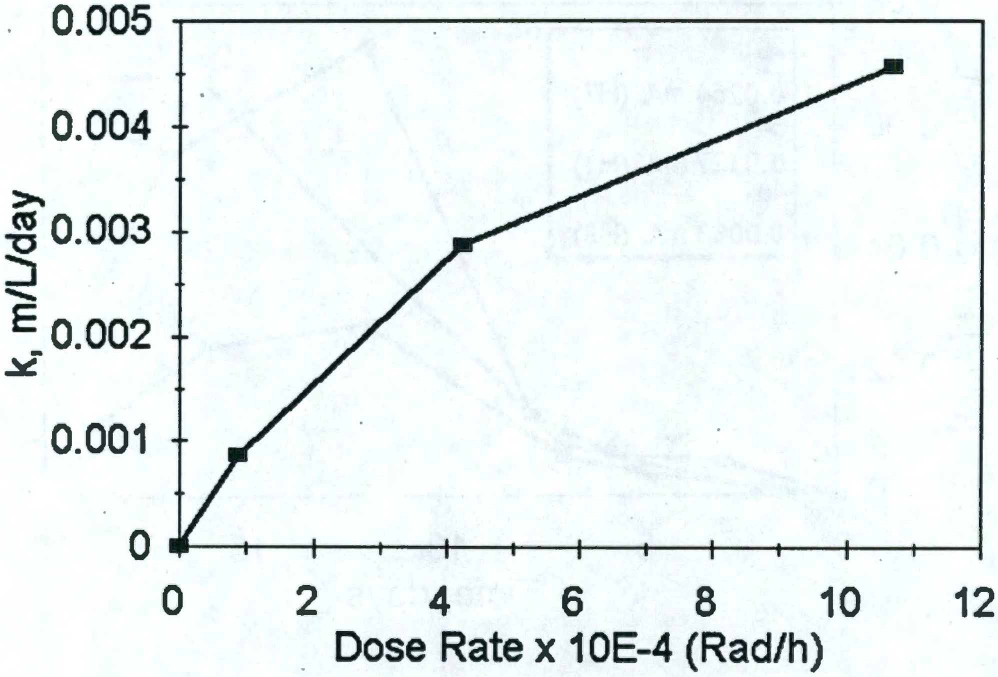


Figure 4-3. Rate Constant for Nitrate Destruction as a Function of Gamma Radiation Dose Rate.



Cyanide Speciation. Work on development of an ion chromatographic analytical method for ferrocyanide species continued during the quarter, and a report summarizing progress in FY 1994 was published (Bryan et al. 1994). Current efforts are directed toward assessing the influence of potential inorganic interferences on cyanide species detection. Solutions containing 250 ppm (0.025 wt% as CN) ferrocyanide [$Fe(CN)_6^{4-}$] and ferricyanide [$Fe(CN)_6^{3-}$] with various amounts of inorganic interferant concentrations were analyzed using the high-pressure liquid chromatography system with an ultraviolet-visible photo-diode array detector system. Reduced levels of ferricyanide and ferrocyanide were detected when the samples contained high concentrations of nitrate and nitrite. The error is probably because the absorbance of the nitrite and nitrate ions within the ultraviolet-visible region is coincident with the absorbance of the ferri- and ferrocyanide complexes. This interference can probably be eliminated by using matrix matched standard solutions containing the same concentration of nitrite and nitrate as the sample solutions. This technique is currently under evaluation.

Ferrocyanide tank waste samples from Tanks C-112 and C-109 have been prepared for evaluation of the FTIR spectroscopy cyanoferrate speciation method with actual waste samples. The evaluation has been delayed by the continuing halt of all radiological laboratory work within the 325 Building.

Determination of Cesium Solubility and the Uptake Capacity of Ferrocyanide Waste Simulants. A report summarizing the influences of cesium, sodium, nickel, and ferrocyanide on the solubility of cesium was published this quarter (Rai et. al. 1994). Tests indicated that cesium does not exhibit retrograde solubility (i.e., decreasing solubility with increasing temperature).

Experimental studies were also conducted to determine the capacity for ^{137}Cs uptake by mixed metal ferrocyanides present in Hanford Site waste tanks and to assess the potential for aggregation of these ^{137}Cs-exchanged materials to form hot spots. A report summarizing the FY 1994 progress was released this quarter (Burgeson et al. 1994).

The results obtained to date indicate that as the mole ratio of cesium to nickel ferrocyanide increases, the effectiveness of nickel ferrocyanide as an exchanger decreases. In the initial scavenging campaign, the mole ratio of cesium to nickel ferrocyanide was approximately 0.006 to 0.003. Under these conditions and with lower ratios, cesium is readily removed from solution. However, at higher ratios of cesium to nickel ferrocyanide, the effectiveness of the nickel ferrocyanide simulant solids as a cesium ion exchanger decreases significantly. However, results from these initial experiments indicate that equilibrium may not have been achieved in all cases. Therefore, selected experiments using longer reaction times are being conducted to assure equilibrium is achieved.

Microconvection Modeling. A report discussing FY 1994 microconvection modeling simulations was published this quarter (McGrail 1994). Results indicated that it is possible for the internal heat generation to establish a bifurcated flow field within the tank. Convective mass transport along the flow streamlines in the flow field would help distribute ^{137}Cs. Therefore, natural mass transport processes do not favor the formation of hot spots.

Comparison of simulated waste with actual ferrocyanide waste. This activity commenced in FY 1994 because waste simulants produced to date represent the actual ferrocyanide waste at the time of its generation over 30 years ago and may not represent the tank waste as it now exists. Because of this concern, Westinghouse Hanford Company requested that PNL compare the measured properties of samples from tanks 241-C-109 and -112 with the ferrocyanide simulants (In Farm 1 and In Farm 2) most representative of the waste added to these tanks in the 1950s.

