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Quarterly Report on Defense Nuclear Facilities Safety Board Recommendation 90-7 for the Period Ending September 30, 1993

J. E. Meacham
R. J. Cash
G. T. Dukelow

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Westinghouse Hanford Company
P.O. Box 1970
Richland, Washington 99352

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QUARTERLY REPORT ON DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7 FOR THE PERIOD ENDING SEPTEMBER 30, 1993

J. E. Meacham
R. J. Cash
G. T. Dukelow

EXECUTIVE SUMMARY

This is the tenth quarterly report on the progress of activities addressing safety issues associated with Hanford Site high-level radioactive waste tanks that contain ferrocyanide compounds. In the presence of oxidizing materials, such as nitrates or nitrites, ferrocyanide can be made to explode in the laboratory by heating it to high temperatures [above 285 °C (545 °F)]. In the mid 1950s, approximately 140 metric tons of ferrocyanide were added to waste now stored in underground high-level radioactive waste tanks. An implementation plan (Cash 1991)[1] responding to the Defense Nuclear Facilities Safety Board Recommendation 90-7 (FR 1990)[2] was issued in March 1991 describing the activities that were planned and underway to address each of the six parts of Recommendation 90-7. A revision to the original plan was transmitted to the U.S. Department of Energy by Westinghouse Hanford in December 1992, and subsequently to the Defense Nuclear Facilities Safety Board in 1993.

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[1]Cash, R. J., 1991, *Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7*, WHC-EP-0415, Westinghouse Hanford, Richland, Wash.:ıgton.

[2]FR, 1990, "Implementation Plan for Recommendation 90-3 at the Department of Energy's Hanford Site, WA," *Federal Register*, DNFSB Recommendation 90-7, Vol. 55, No. 202, pp. 42243-44.

The 1991 implementation plan will be updated and revised next quarter and re-released as a program plan. The program plan will still address the six parts of Recommendation 90-7; however, it will also include all work in the Ferrocyanide Safety Program. The next quarterly report (December 31, 1993) will be reported against the new program plan.

Milestones completed this quarter include: (1) installation of thermocouple trees into the four remaining non-leaking ferrocyanide tanks (241-BX-106, 241-BY-101, 241-C-108, and 241-TX-118); (2) transmittal of a proof of principle report for neutron probe in situ moisture monitoring; (3) demonstration of Raman spectroscopy in the hot cell on actual tank waste; (4) vapor space sampling of tanks 241-BX-106, 241-BY-101, 241-C-108, -111, and 241-TX-118; (5) public release of a data interpretation report for tank 241-C-109; (6) publication of the document, Ferrocyanide Safety Project: Task 3 Ferrocyanide Aging Studies FY 1993 Annual Report, *PNL-8888; (7) a report on cyanide speciation titled,* Cyanide Speciation Studies FY 1993 Annual Report, *PNL-8887; and (8) a report on microconvection modeling, titled* Ferrocyanide Safety Program: Computational Analysis of Fluid Flow and Zonal Deposition in Ferrocyanide Single-Shell Tanks, *PNL-8876.*

On August 12, 1993, an Administrative Hold was placed on all activities in the Hanford Site tank farms. The hold was ordered to allow a reexamination of tank farms safety procedures and conduct-of-operations. Several tasks in the ferrocyanide program will be delayed as a result of the Administrative Hold. Work directly affected by the hold is identified in the text of this report and include, installation of thermocouple trees, vapor space sampling, stabilization, and core sampling.

Thermocouple trees were installed into the four remaining non-leaking ferrocyanide tanks this quarter, tanks 241-BX-106, 241-BY-101, 241-C-108, and 241-TX-118. Comments from the U.S. Department of Energy, Richland Operations Office were incorporated into the safety and environmental assessments for installation of thermocouple trees into the leaker tanks. The predecisional safety and environmental assessments were transmitted to the U.S. Department of Energy, Headquarters in September 1993.

Moisture monitoring proof-of-principle testing for the neutron probe was completed this quarter. Neutron scans were performed in ferrocyanide tanks 241-BY-107, -110, and -111. Results of the scans suggest that the sludge in these tanks contained a uniformly wet sludge with a lower water content saltcake layer on top. Scan data obtained in the saltcake region of tank 241-BY-111 revealed an air annulus between the liquid observation well and saltcake. The air annulus was estimated to range in radius between 12 to 18 cm in the saltcake.

The Center for Process Analytical Chemistry at the University of Washington has completed the first phase of a proof-of-principle study examining potential photo-optic techniques for in situ moisture monitoring. The study concluded that the near infrared spectral region was the most promising. Results indicated an amount of less than 0.5 wt% moisture could be detected and further development work will concentrate on the near infrared spectral region.

Raman spectroscopy data was obtained in a hot cell from actual Hanford Site waste tank material. The Raman probe showed good potential for indicating homogeneity within a core sample. Spiking experiments with simulants and actual waste revealed a potential lower *detection limit of 0.27 wt% and 0.28 wt% for spikes with sodium ferrocyanide and potassium ferrocyanide, respectively.*

Combustible gas analyses for tanks 241-BX-106, 241-BY-101, 241-C-108, and 241-TX-118 revealed flammable gas concentrations below the detection limit (<1% of the lower flammability limit). Ammonia concentration ranged between 10 and 18 parts per million for tank 241-BX-106 and between 9 and 40 parts per million for tank 241-BY-101. Detectable concentrations of noxious gases were not found in the dome spaces of tanks 241-C-108, -111, and 241-TX-118.

Moisture retention tests and modeling continued this quarter. Centrifugation of simulant at 10 and 20 gravities over a fritted porus media yielded final water concentrations of 47 and 46 wt% respectively. A preliminary modeling analysis was performed to evaluate ferrocyanide sludge water loss if allowed to gravity drain. The simple model indicated that the sludge would still contain over 40 wt% water even after 200 to 300 years of drainage. All information to date indicates that drainage will not remove water below about 40 wt% from ferrocyanide sludge.

As part of the accelerated safety initiatives, closure of the ferrocyanide Unreviewed Safety Question has been moved forward to January 1994. Work was started on a ferrocyanide Unreviewed Safety Question closure document this quarter. A draft of the document is scheduled to be submitted to the U.S. Department of Energy for approval by October 1, 1993. Closure of the ferrocyanide Unreviewed Safety Question will rely heavily on strategies *developed by the U.S. Department of Energy and Westinghouse Hanford Company for Unreviewed Safety Question closure and final resolution of the Safety Issue.*

Westinghouse Hanford Company received U.S Department of Energy concurrence for the removal of tanks 241-BX-110, -111, 241-BY-101, and 241-T-101 from the Ferrocyanide Watch List. More information was requested for the removal of two additional tanks, 241-BX-102 and 241-BX-106, from the Watch List. A document, titled Ferrocyanide Safety Program: Rationale for Removing Six Tanks from the Safety Watch List, *was written this quarter to meet DOE's request for further information.*

Aging of ferrocyanide waste continues to be examined as part of the ferrocyanide program. During screening studies conducted this quarter, over 42% of the cyanide in In Farm 1 simulant were converted to ammonia and formate. Results suggested that gamma radiation promotes the hydrolysis reaction. A progress report on waste aging was published this quarter as, Ferrocyanide Safety Project: Task 3 Ferrocyanide Aging Studies FY 1993 Annual Report.

Modeling has revealed that fluid density gradients and/or thermal gradients in ferrocyanide single-shell tanks will result in microconvective mixing. The predicted velocity for fluid convection through the waste and interstitial liquid was 3 m/yr. The effects of diffusion and fluid convection on redistribution of cesium-137 were also evaluated. The report concluded that diffusion and fluid convection would not result in a hot spot of concern.

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LIST OF TERMS

CASS	Computer Automated Surveillance System
CPAC	Center for Process Analytical Chemistry
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DOE-RL	U.S. Department of Energy, Richland Operations Office
DOE-HQ	U.S. Department of Energy, Headquarters
EA	Environmental Assessment
EDTA	Ethylenediaminetetraacetic Acid
EM	Environmental Restoration and Waste Management Division at DOE-HQ
en	Ethylenediamine
FAI	Fauske and Associates, Inc.
FSU	Florida State University
FTIR	Fourier Transform Infrared
FY	Fiscal Year
HEDTA	Hydroxyethylenediaminetriacetic Acid
HEPA	High-Efficiency Particulate Air
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
IDA	Iminodiacetic Acid
LANL	Los Alamos National Laboratory
LLNL	Lawrence Livermore National Laboratory
LOD	Levels of Detection
LOW	Liquid Observation Well
MCNP	Monte Carlo Neutron Photon [Model]
μm	Micrometers
MIT	Multifunctional Instrument Tree
NIR	Near Infrared
NTA	Nitrilotriacetic Acid
PNL	Pacific Northwest Laboratory
ppm	Parts Per Million
PSO	Program Secretarial Officer
RTD	Resistance Temperature Detector
SA	Safety Assessment
SAR	Safety Analysis Report
SRL	Savannah River Laboratory
SST	Single-Shell Tank
TAP	Tanks Advisory Panel
TC	Thermocouple
TMACS	Tank Monitor and Control System
USQ	Unreviewed Safety Question

QUARTERLY REPORT ON DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-8 FOR THE PERIOD ENDING SEPTEMBER 30, 1993

1.0 INTRODUCTION

1.1 PURPOSE

This quarterly report provides a status of the activities underway at the Hanford Site on ferrocyanide waste tank safety issues, as requested by the Defense Nuclear Facilities Safety Board (DNFSB) in their 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 plan was revised and forwarded to the U.S. Department of Energy (DOE) in December 1992 for transmittal to the DNFSB (Borsheim et al. 1992). The plan was subsequently forwarded to the DNFSB in August 1993. All activities in the revised DNFSB *Implementation Plan* are underway or have been completed, and the status of each is described in Section 2.0 of this report.

1.2 QUARTERLY HIGHLIGHTS

- On August 12, 1993, Westinghouse Hanford Company (Westinghouse Hanford) placed an Administrative Hold on all activities in the Hanford Site tank farms. The hold was ordered to allow a reexamination of tank farms safety procedures and conduct-of-operations. Several tasks in the Ferrocyanide Safety Program will be delayed as a result of the Administrative Hold, including installation of thermocouple (TC) trees, vapor space sampling, stabilization, and core sampling.

- TC trees were installed into the four remaining non-leaking ferrocyanide tanks (241-BX-106, 241-BY-101, 241-C-108, and 241-TX-118) this quarter and efforts continue to install TC trees into the 14 "assumed leaker" ferrocyanide tanks. Comments from the U.S. Department of Energy, Richland Operations Office (DOE-RL) were incorporated into the safety and environmental assessments for installation of TC trees into the leaker tanks. The predecisional safety and environmental assessments were transmitted to the U.S. Department of Energy, Headquarters (DOE-HQ) in September 1993.

- Proof-of-principle testing of the neutron probe for moisture monitoring in ferrocyanide tanks was completed this quarter. Neutron scans were performed in tanks 241-BY-107, -110, and -111. Probe response (counts per second) in the sludge region of the tanks was relatively constant and about a factor of three greater than in the saltcake region. Results suggest a uniform water content in the sludge with a lower water content in the saltcake overlaying the sludge. Scan data obtained in the saltcake region of tank 241-BY-111 revealed strong evidence of a changing air annulus between the liquid observation well (LOW) and saltcake. The air annulus was estimated to range in radius between 12 to 18 cm in the saltcake.

- Raman spectroscopy data were obtained in a hot cell from actual Hanford Site waste tank material. Complete interpretation of sample scans from tanks 241-T-111, -107, 241-BY-107, and 241-BX-107 is not complete; however, the Raman probe showed good potential for indicating homogeneity within the core samples. Spiking experiments with simulants and actual waste revealed a potential detection limit of 0.27 wt% and 0.28 wt% for spikes with $Na_4Fe(CN)_6 \cdot 10H_2O$ and $K_4Fe(CN)_6 \cdot 3H_2O$, respectively.

- The Center for Process Analytical Chemistry (CPAC) at the University of Washington has completed the first phase of a proof-of-principle study examining potential photo-optic techniques for in situ moisture monitoring. Near infrared (NIR), mid infrared, and visible light spectral regions were examined for feasibility. The study concluded that the NIR spectral region was the most promising. Results indicated that concentrations of less than 0.5 wt% moisture could be detected in the NIR region. Further development work by CPAC will concentrate on the NIR spectral region.

- A more realistic single-shell tank heat load model was developed this quarter. The model contains several improvements over previously used models including an experimentally measured value for soil conductivity, a curved dome space geometry, and use of a transient thermal history.

- All design for connection of TC trees to the Temperature Monitor and Control System (TMACS) is complete; however, connection of the recently installed TCs has been delayed until the work is authorized under the present Administrative Hold.

- Combustible gas analyses completed this quarter for five tanks (241-BX-106, 241-BY-101, 241-C-108, -111, and 241-TX-118) all showed results below the detection limit (<1% of the lower flammability limit). Ammonia concentration ranged between 10 and 18 parts per million (ppm) for tank 241-BX-106 and between 9 and 40 ppm for tank 241-BY-101. Detectable concentrations of noxious gases were not found in the dome spaces of tanks 241-C-108, -111, and 241-TX-118.

- The data interpretation report for tank 241-C-109 was publicly released this quarter (Simpson et al. 1993a). The data interpretation report for tank 241-C-112 was revised and publicly released this quarter (Simpson et al. 1993b).

- Moisture retention tests using ferrocyanide In Farm waste simulant continued this quarter. Centrifugation at 10 and 20 gravities of the simulant over a glass filter (30 μm openings) yielded final water concentrations of 47 and 46 wt%, respectively. This identified a water content that is well above the minimum empirical value required to prevent propagating reactions (~12 wt%).

- A preliminary modeling analysis was performed to evaluate ferrocyanide sludge water loss if allowed to drain by gravity. The simple model indicated that the sludge would still contain over 40 wt% water even, after 200 to 300 years of drainage.

- As part of the accelerated safety initiatives, closure of the Ferrocyanide Unreviewed Safety Question (USQ) has been moved forward seven months to January 1994. Work started on the Ferrocyanide USQ closure document this quarter. A draft of the document is scheduled to be submitted to the DOE for approval by October 1, 1993. Closure of the Ferrocyanide USQ will rely heavily on strategies developed by DOE and Westinghouse Hanford for USQ closure and final resolution of the Safety Issue.

- Westinghouse Hanford received DOE concurrence in July for the removal of tanks 241-BX-110, -111, 241-BY-101, and 241-T-101 from the Ferrocyanide Watch List. More information was requested for the removal of two additional tanks, 241-BX-102 and 241-BX-106, from the Watch List. A document, *Ferrocyanide Safety Program: Rationale for Removing Six Tanks from the Safety Watch List* (Borsheim et al. 1993), was written this quarter to meet DOE's request for further information.

- Radiolytic and hydrolytic destruction (aging) of ferrocyanide waste continues to be examined as part of the Ferrocyanide Safety Program. During screening studies conducted this quarter, ferrocyanide In Farm waste simulant samples contacted with 4 molar (M) NaOH for three weeks at 90 °C in a field of 1.65×10^5 Rad/hour, resulted in conversion of over 42% of the cyanide groups to ammonia and formate. Results suggest that gamma radiation promotes the hydrolysis reaction.

- Computer modeling predicted that microconvective mixing will occur in ferrocyanide single-shell tanks, because of fluid density gradients and/or thermal gradients. The predicted velocity for fluid convection through the waste and interstitial liquid was 3 m/yr. The effects of diffusion and fluid convection on redistribution of ^{137}Cs were also evaluated. The report concluded that diffusion and fluid convection could not result in a hot spot of concern.

1.3 REPORT FORMAT

The quarterly reports progress of activities under each of the six parts of DNFSB Recommendation 90-7 are arranged in the same order as the original *DNFSB Implementation Plan* (Cash 1991) and the revised *DNFSB Implementation Plan* (Borsheim et al. 1992). The arrangement also follows the same order provided in the recommendation. 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 items of progress:

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

1.4 BACKGROUND

Radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s. During the 1950s, additional tank storage space was required to support the Hanford Site defense mission. To obtain this additional storage volume in a short period of time, while minimizing the construction of additional storage tanks, Hanford Site scientists developed a process to scavenge radiocesium and other soluble radionuclides from tank waste liquids. As a result of implementing this process, approximately 140 metric tons of ferrocyanide were added to a number of single-shell tanks (SSTs).