A report detailing the comparisons was published this quarter (Scheele et al. 1994). Overall, the results indicate that similarity between the simulated In Farm waste relative to the waste in tanks C-109 and C-112 depends on the property of interest. As an example, the In Farm simulants exhibit greater thermal reactivity and have similar qualitative rheological properties, but differ in quantitative rheological properties.

- **Planned Work For Subsequent Months.** Aging experiments will be continued using In Farm flowsheet simulant. Knowledge of factors that impact the free cyanide concentration in solution are important to understanding the mechanism(s) involved in the hydrolysis reactions. Experiments will be conducted to determine factors that may have influenced hydrolysis rates under actual tank waste conditions.

  Cyanide speciation development, including ion chromatography (IC) methods and solution IR methods, will continue until the validated techniques and procedures can be routinely applied to samples in analytical laboratories at PNL and Westinghouse Hanford Company. The studies will include determination of interferences and possible corrections.

- **Problem Areas and Actions Taken.** All laboratory work has been halted within radioactive control areas in the 325 Building since early April. Restart plans were submitted to DOE and restart is anticipated sometime next quarter. The shutdown of radiological work affected completion of the work scope outlined in the FY 1994 test plans.

- **Milestone Status.**

  - **September 30, 1994:** PNL issues report, cleared for public release, on FY 1994 hydrolysis and radiolysis aging experiments with ferrocyanide waste materials. A report (Lilga et al. 1994) was issued on schedule.

  - **September 30, 1994:** PNL issues report, cleared for public release, on solution IR and IC cyanoferrate speciation activities and application for routine measurements in the analytical laboratories. A report on FY 1994 activities has been issued (Bryan et al. 1994), but a final report will not be prepared until all work is complete in FY 1995.

  - **September 30, 1994:** PNL issues a publicly available progress report on FY 1994 work on the solubility of sodium/cesium nickel ferrocyanide compounds. A report (Rai et al. 1994) was completed on schedule.

  - **September 30, 1994:** PNL issues report, cleared for public release, on microconvection modeling and the effects projected to have occurred in the tank waste from this phenomenon during more than 35 years of storage. This milestone was completed this quarter (McGrail 1994).

  - **September 30, 1994:** PNL issues a progress report, available to the public, on FY 1994 studies comparing chemical and physical parameters of ferrocyanide waste simulants with actual waste samples. An interim report (Scheele et al. 1994), summarizing progress in FY 1994 was issued.

- **September 30, 1995:** PNL issues the final report integrating all Ferrocyanide Safety Program hydrolysis and radiolysis aging activities.

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

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

4.5.2 Ferrocyanide Propagation Studies

Ferrocyanide adiabatic calorimetry and propagation tests are continuing at FAI under contract to Westinghouse Hanford Company. The results of these simulant tests are being used to help determine if ferrocyanide waste can ignite and burn to spread and involve additional waste from a potential ignition point. Because the composition of the waste in the storage tanks varies and is not known at all locations, ranges of material compositions have been tested. Present work is focused on the minimum water concentration required to prevent propagation in a stoichiometric ferrocyanide/nitrate simulant mix that represents the most reactive ferrocyanide waste mixture. This data is important for establishment of safety limits for the tank farm ferrocyanide waste.

- **Progress During Reporting Period.** Efforts were directed this quarter at: (1) characterizing a standard ferrocyanide material preparation; and (2) determining the free water content that would bound the onset of propagating reactions for a stoichiometric mix of ferrocyanide and nitrate with no solid diluents. The standard ferrocyanide material was prepared by adding sodium ferrocyanide and nickel sulfate at nominal flowsheet concentrations to distilled water, and adjusting the pH to 9.5. Additional flowsheet chemicals such as phosphates and nitrates were not included in this preparation. The standard material was used to prepare a stoichiometric mix of ferrocyanide and nitrate with no solid diluents for propagation testing.

  The standard material was dried (in vacuum at 60 °C for 48 hours) and analyzed to determine the water remaining (bound water). The bound water was determined to be 17 wt% or 3.76 moles water per $Fe(CN)_6^{4-}$ ion. The water remaining after drying under vacuum did not completely leave the ferrocyanide until heated to 300 °C in an argon atmosphere. The cation composition of the standard is presented in Table 4-2. Cyanide content was determined to be all in the form of ferrocyanide (i.e. no ferricyanide or free cyanide was found). These analyses provided close agreement on balance of charge between anions and cations (1.53 and 1.54, respectively) and on total sample accounted for

(98.3 wt%). The iron and cyanide analyses were in very good agreement for the expected presence of stable hexacyano-ferrate II.

Table 4-2. Composition of Ferrocyanide Standard.

Analyte	Mass After Vacuum Drying (wt%)
Iron	14.0
Nickel	17.1
Sodium	9.1
Cyanide [$Fe(CN)_6^{4-}$]	39.7 [53.7]
Water	17.0
Potassium	0.79
Boron	0.48
Sulfur	<0.15
Calcium	0.016
Chromium	0.005
Lead	0.001
TOTAL	98.2 to 98.4

A report summarizing ferrocyanide propagation tests conducted at FAI was published this quarter (Fauske 1994). Results indicate that the minimum free water concentration required to prevent propagation of a stoichiometric mixture is 20 wt% for an initial temperature of 25 °C. For any mixture of ferrocyanide waste at 25 °C or less, a water content of 20 wt% would be sufficient to prevent a propagating reaction.

- **Planned Work for Subsequent Months. Conduct additional ferrocyanide tests to determine effect of upward propagation, larger diameter sample (50 mm), and initial temperature on effect on onset of propagation.**

- **Milestone Status.**

  - **June 30, 1994:** Westinghouse Hanford Company completes screening tests of In Farm 1 simulant at FAI by varying ferrocyanide and water compositions to define the empirical line that divides propagating and non-propagating mixtures on the triangle diagram (Postma et al. 1994). Tests were completed on schedule at FAI, and a report, cleared for public distribution, was issued this quarter (Fauske 1994).

  - **September 30, 1995:** Westinghouse Hanford Company completes the ferrocyanide calorimetry and propagation test program at FAI as specified by Westinghouse Hanford Company, and prepares reports, available for public release, that support resolution of the Ferrocyanide Safety Issue.

4.6 EMERGENCY 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."

The *Action Plan for Response to Abnormal Conditions in Hanford Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991) was prepared in response to DNFSB Recommendation 90-7.6. The action plan describes the steps to be taken if a temperature increase trend above the tank temperature baseline is measured in any of the ferrocyanide tanks. The document was revised to include the monitoring criteria and responses for abnormal levels of flammable and toxic gases, as well as the reporting requirements, if established criteria are exceeded. The second revision of the plan was released in June 1994 (Fowler 1994).

The *Tank Farm Stabilization Plan For Emergency Response* (WHC 1991) was issued in March 1991. If a radioactive release from a ferrocyanide tank were to occur, it would be detected by one or more radiation monitoring systems. Significant airborne or ground surface releases that spread beyond the immediate tank or tank farm would be detected by the tank farm area radiation detectors. These monitoring systems are on all tank farms. An emergency involving an underground radioactive waste storage tank is a unique event with potentially serious consequences both onsite and offsite. The *Stabilization Plan* provides quick, preplanned actions that can be used to stabilize an emergency event at an underground radioactive waste storage tank.

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

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

- **Progress During Reporting Period.** As noted in previous reports, all of the planned milestones for this task were completed.
- **Planned Work For Subsequent Months.** None planned.
- **Problem Areas and Action Taken.** None.
- **Milestone Status.** All milestones have been completed.

5.0 PROGRAM SCHEDULES AND MILESTONES

Two sets of schedules (Figures 5-1 and 5-2) are presented in this section. The scope of some of the program activities has changed since the FY 1992 program plan (Cash and Dukelow 1992) and the revised implementation plan (Borsheim et al. 1992) were released, and progress should be tracked against the schedules presented here. These are the schedules provided in the March 1994 Ferrocyanide Safety Program Plan (Borsheim et al. 1994).

The first set of schedules reviews milestones for FY 1991 through FY 1994; these have been statused through September 30, 1994. A status line was drawn showing the progress completed on each activity. Actions that have started or been completed are indicated by triangles that are filled in. Work indicated by open triangles has either not started or has not been completed. Diamonds indicate a Tri-Party Agreement milestone.

The second set of schedules reviews out-year milestones for FY 1994 through the expected end of the program in FY 1997. The sequence and anticipated completion dates of the major milestones leading to Safety Issue resolution are presented.