Ferrocyanide is a complex of ferrous ion and cyanide that is considered nontoxic because it is stable in aqueous solutions. However, in the presence of oxidizing materials, such as nitrates and nitrites, near-stoichiometric amounts of ferrocyanide can explode under special conditions in the laboratory by (1) heating it to high temperatures (above 285 °C); or (2) by an electrical spark of sufficient energy to heat the mixture. The explosive nature of ferrocyanide in the presence of an oxidizer has been known for decades, but the conditions under which the compound can undergo an exothermic reaction have not been thoroughly studied. Because the scavenging process involved precipitating ferrocyanide from solutions containing nitrate, it is likely that an intimate mixture of ferrocyanides with nitrates and nitrites[3] and other diluents exists in parts of some of the SSTs.

Efforts have been underway since the mid-1980s to evaluate the potential for a ferrocyanide reaction in the Hanford Site single-shell tanks (Burger 1989, Burger and Scheele 1988). In 1987, the final environmental impact statement for disposal of Hanford Site waste farms was issued (DOE 1987). The environmental impact statement projected that the bounding "worst-case" accident in a ferrocyanide tank would be an exothermic reaction resulting in a subsequent short-term radiation dose to the public of approximately 200 mrem.

A General Accounting Office study (Peach 1990) postulated a "worst-case" accident, with independently-calculated doses greater than the 1987 DOE environmental impact statement. A special Hanford Site Ferrocyanide Task Team was commissioned in September 1990 to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident. On October 9, 1990, then Secretary of Energy James D. Watkins announced that a supplemental environmental impact statement would be prepared that contained an updated analysis of safety questions for the Hanford Site single-shell tanks (including analysis of a ferrocyanide explosion) (DOE 1990).

[3]Nitrite is formed in the tanks from radiolysis of the nitrate. The ratio of nitrate to nitrite is approximately 3:1 in the ferrocyanide tanks.

Using process knowledge and historical records, 20[4] tanks are currently identified at the Hanford Site that contain 1,000 g-moles or more of ferrocyanide as the $Fe(CN)_6^{4-}$ radical. In October 1990, the hazard posed by potential reactions between ferrocyanides and oxidizers was declared a USQ[5], because the safety envelope for these tanks may no longer be bounded by the existing safety analysis report (Bergmann 1986) and the 1987 DOE environmental impact statement. Work in and around any of the ferrocyanide tanks requires detailed planning, together with the preparation of supporting safety and environmental documentation, and approval by DOE management. These restrictions are safety requirements and significantly increase the time required to complete work or install equipment in the tanks.

[4]The ferrocyanide Watch List formerly contained 24 tanks (Hanlon 1993). However, four tanks were removed from the Watch List in June 1993 and two more tanks are pending removal (Meacham et al. 1993).

[5]The USQ designation is a formal procedure required under specific orders from DOE (DOE 1986; DOE 1991). The USQ orders state, "A proposed change, test or experiment shall be deemed to involve an unreviewed Safety Question if:

- 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

- 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."

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2.0 DEFENSE NUCLEAR FACILITIES SAFETY BOARD IMPLEMENTATION PLAN TASK ACTIVITIES

The revised DNFSB Implementation Plan (Borsheim et al. 1992) addresses each task activity established in response to the six parts of DNFSB Recommendation 90-7. In this plan, each part of the recommendation is stated and then progress of Hanford Site activities relating to that part is described.

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

"Immediate steps should be taken to add instrumentation as necessary to the 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."

2.1.1 Instrument Trees

DNFSB Recommendation 90-7.1 requests that actions be taken to add instrumentation to the ferrocyanide waste tanks to measure waste temperatures and to determine if hot spots exist or may develop.

A strategy was initially developed to provide the temperature instrumentation necessary to monitor conditions in five high concern waste tanks on an expedited basis. The strategy was to (1) repair the existing TC elements (where possible); (2) install new instrument trees that would be fabricated from existing drawings; and (3) install multifunctional instrument trees (MITs) in those tanks that have a limited number of risers available. The MITs would provide temperature monitoring, the capability for gas sampling at three elevations, possible pressure monitoring, and access for deployment of fiber optics inside the tanks if desired. The TC trees would provide temperature monitoring but may not provide the option to obtain any additional data. This strategy was later revised to include only repair of existing TC trees and installation of new instrument trees in ferrocyanide waste tanks. There are no plans to install MITs in the ferrocyanide tanks at this time.

- **Progress During Reporting Period.** Installation of TC trees in the last four non-leaking ferrocyanide tanks (241-BX-106, 241-BY-101, 241-C-108, and

241-TX-118) was completed on July 30, 1993. However, connection of these trees to TMACS was delayed by a Administrative Hold placed on all tank farm operation on August 12, 1993. The Administrative Hold was ordered to allow a reexamination of tank farm safety procedures and conduct-of-operations.

The ultra high-pressure bore heads for installing the first two instrument trees into assumed leaker tanks have been designed, ordered, and received. Resistance temperature detectors (RTD) will be used on these instrument trees, instead of thermocouples. This is primarily because of the longer life of RTDs and their small error bands. The final report for the ultra high-pressure bore head testing has been sent out for review and comments are being incorporated. The fabrication of the first four instrument trees for the assumed leaker tanks has been started. All contracts have been placed with the ultra high-pressure equipment vendor for the equipment required to support tree installations into the assumed leaker ferrocyanide tanks.

A heated vapor sampling tube has been added to the instrument tree design for the assumed leaker ferrocyanide tanks. The heated vapor sampling tube extends from outside the riser, through the instrument tree and into the dome space of the tanks (Figure 2-1). The tube will be heated by circulating either hot water or hot gas around the sampling tube. This added feature of the new instrument tree may eliminate the need to install an additional vapor probe. Vapor sampling using the tree could reduce field efforts and the cost of vapor space characterization. If necessary, the vapor sampling tube can also be used for monitoring pressure in the ferrocyanide tanks.

Planning continued for installation of instrument trees in the assumed leaker tanks. Comments from the DOE on safety and environmental documentation that supports installation of instrument trees into the assumed leaker ferrocyanide tanks were incorporated. The documentation has been sent back to the DOE for final approval.

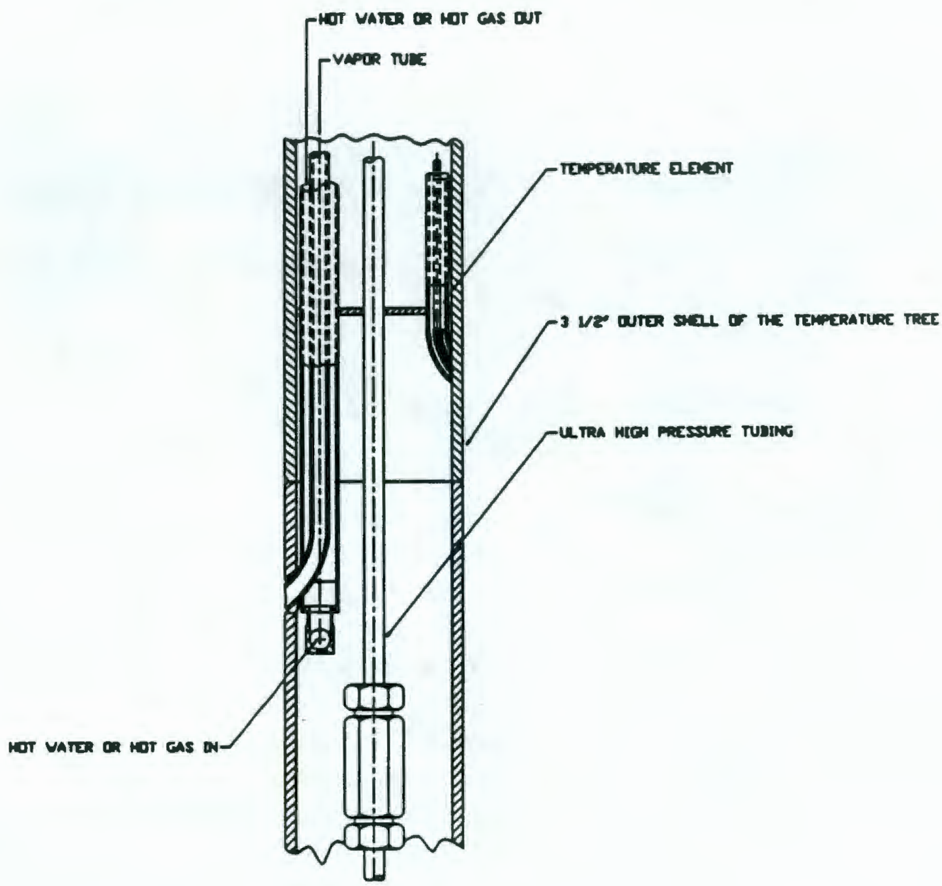
- **Planned Work for Subsequent Months.** Instrument trees for the first four assumed leaker tanks will be fabricated with heated vapor sampling tubes. Two of the four new instrument trees will have the ultra high-pressure bore heads installed in them. Fabrication of these instrument trees will be completed by December 1993.

  The final report for the ultra high-pressure bore head testing will be approved in October 1993.

  All equipment necessary to support the installation of TC trees using ultra high-pressure bore heads will be completed.

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

Figure 2-1. Vapor Sampling Tube for New Thermocouple Tree Design.



- **Milestone Status.**

  - **May 29, 1992**: Install first new TC tree in a ferrocyanide tank, and three additional TC trees by September 30, 1992. The first installation was delayed because the safety and environmental documentation took longer than anticipated for review by DOE and Westinghouse Hanford. The first new TC tree was installed in September 1992.

  - **Septembei 30, 1992**: Install additional TC trees in three ferrocyanide tanks. Three additional TC trees were installed in September 1992 (total of four new TC trees).

- **March 30, 1993:** Submit safety and environmental documentation to DOE for installation of TC trees in assumed leaker ferrocyanide tanks. The safety assessment was completed and transmitted on April 5, 1993. The environmental assessment was finalized and transmitted on June 21, 1993.

- **July 30, 1993:** Complete installation of an additional six TC trees in non-leaker tanks. Two of the six were installed in March and the remaining were installed in July 1993 to meet the milestone.

- **September 30, 1994:** Complete installation of instrument trees in assumed leaker ferrocyanide tanks.

2.1.2 Upgrades to Existing Tank Temperature Monitoring Instrumentation

This task determined the operability and accuracy of previously installed TC elements in the original 24 ferrocyanide tanks at the Hanford Site. The original and newly installed TCs now provide temperature readings 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 was determined by resistance and voltage measurements (Bussell 1991). This work was completed in fiscal year (FY) 1991 with a total of 265 TCs being evaluated. Work in FY 1992 focused on repair and recovery of 92 TCs 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 considered to be complete.

  - **March 31, 1992:** Complete repair of TC elements, as appropriate, on selected ferrocyanide tanks. Only those TC elements in the waste and occasionally one or more elements in the vapor space were slated for repair. The original milestone was delayed because of other high priority safety work and tank farm entry restrictions. This milestone was completed in September 1992.

2.1.3 Alternate Monitoring Technologies

2.1.3.1 Infrared Scanning System. Infrared systems are commercially available from numerous vendors. These systems are sensitive to changes of ±0.28 °C (0.50 °F) or less under ideal conditions, and they may prove to be beneficial 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.

The position paper on the credibility of hot spots and the need for further IR scanning was completed and issued, titled *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Tank Waste by Hot Spots* (Dickinson et al. 1993). This paper examined concentration mechanisms and determined the degree of concentration required to produce temperatures high enough to dry the ferrocyanide waste. The paper concluded that such concentrations were incredible. Based on this report, Westinghouse Hanford recommended to the DOE-RL that no further planning be pursued for infrared scans for the purpose of detecting hot spots.

- **Progress During the Reporting Period.** This task has only one more item scheduled for completion at this time--public release of the report on infrared scans of tank 241-S-110. This report will be released next quarter.

- **Planned Work for Subsequent Months.** The draft report on the infrared scans of tank 241-S-110 will be cleared for public distribution.

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

- **Milestone Status.**

  - **April 10, 1992**: Complete infrared scan of tank 241-S-110. The scan was completed on April 21, 1992, after several delays caused by mechanical and weather-related problems.

  - **May 29, 1992**: Complete a report on the infrared scan of a non-Watch List tank. The report was completed on schedule. DOE comments were incorporated and the document released on January 15, 1993.

  - **December 31, 1992**: Incorporate comments received on report of infrared monitoring of non-Watch List tank 241-S-110 and issue a revised report. The milestone was missed because other safety issues required immediate action. The report was issued to DOE-RL as a predecisional document on January 15, 1993.

- **April 15, 1993**: Make a decision on whether infrared scans will be performed in selected ferrocyanide tanks. A publicly available report concluding that infrared scanning was not required was released on schedule (Dickinson et al. 1993).

2.1.3.2 In Situ Tank Moisture Monitoring. 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 pursued, neutron diffusion and NIR spectroscopy.

Well-logging techniques coupled with computer modeling are being developed and applied to an existing neutron probe to assess this probe and to determine information about moisture levels, material interfaces, and other waste characteristics. The development of a new, improved neutron diffusion based detector system is being investigated. This improved technique would primarily be used to determine the axial moisture concentration profile within the ferrocyanide tanks. The existing neutron probe, used routinely to determine liquid levels, is inserted into closed-bottom LOWs in order to access tank contents.

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 on the order of 0 cm (the source is placed in a ring around the detector) 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). 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 source to detector spacing of the existing probe may be adjusted with the addition of a source extender. Computer modeling of the existing neutron probe system revealed that, in its current configuration, it responds most like a moisture gauge. The probe will operate as a neutron log with the addition of a source extender.

- **Progress During Reporting Period.**

  Neutron Diffusion. Preliminary interpretations of neutron scans obtained in three ferrocyanide tanks (241-BY-107, 241-BY-110, and 241-BY-111) have been completed. Figure 2-2 shows actual neutron probe scans of tank 241-BY-111. The result of dividing the near-field response by the far-field response is superimposed on the actual scans. In order to relate the axial counting rates observed in these scans to an axial moisture concentration profile, the probe response was modeled to best estimate tank 241-BY-104 saltcake and tank sludge for different water concentrations. The density used in the model was 1.6 g/cm^3 for the sludge and 1.7 g/cm^3 for the saltcake.

To perform initial calculations, a calibrated Monte Carlo Neutron Photon (MCNP) model was used, and the LOW material composition was assumed to be identical to that measured in the laboratory. Initial model results for expected near-field (no extender) count rates in high moisture sludge were about 30% lower than those observed. Previous experimental data, obtained with 100% water around the laboratory LOW, reached maximum count rates much lower than those observed in the near-field scans, indicating that the tank LOWs most likely contain less boron than the laboratory sample. This was confirmed by comparisons between the modeling and the data of the probe response to the riser/soil region of the scans. Modeling of an epithermal detector has shown that a system can be assembled that will be insensitive to the boron content in the LOW while maintaining good sensitivity to changing moisture concentrations.

The scans shown in Figure 2-2 have been shifted so that the response is plotted versus the depth in the tank at which the probe is most sensitive to the surrounding media. Five regions of the complete scan have been identified: riser/soil, riser/dome (concrete), tank airspace, saltcake, and sludge. Detector responses in the riser regions of the scan may not be directly compared with responses in the waste because of the air gap, steel riser casing, and the different material compositions and densities. The trends observed in each of these regions are consistent with model expectations.

If the detector system is fully calibrated and the modeled waste composition is representative of the tank material, it should be possible to predict moisture concentrations based on the near- or far-field detector response alone. Further improvement in the moisture prediction is usually gained by making use of the ratio of these two responses. This ratio will often reduce or cancel some systematic uncertainties in the measurement as well as correct for some near-borehole effects.

Figure 2-3 shows the calculated near to far-field response ratio to sludge as a function of the moisture concentration. The curve shown in this figure provides a calculated calibration function that, once confirmed or adjusted by experimental data, may be applied to determine the sludge moisture content as a function of the response ratio of the near and far-field detectors. This calculated calibration curve has not been confirmed with experimental measurements in known moisture waste simulant and must therefore be considered theoretical in nature.

Figure 2-2. Neutron Scans of Tank 241-BY-111 and the Near to Far-Field Response Ratio.