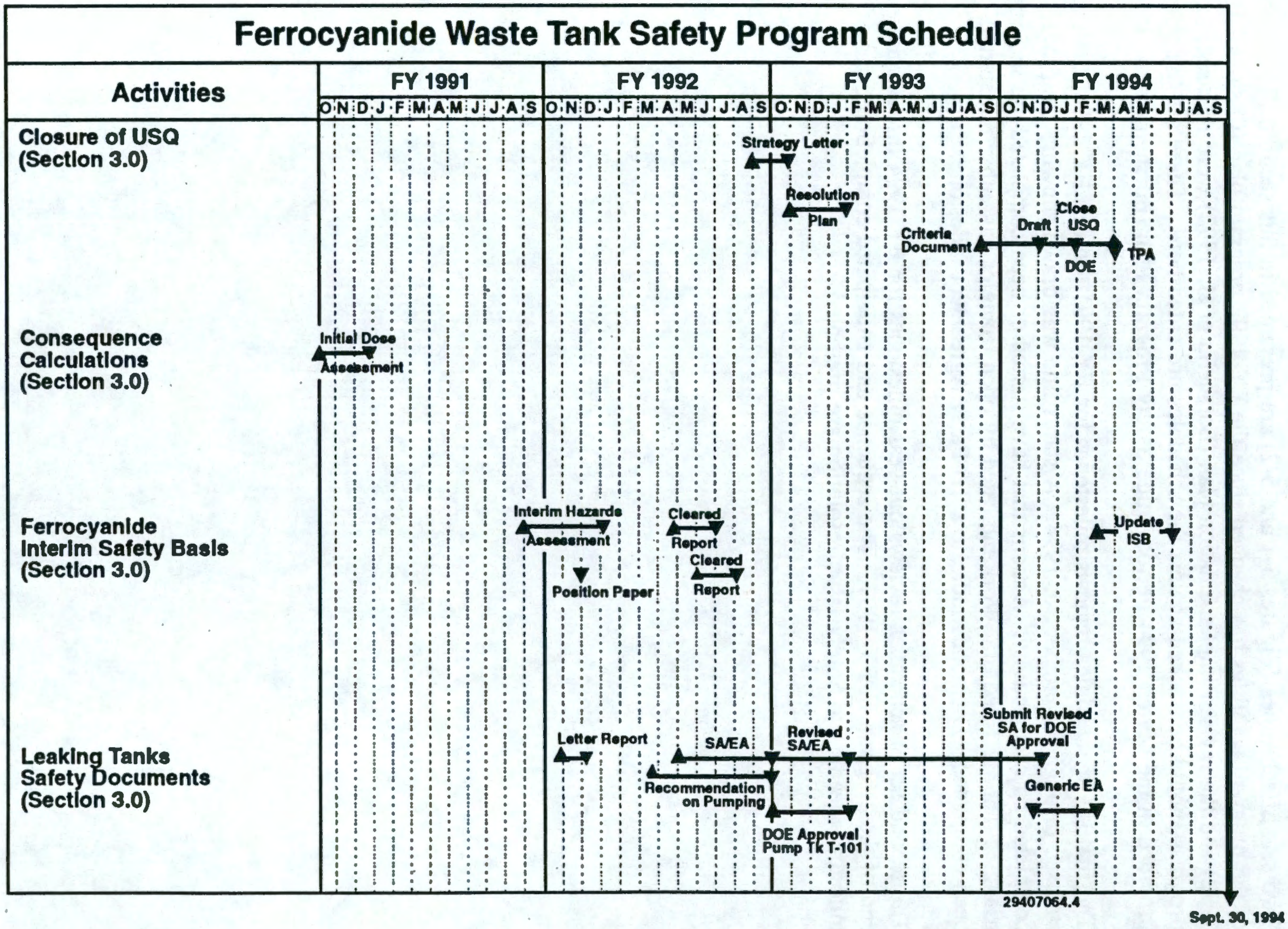


Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 1 of 4)

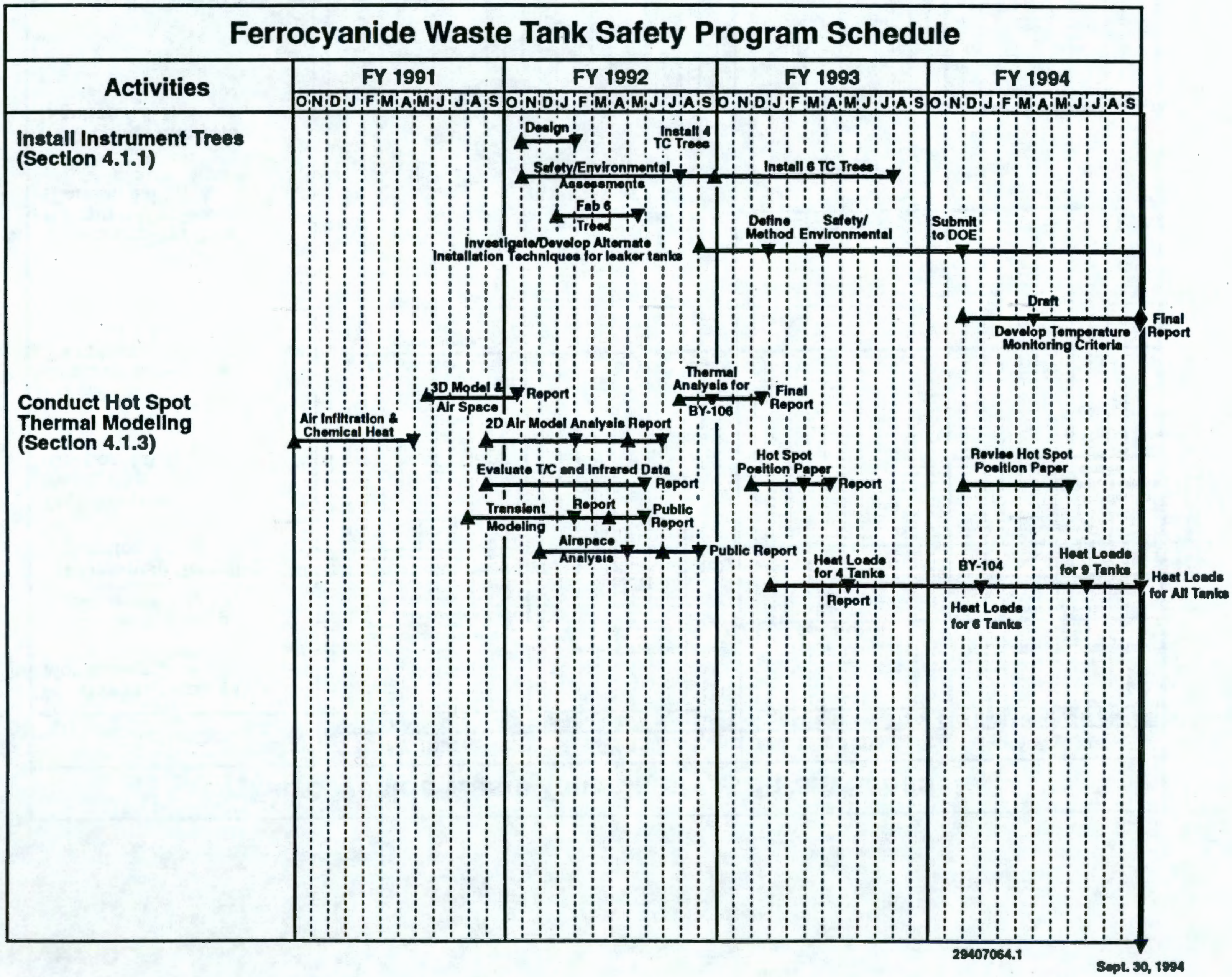


Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 2 of 4)

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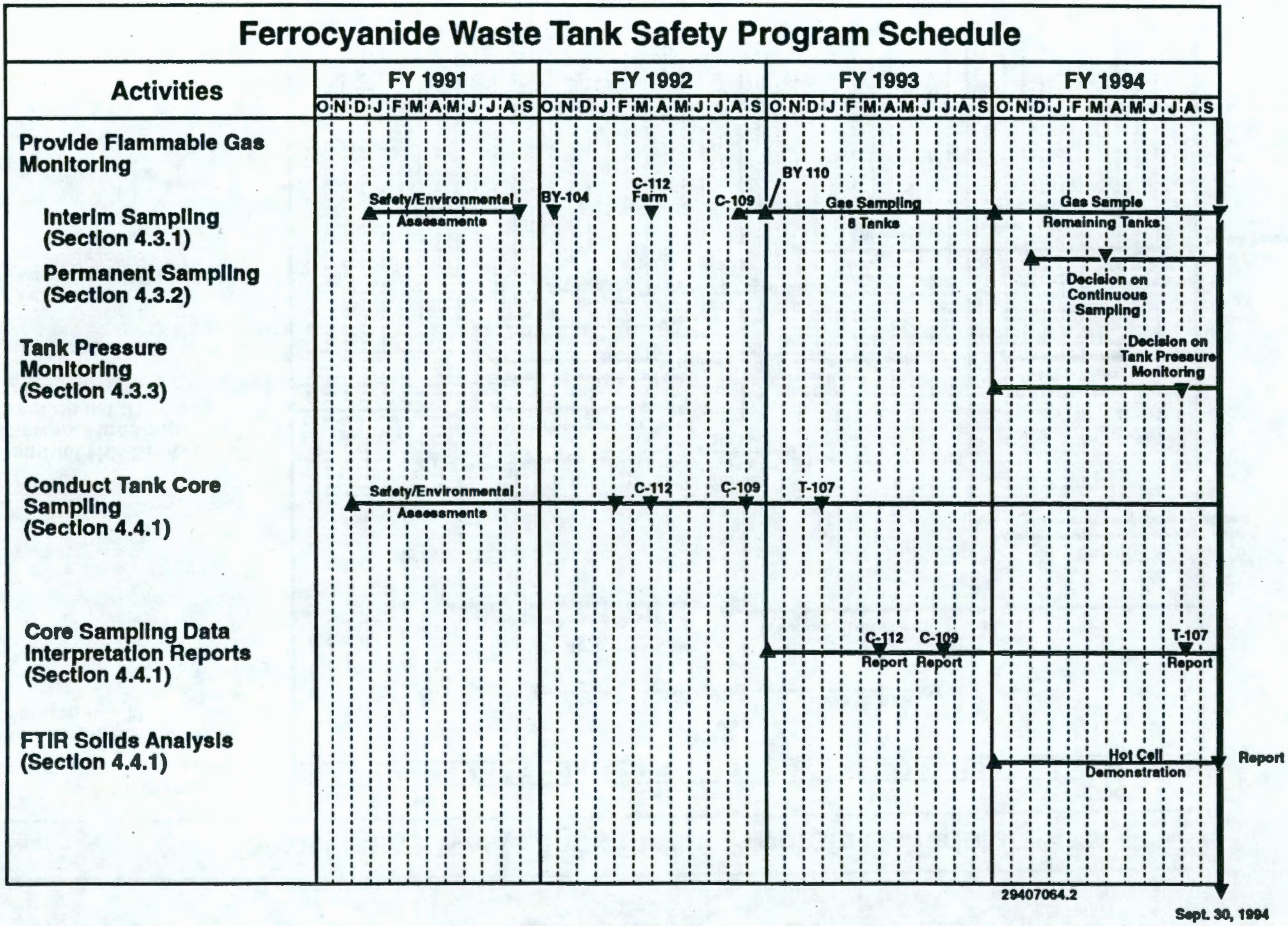

Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 3 of 4)

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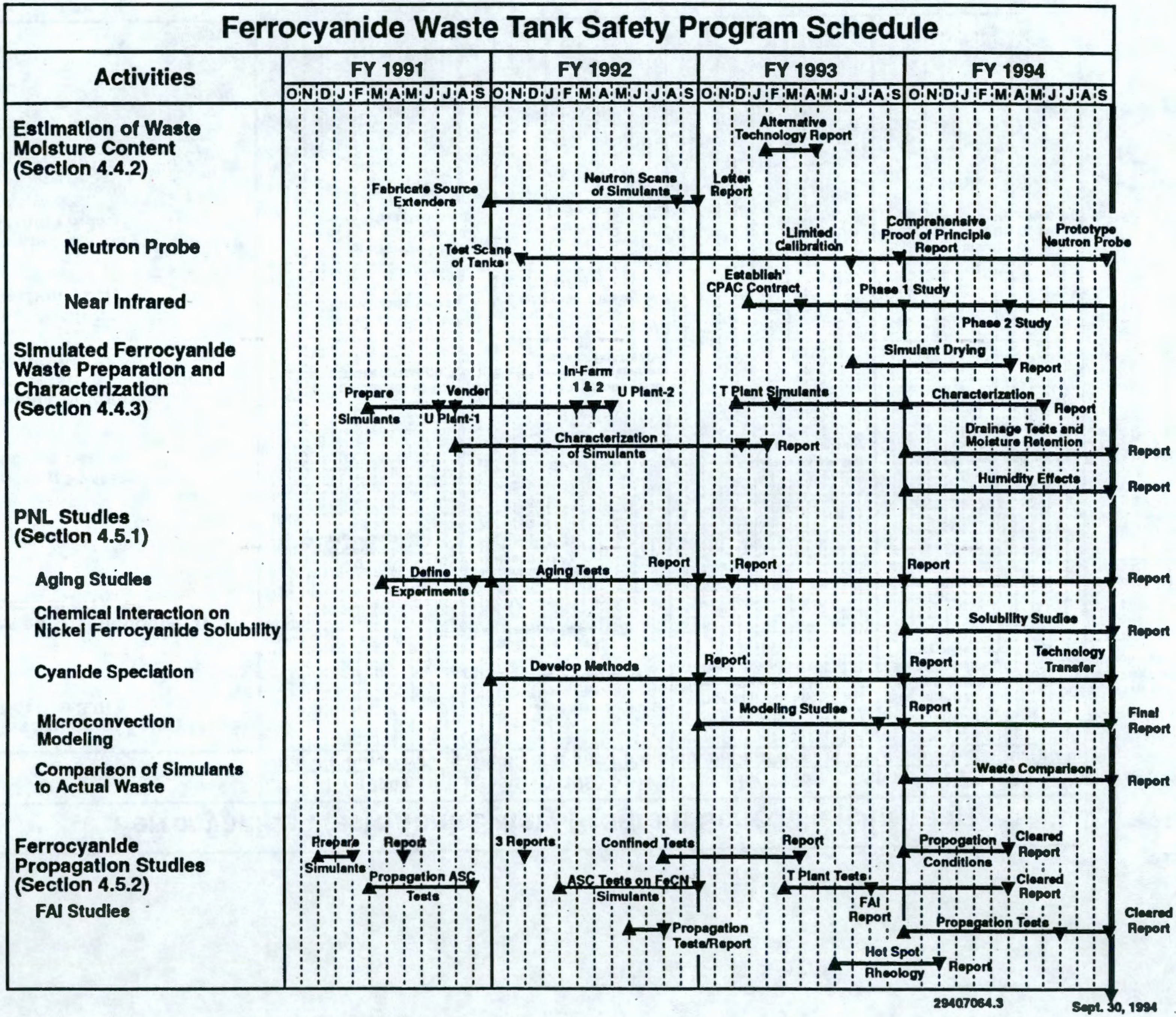