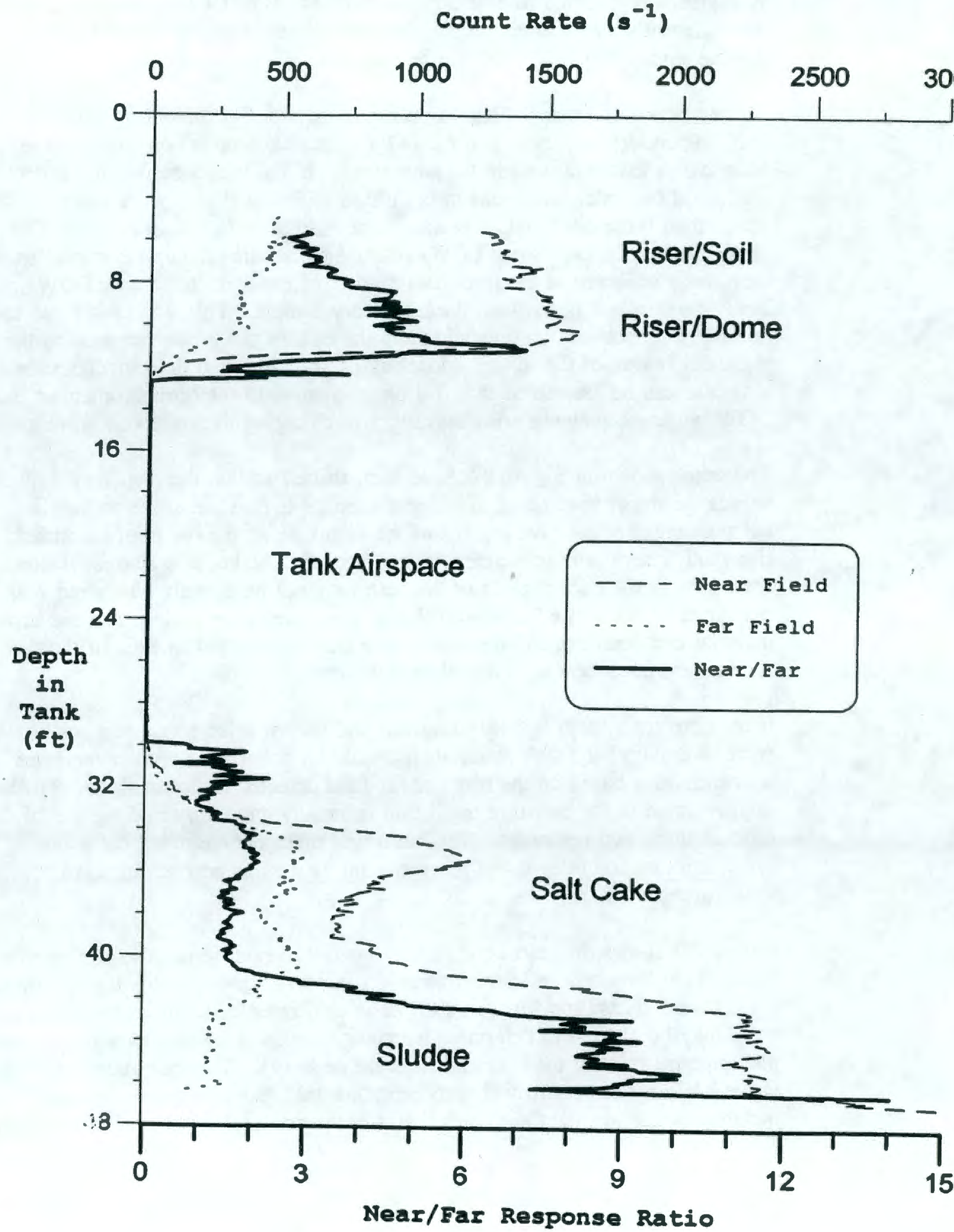
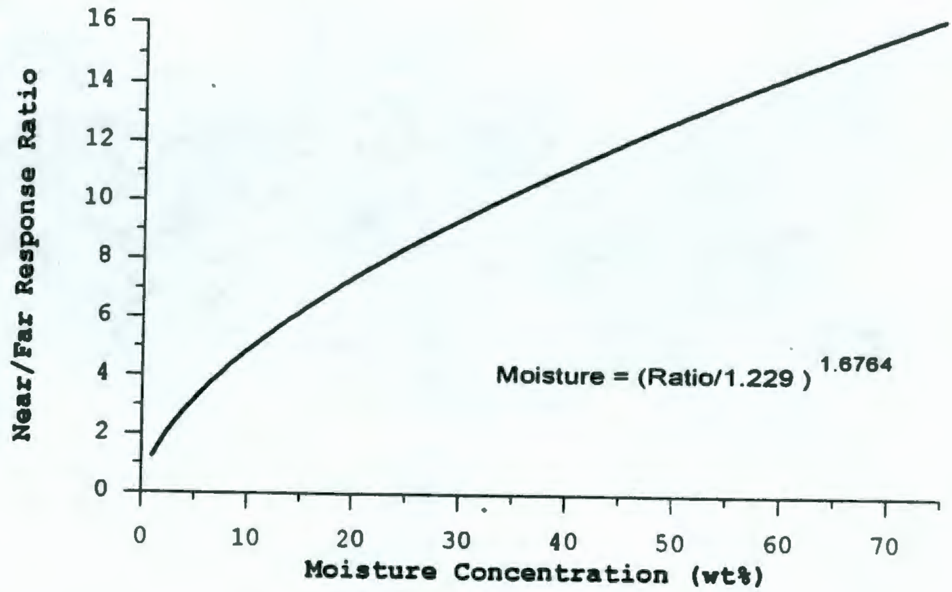


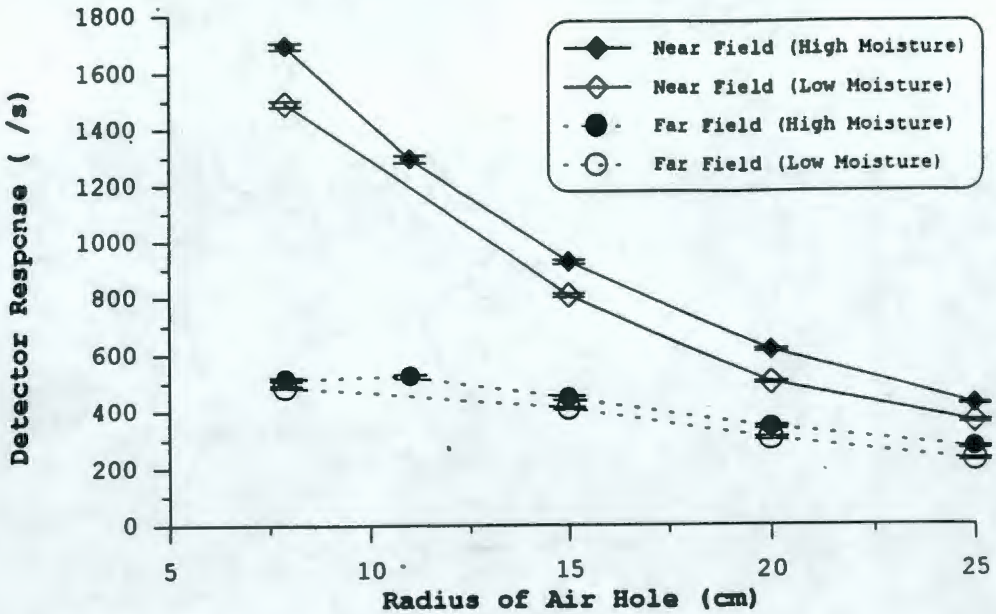
Figure 2-3. Preliminary Calculated Near to Far-Field Ratio Sludge Moisture Calibration Curve.



In general, an increase in the near to far-field response ratio is indicative of an increased hydrogen concentration in the surrounding material. The ratio is observed to be relatively low in the riser/soil region and to increase in the riser/dome region. This is consistent with the expectation of low moisture in the soil and increased bulk density and hydrated water in the concrete tank dome. A more pronounced result is observed in the waste. The detector response ratio in the sludge is about three times larger than in the saltcake and remains relatively constant throughout much of this region. This indicates the tank contains sludge with a uniform water content with a lower water content saltcake overlaying the sludge.

The interpretation of the scan data obtained from the saltcake region of each tank is complicated by the fact that initial installation of the LOW through the hardened saltcake required water lancing to create an opening. In-tank photographs of many LOWs show a saltcake entrance hole larger than the LOW, leaving an annular air gap around the LOW. An annular air gap would affect detector response. It should be possible to correct for such an air gap with modeling and experimental tests. Figure 2-4 shows the predicted responses of both near and far-field detectors to different radius annular air holes between the LOW and low to high moisture saltcake (density = 1.7 g/cm^3).

Figure 2-4. Preliminary Calculated Near and Far-field Responses to Annular Air Holes Between LOW and Saltcake (Low and High Moisture).



The scan data obtained in the saltcake region of tank 241-BY-111 exhibits strong evidence of a varying air annulus between the LOW and saltcake. Because the far-field detector arrangement normally interrogates a larger volume of the surrounding material than the near-field probe, its response is less sensitive to near borehole air gaps until the size of the air gap becomes comparable to the far-field source-to-detector spacing. The near-field count rate initially rises to a plateau of about 1180 per second, while the far-field reaches about 570 counts per second after both probes have completely entered the saltcake. These individual count rates are consistent with those predicted for about a 12 cm radius air annulus surrounded by average moisture saltcake. At a depth of about 38 ft in the tank, the near-field count rate has fallen to about 750 per second and the far-field count rate has dropped to about 430 per second. The count rates and the ratio of the count rates are consistent with those predicted for about an 18 cm radius annular air hole surrounded by average moisture saltcake.

The saltcake scan data are consistent with what would be expected for saltcake containing a relatively uniform moisture concentration throughout its vertical profile, but with a small LOW insertion air hole that increases in size about two feet below the surface of the saltcake. Because of possible air annulus variations, it is likely that the saltcake portion of the scan for each tank will require an individual analysis and interpretation that may not lend itself to the automated use of a single calibration curve. Without the information gained from both the near and far-field detectors, this analysis would be difficult to substantiate.

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

A spectrometer system with a fiber optic probe is being delivered to Westinghouse Hanford by Savannah River Laboratory (SRL). The plan is to integrate the CPAC NIR calibration model with this system for a remote probe moisture sensing system. Non-radioactive (cold) materials will be used to feature test this system. The remote fiber optic probe system has potential application in hot cells and with in situ waste tank penetrometer systems.

- **Planned Work for Subsequent Months.** An experimental test area in which to complete the final development, testing, and calibration of a prototype neutron diffusion-based moisture measurement system is being prepared. This will allow controlled experimental measurements to be made as desired. A two or three detector neutron probe will be assembled and tested. The possibility exists of using a pulsed neutron source for obtaining additional information about the surrounding medium. The air or liquid-filled space immediately surrounding the LOW will be compensated for in future scans. The use of an epithermal neutron detector to eliminate any effects on detector response from the presence of unknown amounts of strong neutron absorbers in the tank waste will be examined. A simulant more representative of the neutronic properties of ferrocyanide waste will be identified and used to obtain probe data as a final check for the MCNP model.

  The integration of a SRL NIR system with the CPAC calibration model will be initiated and materials for cold feature testing will be identified. A report on CPAC Phase 1 moisture sensing feasibility work will be published and Phase 2 work scope optimizing the calibration model will be initiated.

- **Problem Areas and Action Taken.** Final simulants, neutronically equivalent to ferrocyanide waste, with known moisture (hydrogen) concentrations must be acquired for final testing and calibration. In order to correct for non-uniform material around the LOW, experimental results will be needed in simulants arranged to model anticipated material geometries. These results will be used to confirm modeling results for a few selected physical situations and moisture contents.

The effects of nonuniform LOW boron concentrations has led to the conclusion that epithermal detectors should be used in the prototype probe. This would eliminate the uncertainty in moisture measurement due to boron content.

- **Milestone Status.**

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

  - **August 29, 1992:** Completed preliminary neutron probe scans of surrogate tank 241-B-104 using the modified neutron probe.

  - **September 30, 1992:** A letter report documenting the current status of Monte Carlo calculations, tank 241-B-104 test scans, and the increased understanding of the neutron probe was completed. The report also included a description of recommended tasks to be performed, including field activities.

  - **December 1, 1992:** Completed neutron probe test scans of tanks 241-BY-101, -104, -105, and -106 using the modified neutron probe.

  - **March 29, 1993:** Limited moisture simulant drums were completed and available for benchmarking efforts.

  - **April 30, 1993:** A white paper entitled *Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools* (Meacham et al. 1993), was released.

  - **June 25, 1993:** Complete limited calibration using special simulant-filled drums as standards. A letter report documenting the work completed to meet this milestone was written.

  - **September 27, 1993:** The comprehensive neutron probe moisture measurement proof of principle final report was completed September 24, 1993.

2.1.4 Hot Spot Thermal Modeling

The decay of radioactive materials in Hanford Site waste tanks generates heat. A concern has been whether an exothermic excursion and local propagation might occur within the ferrocyanide waste if there was a sufficient concentration of ferrocyanide and a high enough temperature present. There is usually only one or two instrument trees in each ferrocyanide tank (see Table A-1), and the trees are not always at the same location. Consequently, there is some question if significant heat generation could exist in these tanks and not be detected. 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 horizontal location. Sensitivity and parametric analyses are included to determine the magnitude of hot spots that might exist within the waste to cause a propagating reaction to occur.

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

- **Progress During Reporting Period**. A more realistic single-shell tank heat load model was developed this quarter. The model contains several improvements over previously used models. Refinements include; an experimentally measured value for soil conductivity, a curved dome space geometry, and use of a transient thermal history. Including radiant and convective heat transfer to the walls of the tank in the model was found to offer little in the way of increased accuracy. The new model will be used to develop a thermal profile of tank 241-BY-104. Information derived from the analysis of 241-BY-104 will be used for updating the thermal profile of six additional ferrocyanide tanks.

  The technical basis for measuring integrated tank heat loads in the tank dome space is being developed. Preliminary calculations have shown that there is a correlation between total tank heat load and tank dome space temperature. Tank dome space temperature measurements may confer a more representative measure of tank heat load since only a limited number of TC's are available in each tank.

- **Planned Work for Subsequent Months**. The development of the heat transfer/heat load model will be completed and heat load analysis of selected tanks will be performed. A report of the analysis will be prepared and issued. Existing analyses will be updated to include the correction factors being developed.

  Comments made by DOE will be incorporated into the report, *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Waste by Hot Spots* (Dickinson et al. 1993).

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

- **Milestone Status.**

  - **July 31, 1992:** Determine the heat loads and calculated thermal conductivities of the contents for tanks 241-BY-105, -106, -108, -110, -111, and 241-C-109. The upper and lower bound of these parameters were calculated. A final report has been delayed to November 1993 so that heat loads of these tanks can be reevaluated with the updated heat transfer/heat load model.

  - **September 30, 1992:** Performed a detailed thermal analysis of tank 241-BY-106 to determine the response of the tank contents to a hot spot of varying intensities. This analysis included both steady-state and transient analyses. A report of this analysis was issued in May 1993 as "Ferrocyanide Safety Program: Thermal Analysis of Tank 241-BY-106," WHC-EP-0591, Rev. 0.

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

  - **September 17, 1993:** Complete thermal hydraulic analyses of four ferrocyanide tanks to determine heat loads and conductivities of the waste contents and issue a report, available to the public, on the results of the analyses. This milestone has been slipped to November 1993 because of delays in the development of the updated heat transfer/heat load model.

  - **September 24, 1993:** Complete and issue a report, available to the public, of thermal analysis of six ferrocyanide tanks (241-BY-105, -106, -108, -110, 111, and 241-C-109). This milestone was postponed to November 1993 because of delays in the development of the updated model.

2.2 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.2 (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."

2.2.1 Tank Monitor and Control System (TMACS)

This task will provide continuous monitoring of presently installed (and operable) TCs for the ferrocyanide tanks. New TC trees will be connected to the system as they are installed in each tank, resulting in continuous monitoring of all TC trees 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 change in the value of any temperature point. Alarms, if they occur, trigger an audible annunciator and are logged immediately to hard copy. An alarm summary display provides a list of the most recent alarms in order of occurrence. Each alarm can be identified by point and time of occurrence. Operator acknowledgement of the alarm will silence the audible annunciator.

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

Five BY Farm tanks were connected to the system in September 1991, and an additional five in December 1991. These tanks include 241-BY-103, -104, -105, -106, -107, -108, -110, -111, and -112. Tank 241-BY-105 has two operating TC trees. Both were connected to the TMACS. In April 1992, tanks 241-TY-101, -103, -104, and 241-TX-118 were connected to the system and are now operational. Four new TC trees installed in tanks 241-BY-104, -110, -111, and -112 have been connected to the TMACS. This makes a total of 13 ferrocyanide tanks (18 TC trees) that are now monitored by the TMACS. Temperature readings from the working TCs in these tanks are being recorded continuously.

- **Progress During Reporting Period.** All design for connection of the remaining tanks that contain TC trees is complete. Connection to TMACs continued this quarter; however, the Administrative Hold has stopped work in the tank farms.