Figure 5-1. Ferrocyanide Waste Tank Safety Schedule. (Sheet 4 of 4)

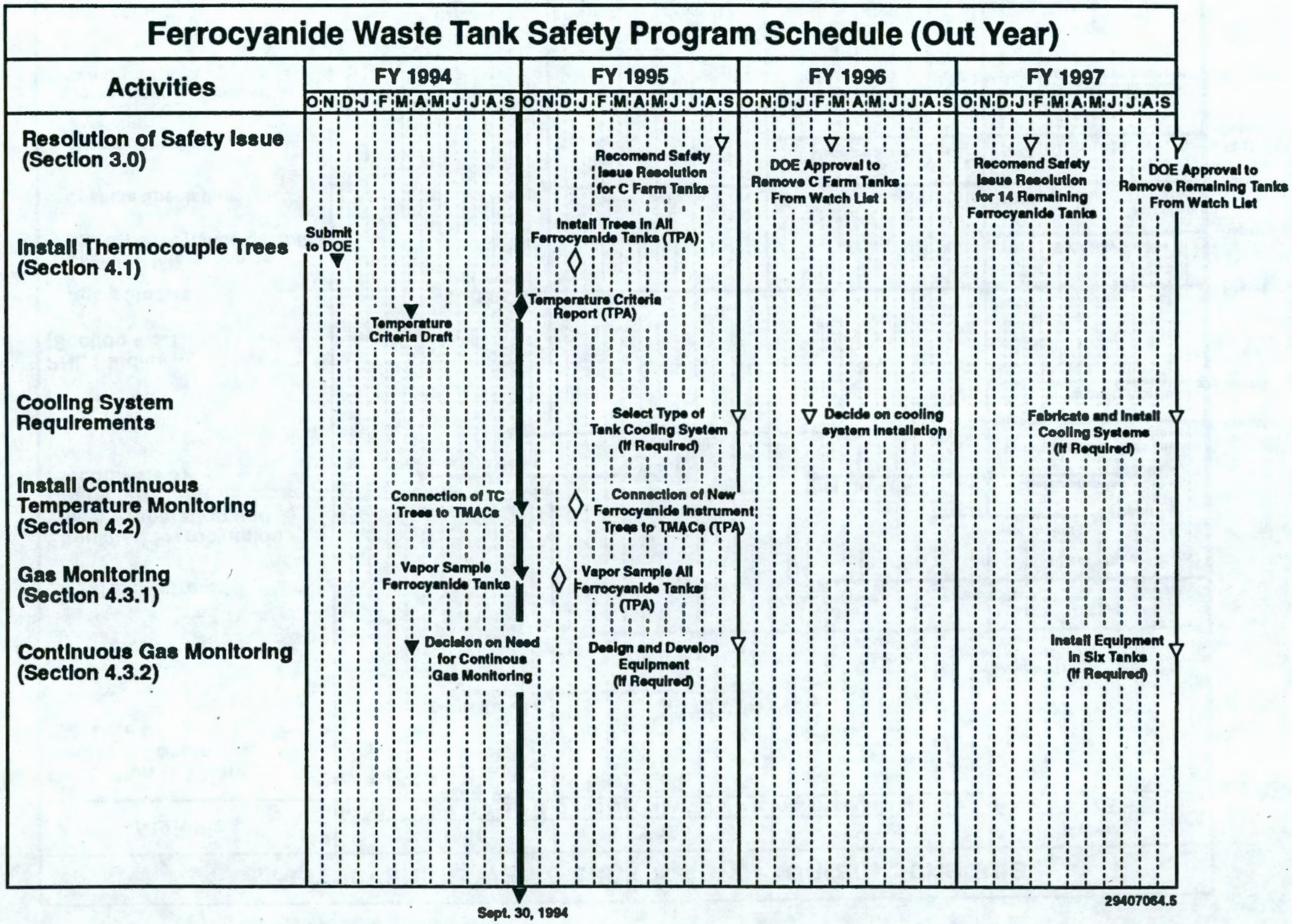

Figure 5-2. Ferrocyanide Waste Tank Safety Schedule (Out Year). (Sheet 1 of 2)