- **Planned Work For Subsequent Months.** Construction will resume in C, T, and BX Farms when the Administrative Hold is lifted.

- **Problem Areas and Action Taken.** Construction within the farms is presently halted because of the Administrative Hold placed on all tank farm work.

- **Milestone Status.**

  - **September 30, 1992:** Completed design of the TMACS for C and T Farms.

  - **July 30, 1993:** Complete installation of the TMACS for the four ferrocyanide tanks in C Farm. All 12 tanks in C Farm are being connected to TMACS. This task is behind schedule and will be completed when the Administrative Hold is lifted.

  - **August 30, 1993:** Complete installation of the TMACS for two tanks in T Farm (241-T-101 and -107). This task is behind schedule and will be completed after the Administrative Hold is lifted.

  - **September 30, 1993:** Complete design and installation of the TMACS for the four ferrocyanide tanks in the BX Farm. This has been delayed because of the Administrative Hold in the tank farms.

  - **September 30, 1993:** Complete installation of the TMACS for new TC trees installed during FY 1993. This has been delayed due to the Administrative Hold in the tank farms.

  - **September 30, 1994:** Incorporate TMACS on new instrument trees installed during FY 1994.

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

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

2.3.1 On-Line Gas Monitoring

Options for installing a gas monitoring capability on new TC trees have been reviewed and a heated vapor sampling tube has been added to the design of future TC trees for ferrocyanide tanks (see Section 2.1.1). However, a definite decision to monitor continuously or just occasionally has not been made. The frequency of gas monitoring and/or the need for continuous monitoring will be determined after a significant number of the ferrocyanide tanks are vapor sampled or if a concern is detected during the sampling program. Evaluation of gas samples secured to date for tanks 241-BY-104, -110, -111, -112, 241-C-108, -109, -111, -112, 241-T-101, -107, 241-BX-106, and 241-TX-118 has indicated no need to continuously monitor for specific gases. The vapor sampling tube design for future thermocouple trees allows vapor space sampling on a continuous or intermittent basis.

2.3.2 Interim Flammable Gas Monitoring

The effort to conduct flammable and toxic gas monitoring and analyses in the ferrocyanide tanks is continuing. This effort was transferred to the waste tank Vapor Program, which is coordinating interim gas monitoring of the ferrocyanide tanks. Tank vapor spaces are measured for flammability using a commercial combustible gas monitor and are monitored for toxic gases using an organic vapor monitor and Dräger tubes as required by the safety assessments and work procedures for a particular activity. Development and validation of alternative technologies for vapor space characterization are in progress using Summa canisters and specific absorption tubes.

Because the safety issue associated with ferrocyanide tanks is listed as a USQ, this activity requires DOE-EM Headquarters Program Secretarial Officer (PSO) approval for performing sampling activities within the tanks. Although past sampling conducted by Westinghouse Hanford Industrial Hygiene Programs with a combustible gas monitor has indicated no flammable gas content above 6 percent of the lower flammability limit, no qualitative measurements were obtained. The combustible gas monitor is calibrated using pentane gas. Readings are assumed to be for hydrogen gas, which is known to be present from the radiolysis of water.

All ferrocyanide tanks are passively ventilated through individual high-efficiency particulate air (HEPA) filters. The "breathing" is dependent on changes in barometric pressure and differences in temperature between the waste tank and the outside air. The pressure change causes a small volume of stagnant air to be replaced with fresh air, which helps control the concentration of chemical vapors inside the tanks.

- **Progress During Reporting Period**. The vapor spaces in five tanks (241-BX-106, 241-BY-101, 241-C-108, -111, and 241-TX-118) were sampled this quarter. Analyses showed no concentrations of flammable gases above the detection limit (<1% of the lower flammability limit) using a combustible gas meter. All flammable gas readings in the ferrocyanide tanks monitored to date have indicated either non-detectable values or concentrations much less than the lower flammability limit. Ammonia was the only gas detectable in the dome space of tanks 241-BX-106 and 241-BY-101 using Dräger tubes. Ammonia concentration ranged between 10 and 18 parts ppm for tank 241-BX-106 and between 9 and 40 ppm for tank 241-BY-101. Detectable concentrations of noxious gases were not found in the dome spaces of tanks 241-C-108, -111, and 241-TX-118. Hydrogen cyanide levels in tanks 241-C-108 and -111 were below 0.04 parts per billion. Table A-2 in appendix A contains gas analyses for the ferrocyanide tanks sampled to date.

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

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

- **Milestone Status.**

  - **September 30, 1992:** Complete flammable gas sampling of 241-C-109, 241-BY-110, and 241-T-107 to support push mode core sampling and TC tree installation. Tank 241-C-109 was sampled on August 26, 1992. Tank 241-BY-110 was sampled on September 27, 1992. Tank 241-T-107 was sampled on October 22, 1992.

  - **September 30, 1993:** Complete flammable gas sampling of eight additional ferrocyanide tanks to support push mode core sampling and TC tree installation. All eight tanks (241-BX-106, -110, -111, 241-BY-101, -111, -112, 241-C-108, and -111) were sampled for flammable gas on schedule.

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

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

2.3.3 Vapor Space Gas Modeling

The possibility that localized concentrations or stratification of gases exist in the tanks has been evaluated. Radiolysis of water generates hydrogen, and the interaction of various chemicals in the tanks may also release hydrogen and other gases. Some of these gases may have the potential to be explosive or otherwise hazardous if their concentrations become large enough and are mixed properly with air. This concern is being addressed through the sampling effort described in Section 2.3.2. A modeling effort to determine airflow patterns in the tank vapor space of tank 241-C-109 was conducted to evaluate the amount of mixing and local gas concentrations that could occur. The results of this analysis were used to evaluate the hazards and risks involved during sampling and other intrusive activities within this and other ferrocyanide tanks.

An analysis of a second tank was deemed unnecessary because of the well-mixed environment calculated for the first tank. The results of this study have shown that the gases in the tank are well mixed and follow Graham's law for gaseous diffusion. A significant exchange of tank gases with fresh air occurs frequently and the accumulation of flammable gases is precluded. Thermal convection was shown to provide a well mixed vapor space within the tanks.

- **Progress During the Reporting Period.** The goals of the project have been met and the task is completed.

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

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

- **Milestone Status.**

  - **February 8, 1993:** Perform an analysis of the airflow patterns in ferrocyanide tank 241-C-109. Determine the potential to have concentrations of flammable gasses that could lead to hazardous conditions and issue a report on the findings. This report was completed and cleared for public release as WHC-SD-WM-ER-183, Rev 0., on schedule.

  - **April 30, 1993:** Complete an analysis, if warranted, of a second tank with greater differential temperatures within the tank and issue a report approved for public release. This activity is not required because analysis of tank 241-C-109 determined that the gases are well mixed. The gases in all ferrocyanide tanks are believed to be well mixed and exchanged frequently with fresh outside air.

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

"The program of sampling the contents of these tanks should be greatly accelerated. The proposed schedule whereby analysis of two core samples from each SST 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."

2.4.1 Ferrocyanide Tank Waste Sampling and Characterization

Characterization of the waste in the ferrocyanide tanks is necessary to (1) guide chemical reaction studies with ferrocyanide waste simulants, (2) provide a basis for estimating the consequences of a runaway ferrocyanide reaction, (3) determine how the ferrocyanide waste can be stored safely in situ until retrieval and disposal actions are completed, and (4) apply the study results to the final remediation of the waste in these tanks. Knowledge of the concentrations and relative positions of various waste constituents is also important to determine their potential for chemical reactions and the consequences of a potential reaction.

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. Their location is also important because they are potential source terms in postulated radiological releases from an exothermic ferrocyanide reaction. The water content of the waste is very important because the high heat capacity and the heat of vaporization of water make it an effective inerting material. Water content can prevent a sustained combustion or a propagating reaction. Wet ferrocyanide material would require drying before it could react or propagate. Other materials (for example, nickel, copper, lead, and the rare earths) may be important as potential catalysts.

Push-mode core sampling is presently the only viable Hanford Site method for waste tank core sampling until it is demonstrated that rotary-drill core sampling will not produce excessive temperatures in the waste. Six ferrocyanide tanks suitable for push-mode core sampling were placed on the list of SSTs to be core sampled in FY 1992 and FY 1993. Three of these tanks, 241-C-112, -109, and 241-T-107 have been core sampled to date. Three additional tanks, 241-C-108, -111, and 241-BX-102 are scheduled for push-mode core sampling in FY 1994. The Administrative Hold prevented the tanks from being sampled in FY 1993 as originally scheduled.

- **Progress During the Reporting Period**. The data interpretation report for tank 241-C-109 was publicly released this quarter (Simpson et al. 1993a). Comments from DOE were incorporated into the data interpretation report for tank 241-C-112 and the report was re-released (Simpson et al. 1993b).

  The Core Sampling truck acceptance test report was released and the truck was moved out to the operability test site. Drilling tests per the operability test procedure were initiated. Exhauster system components were received and assembly work to integrate components onto the skid were completed. Procurement and fabrication were completed for fixed use drill strings, bits, and samplers. Testing was suspended as a consequence of the tank farm Administrative Hold.

  Equipment was removed from the test site and relocated in order for modifications to be incorporated, based on test results to date. The safety and environmental assessments were approved and released by Westinghouse Hanford to the DOE-RL. The DOE-RL submitted review comments that Westinghouse Hanford incorporated and the revised documents are in the release cycle. A readiness review has been started for the first ferrocyanide tank, 241-BY-104, expected to be sampled in the third quarter of FY 1994.

Core sampling of ferrocyanide tanks with saltcake was deferred until the rotary-mode core sample truck is available for field use. Possible push-mode core sampling of tank 241-BY-104 was evaluated. It was recommended that push-mode core sampling not be used on this tank at this time. Tank 241-BY-104 will be rotary-mode core sampled when operations in the tank farms begin again.

- **Planned Work For Subsequent Months.** The data package for tank 241-T-107 is expected to be ready in October 1993. Push-mode core sampling will continue in tanks 241-C-111, -108, and 241-BX-102 when the Administrative Hold is lifted.

  Core sampling of ferrocyanide tanks with saltcake will be deferred until the rotary-mode core sample truck is available for field use.

- **Problem Areas and Actions Taken.** Core sample recovery continues to be a problem for push-mode core sampling of tanks. Although the sampler valve assembly was changed to incorporate a spring-loaded mechanism to close the sampler tightly, one of the three tank 241-C-109 core sample segments still had poor recovery. A third core was taken from tank 241-T-107 because one of the first two cores had poor recovery. Poor sample recovery was also seen in push-mode core sampling of non-ferrocyanide tanks 241-T-105 and -102. Core sampling has been suspended while the core recovery issue is being resolved. Recovery actions include the formation of a core sampling restart team, consultation with an external panel of experts, and comprehensive equipment testing for performance evaluation.

- **Milestone Status.**

  - **August 30, 1992**: Obtain three full-length push-mode core samples from tank 241-C-109. Core sampling was completed on September 7, 1992.

  - **September 30, 1992**: Obtain two full-length push-mode core samples from tank 241-T-107. One core sample was secured in November 1992; however, core sampling was suspended at that time until findings from a DOE-RL audit were satisfactorily resolved. Sampling resumed on February 17, 1993 and was completed on March 15, 1993. A third core sample was taken because one of the original cores showed poor sample recovery.

  - **March 31, 1993**: Complete interpretation of ferrocyanide tank 241-C-112 analytical data and issue a report cleared for public release. This data interpretation report also addressed another milestone and the issue date was deferred to April 30, 1993 to accommodate another required review for the document. That document issue date was met and the document was distributed.

- **April 30, 1993**: Complete interpretation of ferrocyanide tank 241-BY-104 auger surface sample analytical data and issue a report that is cleared for public release. The interpretation report was issued on May 10, 1993 after incorporating some changes requested by DOE-RL.

- **July 31, 1993**: Complete interpretation of ferrocyanide tank 241-C-109 analytical data and issue a report cleared for public release. This milestone was deferred to September 1993, because the validated laboratory analyses data packages were not received until May 14, 1993. This report was released on September 27, 1993.

- **September 30, 1993**: Complete interpretation of ferrocyanide tank 241-T-107 analytical data and issue a report that is cleared for public release. This milestone has been deferred to February 1994 because core sampling and analysis were delayed approximately four months.

- **September 30, 1993**: Obtain two full-length push-mode core samples from three additional ferrocyanide tanks in FY 1993. The following order for sampling in the tanks was planned: 241-C-111, -108, and 241-BX-102. The administrative hold has delayed completion of this milestone until FY 1994.

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

- **September 30, 1995**: Obtain core samples from four ferrocyanide tanks. The schedule for tank sampling is being accelerated to complete all ferrocyanide tanks by FY 1995.

- **September 30, 1996**: Obtain core samples from four ferrocyanide tanks. The schedule for tank sampling is being accelerated to complete all ferrocyanide tanks by FY 1995.

- **September 30, 1997**: Obtain core samples from the remaining ferrocyanide tanks. The schedule for tank sampling is being accelerated to complete all ferrocyanide tanks by FY 1995.

2.4.2 Waste Analysis With Laser Raman Spectroscopy

The objective of this activity is to develop and demonstrate Raman spectroscopy methods for the sensing and measurement of safety related chemical species (free cyanide, ferrocyanide, and ferricyanide) in Hanford Site high-level waste tank materials for both hot cell and in situ waste tank applications. Techniques for in situ measurement of cyanide species using remote sensing via optical fibers, as well as other techniques, will be pursued in addition to ex situ methods, where core samples are analyzed in the analytical laboratory. A secondary objective is to extend any methodology to the analysis of other anions of interest (such as sulfate, nitrate, nitrite, phosphate, and aluminate) and to organic compounds such as ethylenediaminetetraacetic acid (EDTA) and hydroxyethylenediaminetriacetic acid (HEDTA).

Screening studies are being conducted to identify possible sources of interferences and potential limitations of the Raman method. The fluorescence of the products caused by the excitation from the incident laser light can also overwhelm the Raman signals under certain conditions. The effect of pH >8, in addition to the effect of other ions and organics on ferrocyanide signal strength and frequency position is being studied. Tests to establish detection limits and levels of accuracy and precision for ferrocyanide in the presence of other compounds are underway.

- **Progress During Reporting Period.** A milestone was achieved when Raman spectroscopy data were obtained from Hanford waste tank materials. The Raman system was setup in the 200 West area 222-S hot cell laboratory and a fiber optic probe installed in the 1E2 hot cell, as illustrated in Figure 2-5. Figure 2-6 shows the interior of the hot cell and the use of manipulators to position the fiber optic probe within a waste tank sample container. The sample is real waste tank material and has the physical consistency and optical opacity typically inherent with most of tank waste slurries.

Figure 2-5. Hot Cell Raman System Installation With Remote Fiber Optic Probe.

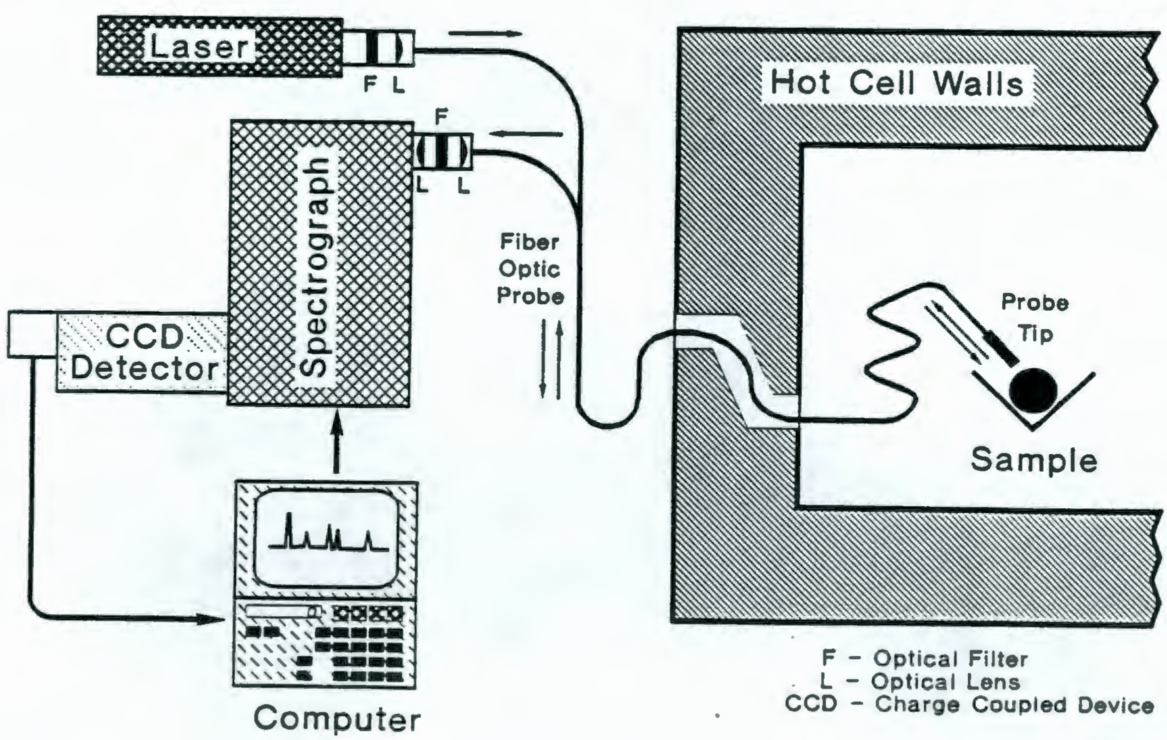
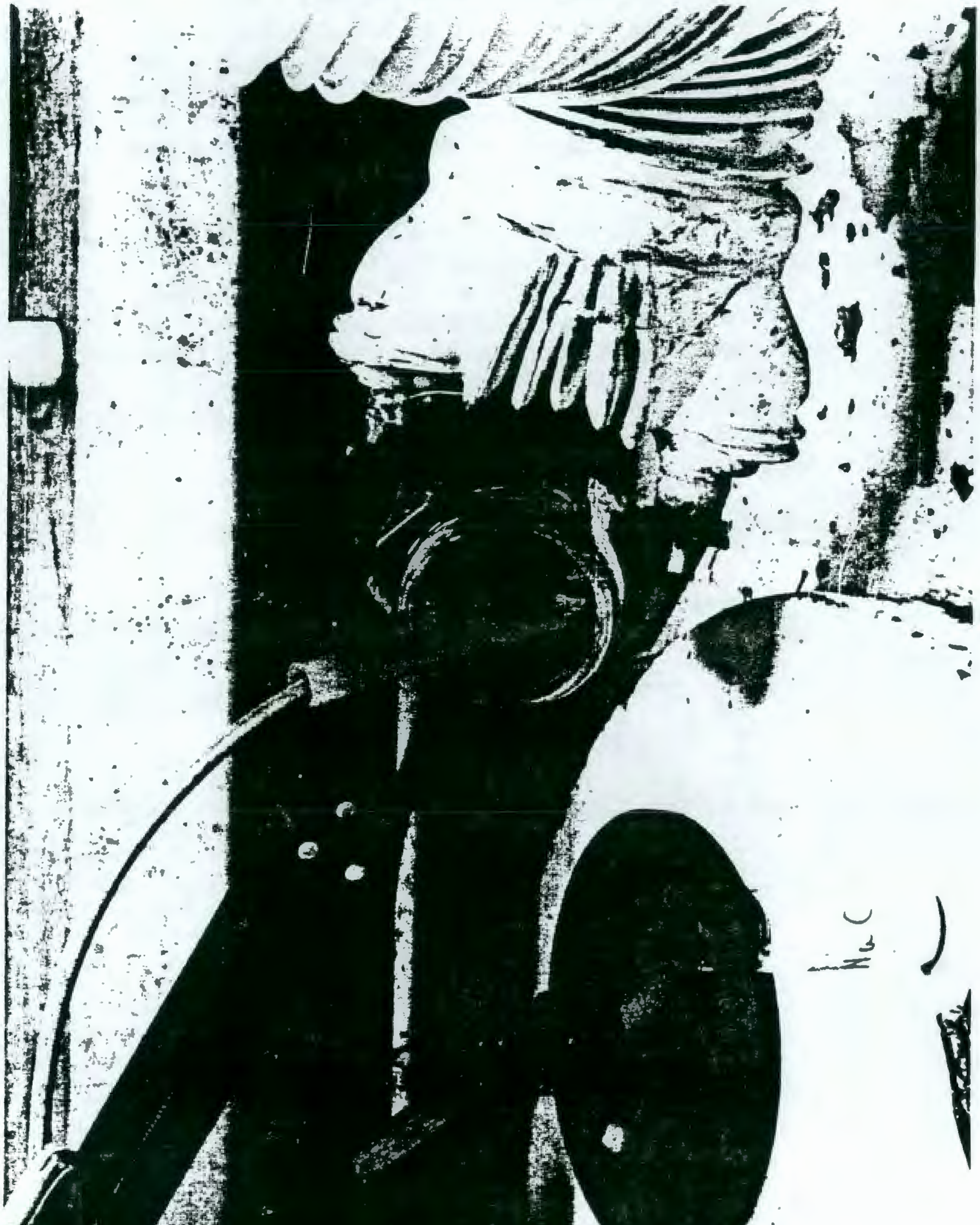


Figure 2-6. Raman Spectrum Hot Cell Interior View, Showing the Raman Fiber Optic Probe Being Positioned Within a Waste Sample Container With the Hot Cell Manipulators.



The hot cell campaigns provided Raman spectral data as well as an operational procedure test data. The first hot cell campaign used a laser diode source, which produced 30 Mw (10^{-3} Watts) at a 826 nm (10^{-9} meters) wavelength at the probe tip. A lack of good Raman sensitivity was evident from the low signal to noise of early spectra obtained from simulant and real waste materials. A second hot cell campaign was completed after the laser was replaced with an argon ion laser that produced 130 Mw of 514.5 nm wavelength at the probe tip. The laser change increased the system response by about a factor of 40.

Examples of Raman spectra obtained from archived samples of 241-BY-104, 241-BX-107, 241-T-107, and -111 wastes are shown in Figures 2-7 and 2-8. The oxianion region is shown in Figure 2-7, while the ferro/ferricyanide active region is shown in Figure 2-8. The spectral peak wavelength position is a function of the molecular species present, while the relative amplitude (within each spectrum) is indicative of the concentration of that species. Although an extensive analysis from these Raman spectra has not been completed, a few observations can still be made. The Raman data in Figures 2-7 and 2-8 show peaks that are common to all spectra, such as the strong nitrate peak in the 241-T-111, -107, and 241-BY-104 samples. The 241-BY-104 appears to have the most unique Raman features in that several of the common peaks in the 241-T-111 and -107 wastes are not visible. All the waste materials examined appear to lack Raman peaks in the ferro/ferricyanide region, indicating the absence of these expected analytes.

All of the real waste materials tested in the hot cell campaigns exhibit a degree of fluorescence with the 514.5 nm laser light. For most of the materials tested the fluorescence levels were small and did not strongly impact the Raman signals. However, this appears not to be the case for the 241-BX-107 samples examined in the hot cell with the 514.5 nm laser. The 241-BX-107 Raman spectra in Figures 2-7 and 2-8 appear to have been overpowered by fluorescence effects.

The previous data for 241-BX-107, obtained with the 826 nm laser, did not exhibit this same response as indicated in Figure 2-9. Further studies are planned since there was some indication of an inter-relationship between the probe's silica Raman response and the fluorescence response. This early work keynotes the need for continued optimization work to improve Raman signal to noise levels. Future tests with optical filtering and use of longer (for example 530 nm NdYAG doubled laser light) wavelength lasers are planned.

A further illustration of the potential for using a Raman probe to indicate homogeneity within a core sample is shown in Figure 2-10. This shows the Raman response for different positions within the 241-T-107 material container. Spectrum A, B, and C were each obtained after resetting the probe in the T-107 material container, while D is a sodium nitrate reference. There are major differences in Raman peak levels between the spectra.

Figure 2-7. Raman Spectra for 241-T-111, -107, 241-BY-107 and 241-BX-107 Waste Tank Samples for the Expected Oxianion Active Region.

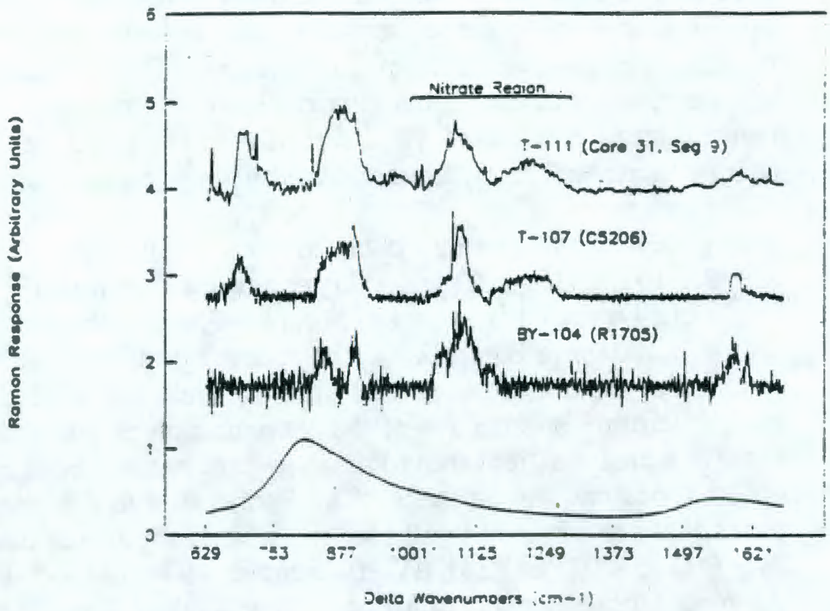


Figure 2-8. Raman Spectra for 241-T-111, -107, 241-BY-107 and 241-BX-107 Waste tank Samples for the Ferro/Ferricyanide Raman Active Region.

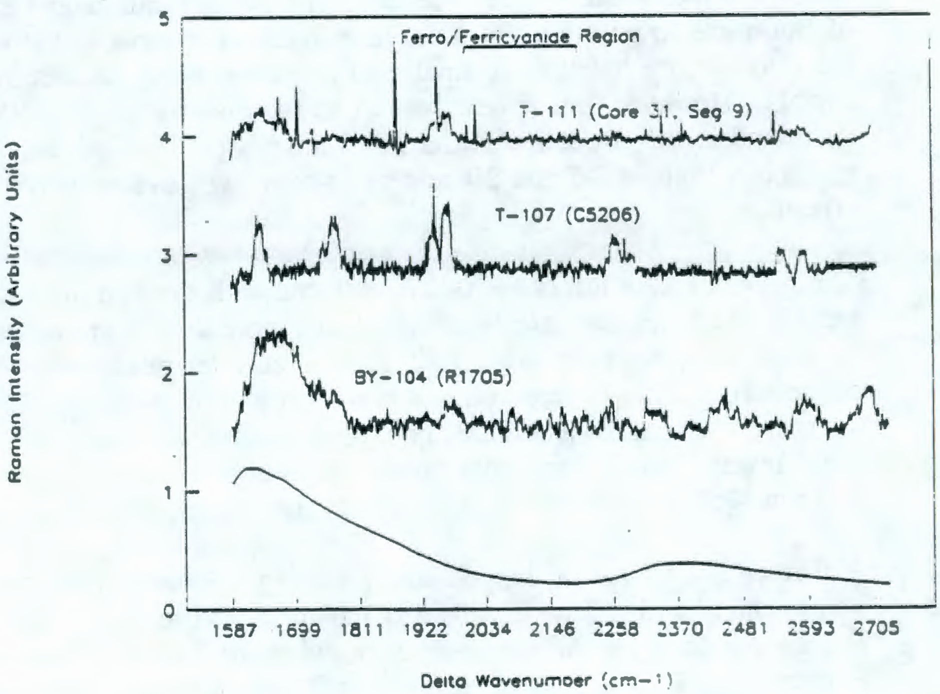


Figure 2-9. Raman spectra from 241-BX-107 waste material obtained with a 826 nm laser diode.

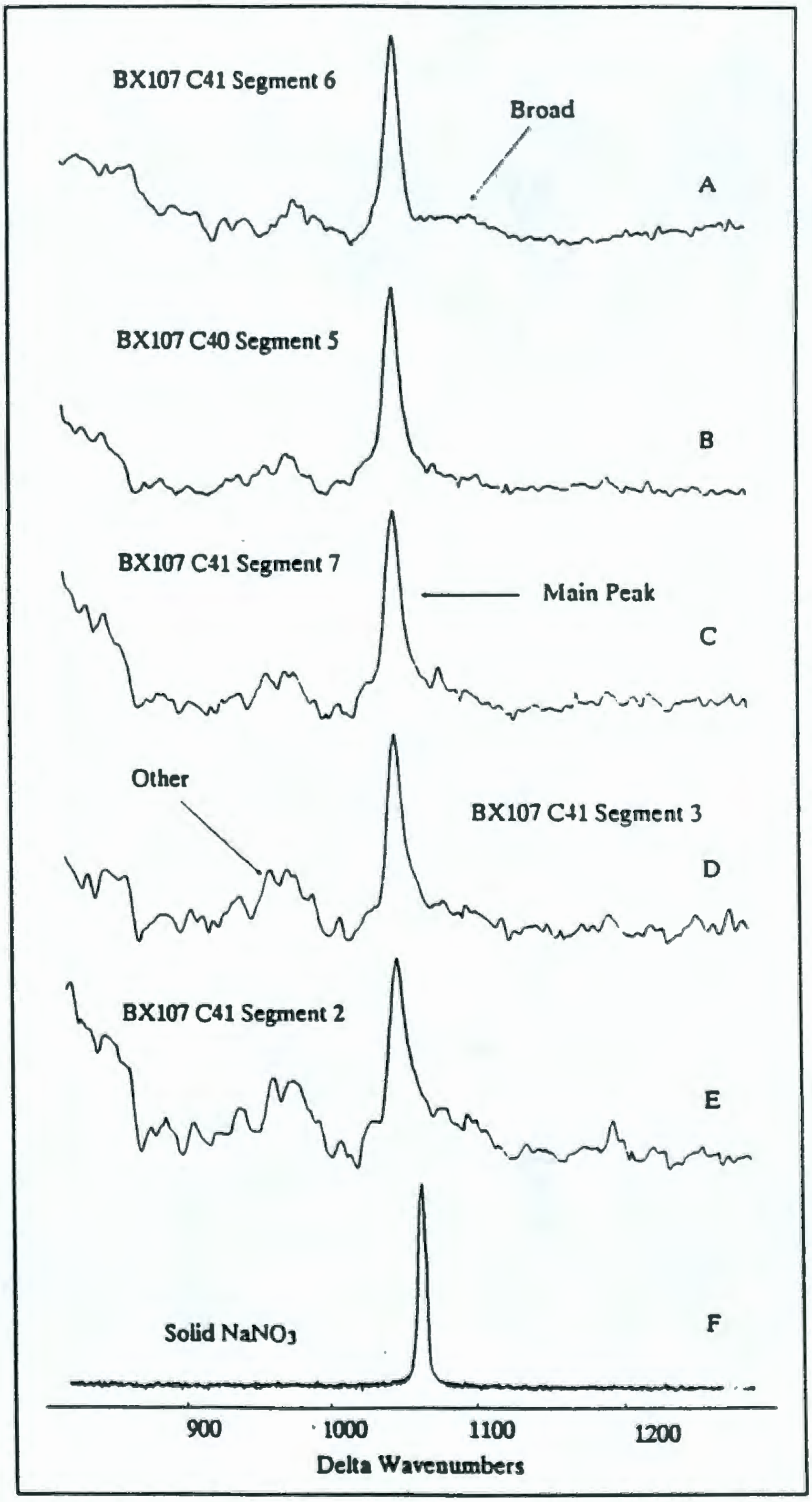
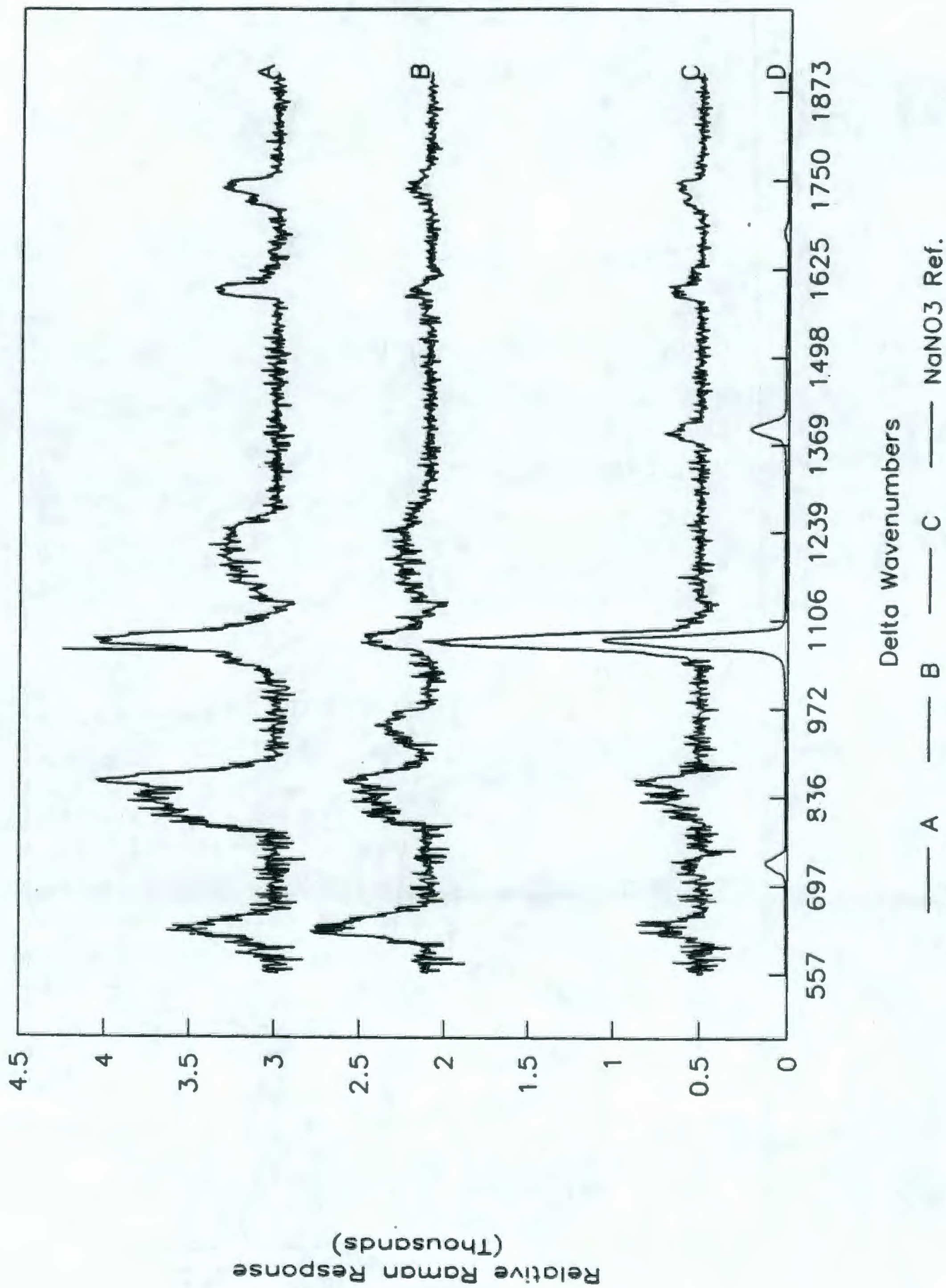