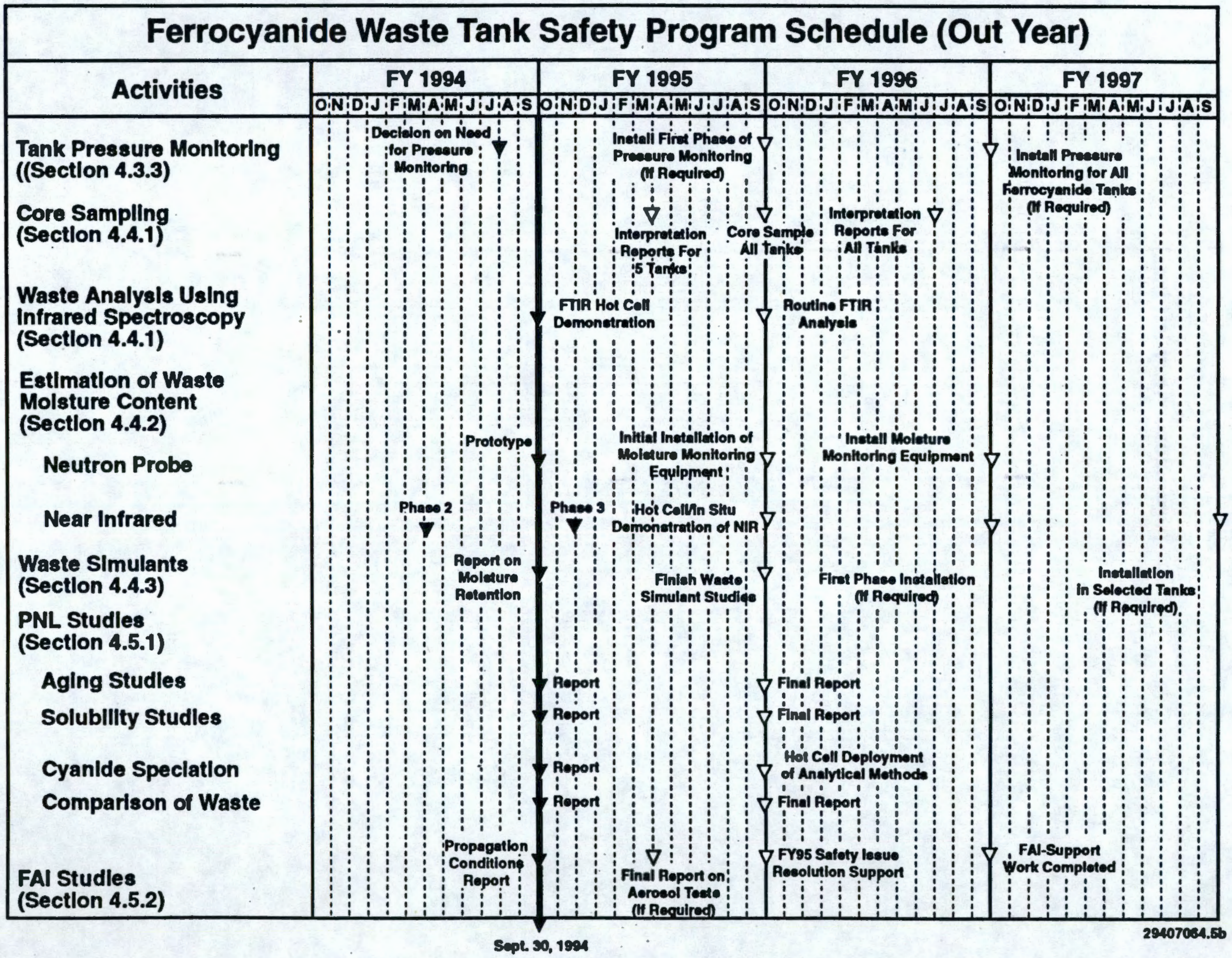

Figure 5-2. Ferrocyanide Waste Tank Safety Schedule (Out Year). (Sheet 2 of 2)

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APPENDIX

FERROCYANIDE TANK INFORMATION SUMMARY

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Table A-1. Summary of Contents and Status of Ferrocyanide Tanks[a].

Tank	Total waste volume (1,000 L)	FeCN[b] (1,000 g-mole)	Heat load (kW)[c]	Maximum temp. (°C)	(°F)	Status of tanks[d]
BX-102	363	<1	0.8	23	73	IS; AL
BX-106	174	<1	0.7	22 22[e]	72 71	NS; Sound
BY-103	1510	66	1.6	27	80	NS; AL
BY-104	1540	83	2.6	52 46[e]	126 114	IS; Sound
BY-105	1900	36	2.6	45 49	113 119	NS; AL
BY-106	2430	70	3.0	53	127	NS; AL
BY-107	1010	42	2.6	36 --[f]	97 --	IS; AL
BY-108	863	58	2.7	42	108	IS; AL
BY-110	1510	71	2.0	48 42[e]	118 107	IS; Sound
BY-111	1690	6	1.6	31[g] 28[e]	87 83	IS; Sound
BY-112	1100	2	1.8	29[g] 32[e]	84 89	IS; Sound
C-108	250	25	1.8	27 28[e]	80 82	IS; Sound
C-109	250	6.8[h]	2.1	30 29[e]	86 85	IS; Sound
C-111	216	33	2.0	23	80	IS; AL
C-112	394	11.5[h]	2.2	31 31[e]	88 87	IS; Sound

Table A-1. Summary of Contents and Status of Ferrocyanide Tanks[a].

Tank	Total waste volume (1,000 L)	FeCN[b] (1,000 g-mole)	Heat load (kW)[c]	Maximum temp. (°C)	(°F)	Status of tanks[d]
T-107	681	5	0.9	23	73	NS; AL
TX-118	1310	<3	1.4	25 --[f]	77 --	IS; Sound
TY-101	447	23	0.9	22	72	IS; AL
TY-103	613	28	1.2	23	73	IS; AL
TY-104	174	12	0.9	22	71	IS; AL

[a] Reflects removal of four ferrocyanide tanks from Watch List in July 1993. Tank information and temperature data as of September 1994.
[b] Inventories from Borsheim and Simpson (1991).
[c] Heat load values from Table 7-1 in Crowe et al. (1993).
[d] IS - Interim Stabilized Tank; NS - Not Stabilized; AL - Assumed Leaker Tank; Sound - Non-Leaking Tank.
[e] Readings from new instrument trees; tank 241-BY-105 already had two trees.
[f] Readings have not yet been taken on this new instrument tree.
[g] Reading from TC element in LOW.
[h] Calculated as ferrocyanide [$Fe(CN)_6^{4-}$] based on the total cyanide values reported in Simpson et al. (1993a, 1993b).