Figure 2-10. 241-T-107 nitrate region, Raman spectra showing spectral changes from resulting from changing the probe position in the waste container



A final report is being prepared that summarizes the results of the FY 93 Raman work and demonstration tests completed with ferro/ferricyanide materials and simulants. The spiking experiments with simulant and real materials illustrate the potential levels of detection for ferro/ferricyanide materials. For example, baseline tests with the 826 nm diode laser source indicated levels of detection (LOD) of 0.27 and 0.28 wt% for spikes of $Na_4Fe(CN)_6 \cdot 10H_2O$ and $K_4Fe(CN)_6 \cdot 3H_2O$ in pure sodium nitrate. Sensitivities were found to be very much dependent on the Raman signal and noise levels which were much poorer for the 826 nm laser diode source than for the 524.5 nm argon ion source.

Using the 826 diode laser, the results of standard additions of $Na_2NiFe(CN)_6$ and $Na_4Fe(CN)_6$ to 241-BX-107 wastes indicated detection limits of 9.9 and 13.6 wt%, respectively. With the 514.5 nm argon laser, a LOD of 0.63 wt% was obtained with $Na_4Fe(CN)_6$ spiked into a 241-BY-104 simulant. The Raman signals from the spike tests with the 241-BY-104 simulant indicated that the $Na_2NiFe(CN)_6$ was undergoing decomposition to $Na_4Fe(CN)_6$. A further indication of a chemical interaction was from the strong ammonia vapors detected after the spike material was added to the 241-BY-104 simulant. Additional work is needed as this initial test indicates there may be some material matrices where suspected forms of ferro/ferricyanide are not tolerated and only breakdown products would be present.

- **Planned Work For Subsequent Months**. Identify and initiate Raman systems optimization modifications, including the procurement and feature testing of a doubled NdYAG laser with single line emission at 530 nm.

  Support Lawrence Livermore National Laboratory in the setup of a environmentally hardened Raman system at Hanford and receive training on system maintenance and operation.

  Plan and complete hot cell testing campaigns with all available archived waste tank samples. Re-test 241-BX-107 waste materials to resolve fluorescence issue and evaluate new laser systems response with real waste materials.

  Verify hot cell work and validate spectral data from real waste tank materials for samples containing ferrocyanides.

- **Problem Areas and Actions Taken**. The Administrative Hold at the tank farms will impact the availability of new waste materials for hot cell Raman tests and evaluations. In addition, the goal to complete a Raman campaign during extrusion of a waste core may not be achievable. Work will continue using available, archived samples taken from prior waste tank core campaigns.

- **Milestone Status.**

  - **January 31, 1993:** The Florida State University (FSU) contract was renewed and new scope items identified.

  - **February 28, 1993:** An environmental specification document for a hot cell and waste tank deployable spectroscopy system was issued on February 11, 1993.

  - **August 31, 1993:** Obtain Raman system performance data with actual waste tank materials. Two hot cell campaigns were completed with archived real waste tank materials.

  - **September 15, 1993:** Two hot cell campaigns were completed with actual waste tank materials. Data was obtained that demonstrates the potential for a hot cell Raman spectroscopy system with ferro/ferricyanide and nitrate/nitrite materials.

2.4.3 Simulated Ferrocyanide Waste Preparation and Characterization

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 any safety concerns of the sludge in each of the ferrocyanide tanks with a great deal of assurance. The results will also provide a technical basis for (1) safety measures to be taken, (2) decisions on appropriate actions leading to resolution of the Ferrocyanide USQ, and (3) eventual remediation of the waste.

Five waste simulants (without radioactive species) are being used to represent the variety of waste produced in the mid-1950s and stored in SSTs. The wastes produced at the Hanford U Plant are 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. Each U Plant batch was about 2,300,000 L (600,000 gal). 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 size In Farm batch was approximately 1,500,000 L

(400,000 gal). It should also be noted that six of these 29 scavenging batches did not contain any ferrocyanide, but did contain nickel sulfide to enhance precipitation of ^{60}Co.

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

Three main 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 mole ratio of nitrite/nitrate, to account for nitrite buildup over time in the wastes by radiolysis of nitrate; (2) the waste simulants prepared or being prepared for characterization do not or will 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 centrifuged at a force of 2,500 g to mimic an equivalent 30 gravity year settling period.

- **Progress During Reporting Period.** The T Plant simulant fractions and supernatant were analyzed for chemical composition. The chemical composition of dried T Plant simulant top and bottom fractions are listed in Table 2-1 along with the compositions of the associated supernatant. Analytical methods used were IC, Inductively Coupled Plasma (ICP), X-ray florescence, X-ray diffraction and atomic adsorption. These results indicate that the T Plant bottom fraction contains little fuel and the dried top fraction simulant contains ~9 wt % disodium mononickel ferrocyanide and excess nitrate/nitrite. The fuel in the T Plant simulant is much less concentrated than the In Farm simulants. The cesium content of the supernatant was less than 0.1 ppm.

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

Table 2-1. Composition of T Plant Supernatant and Dried T Plant Simulant Fractions. (sheet 1 of 2)

Constituent	T Plant Top (wt%)	T Plant Bottom (wt%)	Supernatant (wt%)
Bound Water	~4	~1	----
Nitrate	19.3	4.03	7.77
Nitrite	4.76	0.98	1.92
Sulfate	1.38	0.33	0.547

Table 2-1. Composition of T Plant Supernatant and Dried T Plant Simulant Fractions. (sheet 2 of 2)

Constituent	T Plant Top (wt%)	T Plant Bottom (wt%)	Supernatant (wt%)
Phosphate	13.1	13.4	2.47
Hydroxide*	6.9	3.1	0.0
Sodium	19	3.5	5.2
Sulfur	0.55	0.15	0.16
Iron	9.8	2.3	5.5E-3
Nickel	1.95	0.36	<3E-5
Bismuth	1.2	39	3.8E-4
Silicon	4.8	1.50	1.2E-2
Chromium	1.02	0.29	3.3E-4
Zirconium	0.1	0.2	7E-5
Cesium	0.10	1.25E-2	<1E-5

*Approximated from excess iron

Tests continue to determine the amount of moisture remaining in the simulants in the event of a free flowing drainage, such as a tank leak or deep well pumping of liquids for tank stabilization. A free flowing liquid drainage test using In Farm 2 top fraction simulant at one atmosphere pressure has completed 16 months. The volume of simulant being tested consists of a column 4 inches in diameter and an initial height of 8 inches. The initial water content of the simulant was 53 wt%. Calculations from the measured liquid drained to date indicate that the remaining material has a water content of about 48 wt%. Liquid is continuing to drain very slowly from this material with no apparent termination anticipated in the near future. Some consolidation of the sludge has been observed.

A scoping, vented centrifugation test conducted at 10 gravities centrifugal force with In Farm simulant on a fritted porus media (30 μm sized openings) resulted in a final water content of 47 wt%. An additional vented test conducted at 20 gravities indicated an end point of 46 wt % at this force. This identifies a final water content which is well above the minimum water content required to prevent propagation of the most concentrated ferrocyanide simulant.

A preliminary modeling analysis was performed to evaluate ferrocyanide sludge water loss if allowed to gravity drain. The model simulated flow of a highly concentrated solution of nitrate salts through an unsaturated porous medium. Data from a the small column and centrifugation experiments were used to estimate the hydraulic properties that control liquid flow in the sludge. Figure 2-11 shows water remaining as a function of time for an 8 feet deep sludge layer. The model indicated that the sludge would still contain 40 wt% water even after 200 to 300 years of drainage.

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

The energy required for water release from vacuum dried (60 °C for 18 hrs) In Farm 2 simulant was determined to be 12.6 J/g water for water release up to 170 °C and 98.4 J/g water for water release above 170 °C.

- **Planned Work for Subsequent Months.** A ferrocyanide waste simulant based on characterization of actual tank waste samples will be prepared, analyzed, and tested. Simulant drainage and centrifugation tests will continue. The effects of relative humidity in air on the loss and absorption of moisture will be evaluated under geometric conditions representative of the SSTs.

  A report on the three methods used for drying the ferrocyanide waste simulants will be prepared and issued. This evaluation was completed earlier in FY 1993 and reported in WHC-EP-0474-9 (Cash et al. 1993).

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

- **Milestone Status.**

  - **December 31, 1992**: Issued draft report on the flowsheet waste simulant compositions and ferrocyanide species characterization.

  - **January 30, 1993**: Issued final report (Jeppson and Wong 1993) on the flowsheet waste simulant compositions and ferrocyanide species characterization.

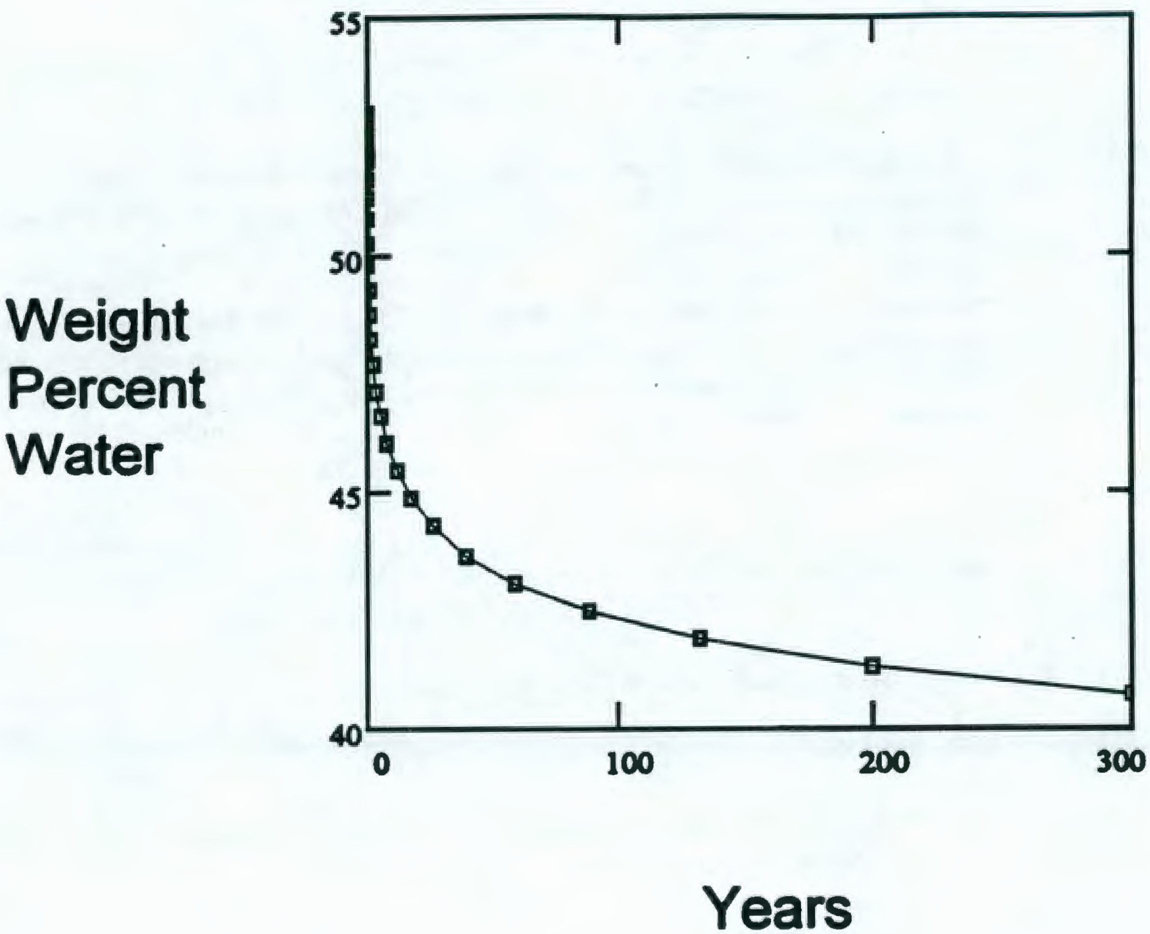
  - **March 31, 1994:** Issue a report, available for public release, on the evaluation of the three waste simulant drying methods.

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

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

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

Figure 2-11. Water Concentration at the Surface of an Eight Foot Column of Ferrocyanide Sludge as a Function of Time.



2.4.4 Position Paper on Safety of Ferrocyanide Tanks

In June 1991 the Tanks Advisory Panel (TAP) requeste that Westinghouse Hanford prepare a position paper on the state of knowledge concerning the Ferrocyanide Safety Issue. The paper was to document what was known about continued safe storage of the ferrocyanide waste in the high-level waste tanks at the Hanford Site. The primary focus of the report was to assess if it was possible for a significant exothermic chemical reaction to occur in the tanks under existing conditions and whether the reaction could reach a runaway state in which radioactive aerosols would be expelled from the tank, as postulated in the General Accounting Office (Peach 1990) report. The safety of continued storage is of interest for all long-term storage, mitigation, remediation, or treatment options because significant storage time will still accrue before options can be selected and completed that modify the waste form and render it safe.

The ferrocyanide position paper and subsequent revisions represent a snapshot in time of (1) what is known about ferrocyanide wastes stored in underground tanks at the Hanford Site, (2) what this information means in terms of storage safety, (3) what key uncertainties exist, and (4) what must be done to close the USQ. The position paper is an overview document with technical backup provided by the ferrocyanide hazards assessment document (Grigsby et al. 1992) or, in the future, by the technical basis document.

A draft position paper was issued November 27, 1991 for DOE and TAP review. Comments were received by May 1992 and the document was revised and cleared for public release on July 24, 1992 (Postma et al. 1992). Updates of the position paper will be issued as significant new information becomes available and as results of core sample analyses are reported.

- **Planned Work for Subsequent Months.** Work on the updated ferrocyanide position paper will commence during FY 1994. An updated position paper on the status of the Ferrocyanide Safety Issue will be completed in June 1994.

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

- **Milestone Status.**

  - **November 27, 1991**: Issue position paper on current understanding of Ferrocyanide Safety Issue. This was completed on schedule.

  - **March 15, 1992**: Issue position paper as a document cleared for public release. This was delayed because review comments were not received on the requested schedule. The deadline was revised to July 1992. The position paper was released as a public document on July 24, 1992.

  - **December 31, 1993**: Issue a ferrocyanide position document, approved for public release, that updates the current understanding of the Ferrocyanide Safety Issue. This will be a revision of WHC-EP-0531, Rev. 1, (Postma et al. 1992). The update of this document has been deferred to September 1994 in order to concentrate efforts on closure of the Ferrocyanide USQ in January 1994.

2.4.5 Ferrocyanide Waste Tanks Hazards Assessment

The scope of the ferrocyanide hazards assessment task was to provide a technical assessment and periodic updates of the ferrocyanide waste tank safety concerns and progress towards closure of the USQ. These assessments are based on information as it becomes available from the Ferrocyanide Safety Program. Contributions are included from Fauske and Associates, Inc. (FAI), Los Alamos National Laboratory (LANL), Pacific Northwest Laboratory (PNL), Westinghouse Hanford, and other sources.

A predecisional interim report assessing the ferrocyanide waste tank hazards was issued on December 3, 1991 for review and comment by TAP, DOE-HQ, and RL. Comments were incorporated into a new revision, approved for public release, and the document was issued on July 24, 1992 as WHC-SD-WM-RPT-032, Rev. 1 (Grigsby et al. 1992). The report reviews the understanding of the ferrocyanide hazard at the time the report was prepared. It presents an integrated evaluation and interpretation of (1) historical data and (2) acquired information. These interim reports will continue to be revised and expanded as additional information becomes available through ongoing work.

Several review comments received on the draft document could not be resolved in the July 1992 release because sufficient information was not available at the time the report was written. These comments will be incorporated into the next revision of the document.

- **Progress During the Reporting Period.** The effort to update the ferrocyanide hazards assessment document was redirected last quarter towards preparation of a safety criteria document to close the Ferrocyanide USQ by January 1994. Since the USQ closure milestone was advanced by seven months and a technical basis for closing the USQ must be included, it was decided that the updated hazards assessment document is not necessary at this time. An update of the document will be prepared later as part of the process for resolving the Ferrocyanide Safety Issue.

- **Planned Work For Subsequent Months.** Preparation of the technical basis for closure of the Ferrocyanide USQ will continue through the next quarter. Technical information from all the Ferrocyanide Safety Program tasks will be gathered into the USQ closure document. The planned approach and key safety criteria that must be met for closure (see Section 2.4.6) will be addressed in detail. The objective of the technical data presented will be to show that in situ storage of the waste is safe and to determine what controls should be implemented to ensure safety.

  After closure of the Ferrocyanide USQ has been accomplished in FY 1994, the Aerosol Experts Panel will be reconvened to review the current status of information available on the Ferrocyanide Safety Issue. The Panel will be asked for their recommendation on the need for conducting small-scale aerosol tests.

Plans for such testing will depend on their recommendations. Tentatively, the Aerosol Experts Panel meeting is planned for March 1994.

A report describing the consequences of hypothetical burns of differing sizes in a ferrocyanide tank is being prepared. The report will be issued in July 1994 and will satisfy the milestone originally set for September 30, 1993.

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

- **Milestone Status.**

  - **May 31, 1993**: Complete the first update of the ferrocyanide hazards assessment document (Grigsby et al. 1992) and issue as an approved public report. This milestone has been deferred for the present time and will become part of the process to resolve the Ferrocyanide Safety Issue now anticipated in FY 1995 and FY 1996.

  - **May 31, 1993**: Complete small-scale aerosol tests and complete final aerosol report. This work was not authorized in the ferrocyanide program budget approved for FY 1993. The need for aerosol tests will be determined by the Aerosol Experts Panel during a meeting tentatively planned for March 1994. Funding for these tests has been allocated in the FY 1994 Ferrocyanide Safety Program budget.

  - **July 31, 1993**: Complete parametric and aerosol tests on the most reactive (In Farm 1) flowsheet simulant at FAI and issue a test report approved for public release. This work was published in two reports issued in June 1993 (Fauske 1993a, 1993b).

  - **September 30, 1993**: Complete a final report, approved for public release, on effects and consequences of various in situ ferrocyanide tank waste burns. This milestone has been deferred until July 1994 because work on the USQ closure document and an update of the hot spot document are considered higher priority.

  - **June 24, 1994:** Issue an Interim Safety Basis Level 1 report to DOE which provides the safety basis for safe operation of ferrocyanide tanks.

  - **July 1994**: Issue an update of the ferrocyanide hazards assessment document. This milestone will be deferred to FY 1994 or canceled pending disposition of the Ferrocyanide USQ closure document and the timing for resolving the Safety Issue.

2.4.6 Closure of the Ferrocyanide Unreviewed Safety Question

Since the inception of the Ferrocyanide Safety Program at Westinghouse Hanford, the ultimate objective of the program has been to resolve the Ferrocyanide Safety Issue and determine if storage of the waste in the tank is safe until final disposal in the Hanford Waste Vitrification Plant. To accomplish that goal the USQ must be closed.

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 the facility Safety Analysis Report (SAR) and other safety analyses, Hazard Classification Documents, Technical Safety Requirements, DOE-issued safety evaluation reports, and facility-specific commitments, such as the safety assessments (SAs). The potential hazards of a ferrocyanide-nitrate/nitrite reaction were discovered to represent an inadequacy in the authorization basis. Therefore, a USQ was declared for the Ferrocyanide Safety Issue, and activities in the waste tanks that could increase the likelihood of an accident involving the ferrocyanide-nitrate/nitrite reaction were restricted (Deaton 1990). Until the USQ is closed, proposed intrusive activities that may impact the safety of the ferrocyanide tanks must be assessed for potential safety and environmental consequences. Furthermore, these activities must be authorized by DOE.

SAs are documents prepared to provide the technical basis to assess the safety of a proposed activity and to provide proper controls to maintain safety. The SA, along with the accompanying Environmental Assessment (EA), provides the basis for DOE authorization of the proposed activities.

Since inception of the Ferrocyanide Safety Program, SAs have been completed for vapor space sampling of all ferrocyanide tanks, waste surface sampling, push-mode core sampling, TC tree installation in sound and leaker tanks, and removal of pumpable liquid from leaking tanks (also known as interim stabilization).

A decision was made to revise the existing SA for installing TC trees in sound (non-leaking) ferrocyanide tanks so that installation in leaker tanks was addressed as well. A study to evaluate and identify alternative methods for installation of TC trees in assumed leaker ferrocyanide tanks was completed. The previous method used relatively large volumes of water to sluice the TC tree through the waste. An ultra high pressure concept that uses minimal quantities of water was chosen for final testing and design. These documents were transmitted to DOE in April 1993.

Preparation of safety and environmental assessments for rotary-core sampling of ferrocyanide and other Watch List tanks that contain hard waste (e.g., saltcake) is necessary. The rotary drill system is expected to be deployed for field operation in mid FY 1994.

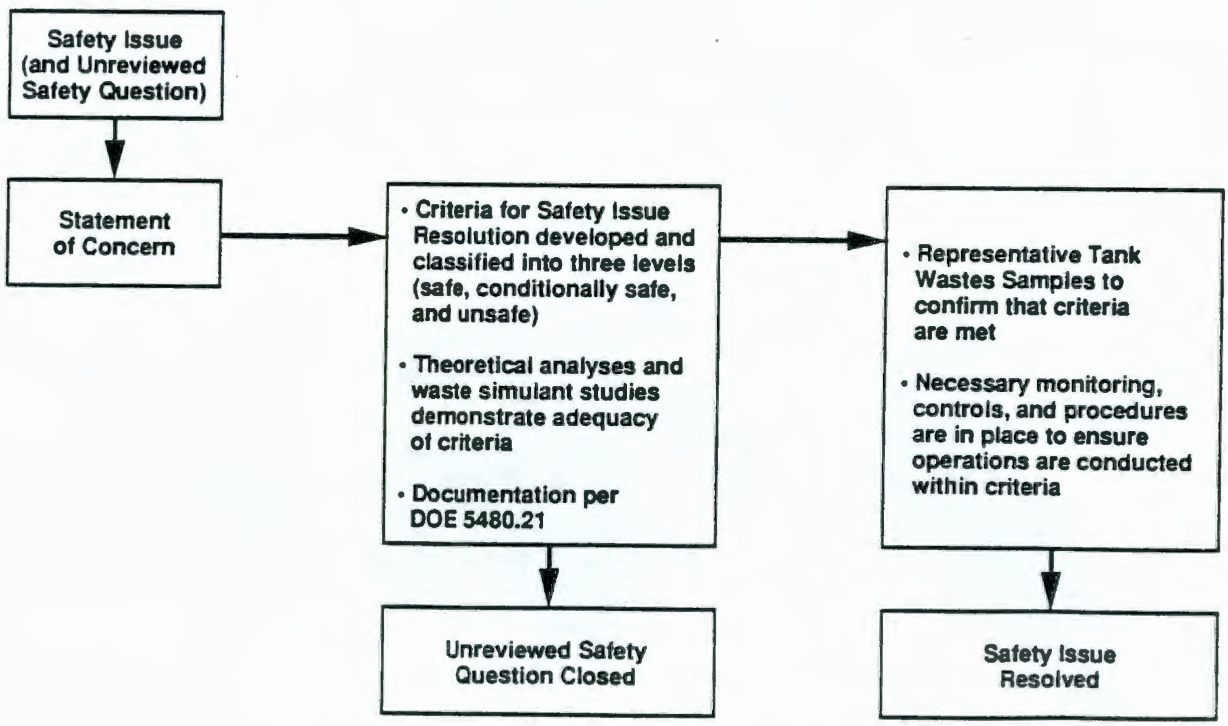
- **Progress During the Reporting Period.** As part of the accelerated Safety Initiatives, closure of the Ferrocyanide USQ has been moved forward to January 1994. This, coupled with a new strategy for USQ closure, resulted in a new path for USQ closure.

The effort to close the USQ has been redirected by DOE and there are no plans to publish the original Ferrocyanide Resolution plan. Instead, work started this quarter on a safety criteria document that incorporates the strategy and logic laid out by DOE to DNFSB (Figure 2-12).

The logic uncouples USQ closure from safety issue resolution. As indicated in Figure 2-12, USQ closure is a milestone on the path to resolving the safety issue. The USQ will be closed using a criteria document that identifies safety criteria for each level of tank safety ("Safe, Conditionally Safe, and Unsafe") and the technical basis for the criteria.

To close the USQ, each ferrocyanide tank would be classified into one of the three levels of safety using these criteria. The safety issue would be resolved after waste from the tanks is characterized and necessary monitoring and controls are put in place to ensure operations are conducted within the safety criteria envelope for the "Safe" or "Conditionally Safe" levels. While the closure of the Ferrocyanide USQ is a near-term objective, resolution of the Ferrocyanide Safety Issue will require a longer timeframe because it requires that waste samples be taken from representative tanks and analyzed, and that other characterization data on the tanks be available.

Figure 2-12. Strategy for Closure of the Ferrocyanide USQ and Resolution of the Safety Issue



The steps leading to closure of the Ferrocyanide USQ are presented in Figure 2-13. The major effort in the approach is the determination of criteria for the safety classes or levels. The criteria are formulated on the basis of defined safety classes, the safety objective, and an understanding of hazard phenomenology. After the criteria have been quantified, currently available waste characterization data are evaluated in light of the criteria. The document that quantifies the work steps depicted in Figure 2-13 provides the basis for closure of the USQ.

The waste parameters on which criteria are to be established have been identified from known requirements for exothermic oxidation/reduction reactions. These are:

-FUEL
-OXIDANTS
-MOISTURE
-WASTE TEMPERATURE

At present it is envisioned that the tanks would be classified into three levels:

LEVEL 1 - <u>SAFE</u>
- fuel content ≤ A%
- oxidants - not limiting
- moisture - not limiting
- waste temperature - not limiting

LEVEL 2 - <u>CONDITIONALLY SAFE</u>
- fuel content > A%
- oxidants - not limiting
- moisture ≥ B%
- waste temperature ≤ C °C

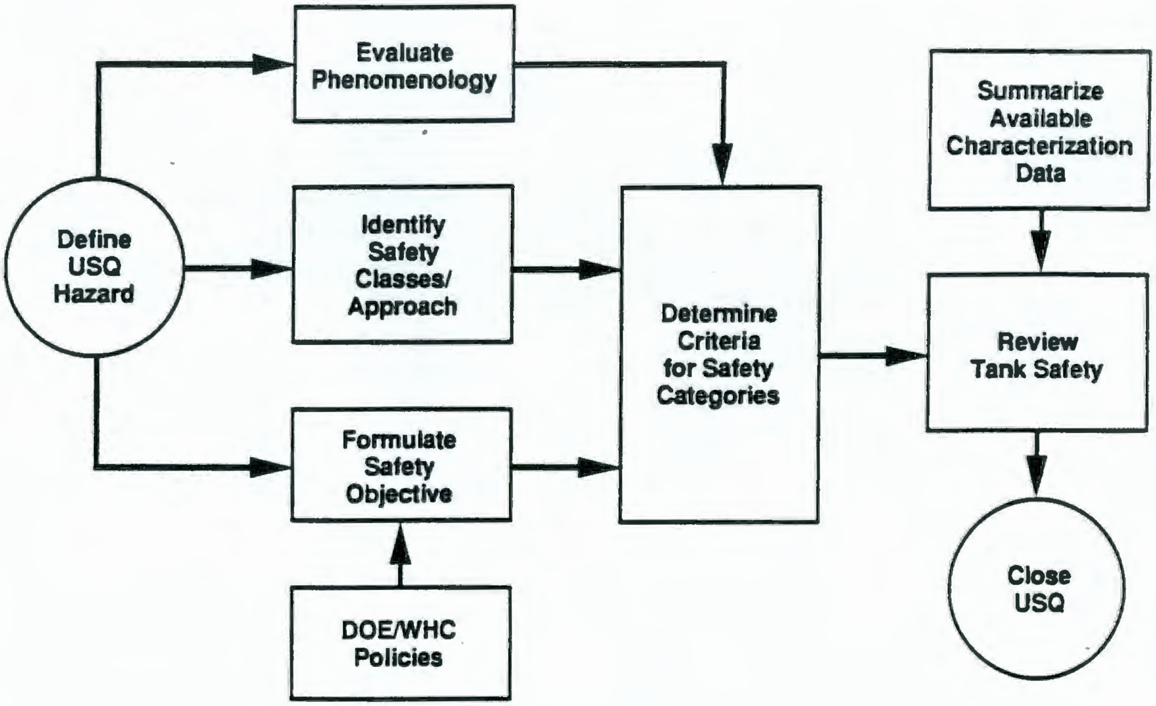
LEVEL 3 - <u>UNSAFE</u>

- criteria for level 1 and level 2 are not met

Numerical values for A, B, and C will be chosen on the basis of theoretical studies and experimental results conducted on waste simulants.

- **Planned Work for Subsequent Months.** A draft of the Ferrocyanide USQ criteria document will be submitted for final DOE review by December 1, 1993. This is part of the accelerated DOE safety initiative that calls for closure of the Ferrocyanide USQ by January 31, 1994.

Figure 2-13. Information Required for Closure of the Ferrocyanide USQ.



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

- **Milestone Status.**

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

  - **October 31, 1992**: Issue SA and EA documentation to DOE for rotary-mode core sampling of ferrocyanide tanks. The SA and EA documentation was completed and transmitted to DOE for approval on July 8, 1993.

  - **January 29, 1993**: Submit predecisional USQ closure plan to DOE providing details on the proposed approach for closure the Ferrocyanide USQ. This milestone was completed on schedule.

  - **February 1, 1993**: Receive authorization from DOE, based on revised SA and EA documentation, to proceed with pumping of ferrocyanide tank 241-T-101. This milestone was deferred to February 26, 1993, because the revised SA was not transmitted to DOE until January 29,

1993. Authorization to pump 241-T-101 was received from DOE in early March, and pumping commenced on March 12.

Comments were received on the SA from DOE in July on one issue that required further analysis. The final SA is now scheduled to be resubmitted to DOE by November 1993.