Table A-2. Ferrocyanide Tank Vapor Sampling Summary

Tank	Date Sampled (Type Sample)[a]	Flammability (% LEL)[b]	Organic Vapor (ppm)[c]	NH_3 (ppm)[d]	NH_3 (ppm)[e]	HCN (ppm)[d]	$NO+NO_2$ (ppm)[d]	TNMHC (mg/m^3)[f]	H_2 (ppm)[g]	N_2O (ppm)[g]	CO (ppm)[g]
BX-106	06/17/93 (1)	<1	12	18	--[h]	<2	<0.5	--	--	--	--
BY-103	05/05/94 (2)	<1	1.2	25	30.7	<2	<0.5	5.2	21.4	49.2	<1
BY-104	10/30/91 (*)	1	37	250	--	<2	>10	--	--	--	--
	04/22/94 (2)	<1	26	200	--	--	<0.5	--	--	--	--
	06/24/94 (3)	--	--	--	248	--	--	61	295	201	1
BY-105	05/09/94 (2)	<1	4.9	40	--	--	--	--	--	--	--
	07/07/94 (3)	--	--	--	43	--	--	12.7	--	49.5	0.4
BY-106	05/04/94 (2)	<1	5.7	60	--	--	--	--	--	--	--
	07/08/94 (3)	--	--	--	74	--	--	9.9	43.5	70.6	0.5
BY-107	03/25/94 (2)	3 - 4	67	97	--	--	--	173	692	802	<5
BY-108	03/28/94 (2)	1	97	700	--	--	<0.5	594	644	757	<5
BY-110	09/27/92 (1)	<1	350	612	--	<2	<0.5	--	--	--	--
BY-111	03/25/93 (1)	<1	6.3	10	--	<2	<0.5	--	--	--	--
	05/11/94 (2)	<1	8.9	60	--	--	--	9.6	67	99	<1
BY-112	03/26/93 (1)	<1	5.9	10	--	<2	<0.5	--	--	--	--
C-108	07/23/93 (**)	<1	1.2	<2	--	<2	<0.5	--	--	--	1
	07/07/94 (2)										
	08/05/94 (3)	--	--	--	2.7	--	--	0.3	15.3	344	0.1
C-109	08/26/92 (1)	<1	--	<5	--	<2	<0.5	--	--	--	--
	06/23/94 (2)	<1	1.0	4	--	--	--	--	--	--	--
	08/09/94 (3)	--	--	--	10.1	--	--	0.6	125	369	0.4
C-111	08/12/93 (**)	<1	<0.2	<2	--	<2	<0.5	--	--	--	--
	06/20/94 (2)										
	09/13/94 (3)	--	--	--	0.3	--	--	0.18	12.4	99	--

Table A-2. Ferrocyanide Tank Vapor Sampling Summary (Continued)

Tank	Date Sampled (Type Sample)[a]	Flammability (% LEL)[b]	Organic Vapor (ppm)[c]	NH_3 (ppm)[d]	NH_3 (ppm)[e]	HCN (ppm)[d]	$NO+NO_2$ (ppm)[d]	TNMHC (mg/m^3)[f]	H_2 (ppm)[g]	N_2O (ppm)[g]	CO (ppm)[g]
C-112	03/18/92 (1)	<1	<0.2	<5	--	<2	<2	--	--	--	--
	06/24/94 (2)	<1	<0.2	4	--	--	--	--	--	--	--
	08/11/94 (3)	--	--	--	22.8	--	--	3.4	204	554	0.9
T-107	10/22/92 (1)	<1	24	203	--	<2	<0.5	--	--	--	--
TX-118	07/28/93 (**)	<1	0.3	10	--	<2	0.5	--	--	--	--
	09/07/94 (2)	<1	7.8	28	2	--	--	9.3	97	17.2	2.5
TY-101	08/04/94 (2)	<1	4	12	3	--	--	--	--	--	--
TY-103	08/04/94 (2)	<1	5	30	1	--	--	--	--	--	--
TY-104	08/05/94 (2)	<1	2.5	24	1	--	--	--	--	--	--

[a] Sample Type:

- * Vapor samples taken downstream of tank primary HEPA filter utilizing vapor sampling cart.
- ** Vapor samples taken from in-tank, non-heated tubes utilizing vapor sampling cart (SUMMA™ only - no NH_3).
- 1 Monitoring performed by Industrial Hygiene technicians using three varying length, non-heated sampling tubes into the tank headspace to evaluate for flammability and toxic vapors.
- 2 Sampling is performed by lowering gas and vapor collection devices into the tank headspace; requires a handcart of equipment.
- 3 Sampling involves the mobile vapor sampling laboratory, heated transfer lines, and installation of a water-heated sampling probe into the tank.

[b] Measured using a combustible gas meter; LEL = Lower Explosive Limit.

[c] Measured using a Organic Vapor Monitor (OVM). OVM readings are affected by ammonia; OVM ammonia response is about 13:1, so that 13 ppm of ammonia is indicated as 1 ppm of organic vapors.

[d] Measured using colorimetric (Dräger™) tubes (values are estimated, and not quantitative).

[e] Analyses of ammonia sorbent trap samples.

[f] Total non-methane hydrocarbon (TNMHC) concentrations measured for SUMMA™ canister samples.

[g] Analyses of SUMMA™ canister samples.

[h] -- Not Available.

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