- **March 30, 1993**: Submit SA and EA documentation for installation of TC trees in assumed leaker ferrocyanide tanks to DOE for review and comment. The SA and EA were completed and submitted to DOE in April 1993; see also Section 2.1.1.
- **September 1, 1993**: Receive authorization from DOE, based on revised SA and EA documentation, to install remaining TC trees in assumed leaker ferrocyanide tanks. This task was delayed as a result of the Tank Farm Administrative Hold and has been rescheduled for February 28, 1994.
- **December 1, 1993**: Submit draft of Ferrocyanide USQ closure criteria document for final DOE review.
- **January 31, 1994**: Close Ferrocyanide USQ based on approval of the Ferrocyanide USQ closure criteria document.

2.4.7 Concepts for Resolution of the Ferrocyanide Safety Issue

A draft report on three approaches evaluated for resolution of the Ferrocyanide Safety Issue was issued by Westinghouse Hanford in November 1991. Comments were received on the report from TAP, DOE-HQ, and RL in May 1992. Work on this task since then was directed to revising the report to reflect the latest information available on the Ferrocyanide Safety Issue. Based on this information, Westinghouse Hanford has taken the position that in situ safe storage is the safe and viable choice for all the tanks on the Ferrocyanide Watch List.

In January 1993, Westinghouse Hanford requested that DOE remove six tanks from the Ferrocyanide Watch List; 241-BX-102, -106, -110, -111, 241-BY-101, and 241-T-101. Historical records for five of the six tanks (241-BX-102, -106, -110, -111, and 241-BY-101) show that none of these tanks received any ferrocyanide sludge, although supernatant from other ferrocyanide receiver tanks was temporarily routed to these tanks. Waste transfer records for tank 241-T-101 showed that it received about 10,000 gram moles of ferrocyanide sludge; however, it was subsequently sluiced and emptied (Borsheim et al. 1993). If the list of tanks that contain ferrocyanide were to be generated today and the same 1000 g-mole criteria applied, these six tanks would not be included on the list.

- **Progress During Reporting Period.** Westinghouse Hanford received DOE concurrence for the removal of tanks 241-BX-110, -111, 241-BY-101, and 241-T-101 from the Ferrocyanide Watch List. Close review of waste transfer records revealed that these tanks contained either a trivial amount of ferrocyanide or no ferrocyanide.

  More information was requested for the removal of two additional tanks, 241-BX-102 and 241-BX-106, from the Watch List. A document, *Ferrocyanide Safety Program: Rationale for Removing Six Tanks from the Safety Watch List* (Borsheim et al. 1993), was written this quarter to address DOE concerns. The document reviews transfer histories for the tanks and includes the documentation used for DOE's decision to authorize stabilization of 241-T-101. A request for DOE concurrence in removing tanks 241-BX-102 and -106 from the Ferrocyanide Watch List was included in the cover letter.

- **Planned Work for Subsequent Months.** The report on selected concepts and recommendations will be updated to reflect the latest information supporting the in situ safe storage option for the ferrocyanide tanks. The report will be cleared for public release and issued.

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

- **Milestone Status.**

  - **November 30, 1992:** Issue a report, approved for public release, on selected concepts and recommendations for resolution of the Ferrocyanide Safety Issue. This milestone was delayed to address other higher priority issues in the Ferrocyanide Safety Program. Release of the report is expected within the first nine months of FY 1994.

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

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

Chemical reaction studies on ferrocyanide waste simulants are being conducted by Westinghouse Hanford, PNL, LANL, Washington State University, and FAI. Westinghouse Hanford and PNL have produced flowsheet simulant materials for testing and characterization. PNL is also administering the subcontract with LANL. In FY 1992, LANL completed chemical reaction sensitivity tests on ferrocyanide waste simulants to identify what stimuli (emphasizing non-thermal) may cause a reaction to occur. FAI is conducting adiabatic calorimetry and propagation tests on these same replicated flowsheet materials. The FAI scope of work was expanded in FY 1993 to include selected aerosol studies.

2.5.1 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 speciation of cyanides found in the actual tank waste; (2) the aging effects of more than 35 years of storage in the tanks; (3) the influence of chemical interactions and physical changes on the solubility of sodium and cesium nickel ferrocyanides; (4) possible microconvection mechanisms that may have allowed mixing of the ferrocyanide sludge with caustic solutions added to the tanks at a later time; (5) the reaction kinetics of mixtures of sodium nickel ferrocyanide and sodium nitrate/nitrite; and (6) modeling of hydro-geologic drainage of ferrocyanide waste simulants.

- **Progress During Reporting Period.**

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

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

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

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

  Samples of the simulant were contacted with 4 M NaOH for three weeks at 90 °C in a field of 1.43×10^5 Rad/hour. An identical reaction mixture was heated to 90 °C outside the gamma irradiation source as a control. Both the sample and control solutions were sparged with argon before sealing and neither solution was stirred mechanically. Analytical data for the reaction mixtures are shown in Table 2-2.

  The final reaction solutions were analyzed for ammonia using an ammonia selective electrode technique. From Table 2-2, the ammonia concentration in the gamma-irradiated solution (0.0938 M) was 8.6 times that found in the control

(0.0109 M). The results indicate a hydrolysis of approximately 42% of the cyanide to ammonia in the gamma field and 4.8% in the control, based on the solution concentrations. These results strongly suggest that gamma radiation promotes the hydrolysis of ferrocyanide, possibly by facilitating the dissociation of cyanide from the ferrocyanide complex.

Table 2-2. Solution Analytical Data for Reaction Products from Hydrolysis of In Farm 1A, Rev. 4.

ANALYTE	CONTROL (Moles/liter)	Gamma Irradiated (Moles/liter)
NH_3	0.011	0.094
HCO_2^-	0.014	0.012
NO_3^-	0.18	0.15
NO_2^-	0.090	0.40
Fe	1,670 ppm	890 ppm
Cs	5.1 ppm	8.8 ppm

The concentration of formate [HCO_2^-] in the control solution was in excellent agreement with the concentration of ammonia measured in solution. The one-to-one correlation was not observed in the gamma-irradiated solution, which contained a formate concentration about 8 times lower than the ammonia concentration. Gamma radiation degrades formate to carbonate. This was consistent with infrared spectra of the insoluble solids from the samples, which indicated more carbonate present in the solids from the gamma irradiated sample than in the solids from the control.

The concentration of soluble iron was 1,675 ppm and 890 ppm for the control and gamma solutions, respectively. The lower iron concentration in the gamma sample is consistent with more extensive hydrolysis, which should result in the precipitation of iron oxides. A small amount of cesium was detected in solution at concentrations of 5.14 and 8.73 ppm for the control and gamma experiments, respectively, corresponding to 2.3% and 3.9% Cesium dissolution.

The dissolution temperature dependance of the In Farm 1A simulant was also investigated during the quarter. The dissolution temperature dependance was determined at 60 °C and 90 °C using pH 13 solutions adjusted to 1 M sodium ion with $NaNO_3$. At 60 °C and 90 °C, the reaction apparently approaches equilibrium dissolution of about 47% and 63%, respectively. Atomic absorption analysis of the solution phase indicated none of the cesium dissolved.

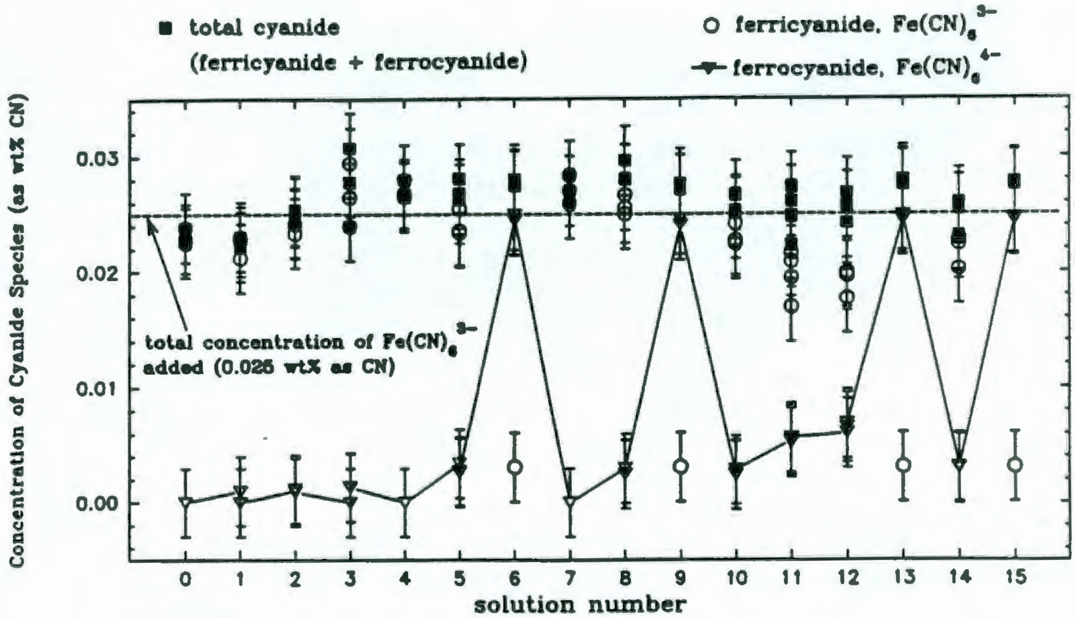
Cyanide Speciation. A report summarizing the progress on cyanide speciation was published this quarter, *Cyanide Speciation Studies FY 1993 Annual Report* (Bryan et al. 1993). Two solution techniques were developed as analytical methods. These methods were based on Fourier Transform infrared (FTIR) spectroscopy and ion chromatography (IC) analytical techniques. Both methods were able to quantify cyanide to about 0.1 wt%.

The effect of potential interferences on the speciation analyses by other constituents present in the dissolved ferrocyanide waste is under investigation. Tests already concluded have shown that cyanide speciation is insensitive to inorganic constituents such as nitrate, carbonate, hydroxide, phosphate, etc.. Possible organic interferants are now being examined.

Influence of Probable Organic Chemical Interferences on Ferrocyanide and Ferricyanide Analysis. The effect of organic constituents which could be present in ferrocyanide waste tanks are also being investigated for their potential interferences on the cyanide species analyses. The presence of various organic species had no appreciable effect on the measured concentration of ferrocyanide. However, as indicated in Figure 2-14, several organic constituents had a major effect on the measured concentrations of ferricyanide. An accurate measure of ferricyanide is important since it produces a more energetic reaction with nitrate than does ferrocyanide.

The organic compounds that showed dramatic ferricyanide to ferrocyanide conversion, nitrilotriacetic acid (NTA), HEDTA, EDTA, iminodiacetic acid (IDA), glycine, and ethylenediamine (en), all contain organic amine functionalities within their molecular structure. Several of the non-amine complexes also showed some ferricyanide to ferrocyanide conversion. They included sodium oxalate, sodium glycolate, and n-butanol. Even though these conversion rates are relatively slow when compared to the amine based conversion, ample time has passed during waste storage for the reduction of ferricyanide to ferrocyanide to occur.

Figure 2-14. Concentrations of Cyanide Species in Solutions Initially Containing Only Ferricyanide and Potential Organic Interferants.



all solutions initially contained 0.025 wt% $Fe(CN)_6^{3-}$ and 2.5 wt% organic additive

0. $Fe(CN)_6^{3-}$ (0.025 wt%, CN)
1. sodium citrate
2. sodium acetate
3. sodium formate
4. NPH
5. sodium oxalate
6. HEDTA
7. TBP
8. glycerin
9. EDTA
10. sodium glycolate
11. IDA
12. glycine
13. NTA
14. n-butanol
15. ethylendiamine (en)

Microconvection Modeling. A report on microconvection modeling was released this quarter, *Ferrocyanide Safety Program: Computational Analysis of Fluid Flow and Zonal Deposition in Ferrocyanide Single-Shell Tanks* (McGrail et al. 1993). Computer simulations predicted that microconvective mixing will occur in ferrocyanide single-shell tanks, because of fluid density gradients and/or thermal gradients. The predicted velocity for fluid convection through the waste and interstitial liquid was 3 m/yr for sludge with 50% porosity, a permeability of 0.002 Pa·s, and a density difference of 50%. Thermal convective mixing was predicted to be much slower, about 10^{-5} to 10^{-2} m/yr.

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

- **Planned Work For Subsequent Months.**

  - Continue the aging study radiolysis and hydrolysis experiments using ferrocyanide flowsheet simulant (In Farm 1A, Rev 4). Parameters such as temperature and pH will be evaluated during gamma pit experiments.

  - Continue work on cyanide speciation analytical methods including IC methods and solution IR methods. Determine probable interferences that may be encountered in developing analytical methods for actual waste samples. Work will also continue on solids speciation methods using IR and Raman techniques. These methods will be explored further using flowsheet materials.

  - Expand microconvection modeling studies and assemble information that contains key physical and chemical properties of waste.

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

- **Milestone Status.**

  - **November 27, 1992:** Transmit a final, cleared report on FY 1992 Aging Studies to DOE. The report (Lilga et al. 1992) was issued on November 25, 1992.

  - **January 22, 1993:** Transmit a draft report on FY 1992 PNL catalyst, initiator, and diluent screening studies to Westinghouse Hanford for review and clearance. The draft report was submitted to Westinghouse Hanford on January 22 for review.

  - **April 30, 1993:** Issue a final PNL report on catalyst, initiator, and diluent studies that is approved for public release. This report, PNL-8649 (Scheele et al. 1993), was issued on schedule.

  - **June 30, 1993:** Issue the final, cleared report on small-scale sensitivity tests of ferrocyanide flowsheet simulants conducted by LANL. This report, LA-12589-MS (Cady 1993), was issued on schedule.

  - **September 20, 1993:** Issue a final PNL report of FY 1993 ferrocyanide microconvection modeling activities at PNL; approved for public release. This report was released on schedule as PNL-8876 (McGrail et al. 1993).

  - **September 20, 1993:** Issue a PNL report, approved for public release, on ferrocyanide speciation method development and deployment of a system in PNL hot cells or laboratory hoods. This report was released on schedule as PNL-8887 (Bryan et al. 1993) and describes work completed in FY 1993.

- **September 30, 1993**: Issue a final cleared PNL report on the results of aging studies on ferrocyanide waste to Westinghouse Hanford for transmittal to DOE. This report was released on schedule as PNL-8888 (Lilga et al. 1993).

2.5.2 Ferrocyanide Propagation Studies

Ferrocyanide adiabatic calorimetry and propagation tests are continuing at FAI under contract to Westinghouse Hanford. The results of these tests are being used to help determine if Hanford Site ferrocyanide waste will ignite and burn to spread and involve additional waste from a potential ignition point and to determine the potential for release of radioactive species under postulated accident conditions. Tests were conducted with dried simulant to evaluate safety concerns associated with postulated hot spot accident conditions. The propagation velocity is a key parameter in determining safety consequences of postulated burns, including a potential radioactivity release from confinement.

Because the composition of the waste in the storage tanks varies and is unknown at all locations, ranges of material compositions have been tested. Present work is focused on the T Plant and the more reactive In Farm 1 simulants. Sludge produced by the In Farm flowsheet was stored in four C Farm tanks and represents about 26% of the total ferrocyanide used in the Hanford scavenging processes. Sludge produced by the T Plant flowsheet was stored in three TY Farm tanks and represents about 8% of the total ferrocyanide used during the Hanford scavenging processes. Adiabatic calorimeter tests have also been initiated to assess the organic contributions to energy releases from ferrocyanide sludges during heat up.

The present concentration of ferrocyanide in the sludge is in question because ferrocyanide has been shown to hydrolyze in the presence of high pH waste (see Section 2.5.1). Initial sample results of C Farm tank waste indicate that the waste ferrocyanide concentrations are at considerably lower concentrations than the In Farm simulants being tested (Simpson et al. 1993a, 1993b)

- **Progress During Reporting Period.** T Plant simulant was prepared and sent to FAI for adiabatic calorimetry tests. The ferrocyanide concentration in the upper fraction of T Plant simulant is expected to be similar to the U Plant simulant in exothermic behavior. The lower fraction did not exhibit exothermic properties during DSC tests.

  A series of tests were conducted at FAI this quarter to determine the minimum concentration of sodium nickel ferrocyanide required to sustain a propagating reaction. In Farm 2 simulant was mixed with sodium nitrate or alumina to concentrations of 15 and 18 wt% $Na_2NiFe(CN)_6$. For dilutions containing both sodium nitrate and alumina, simulant containing 15 wt% $Na_2NiFe(CN)_6$ would not propagate. However, simulant containing 18 wt% $Na_2NiFe(CN)_6$ did propagate. These experiments were conducted to delineate an empirical value for the concentration criteria for sodium nickel ferrocyanide (see Section 2.4.6).

- **Planned Work for Subsequent Months**. Screening tests will be conducted in early FY 1994 to determine propagation limits for ferrocyanide simulants as a function of ferrocyanide concentration and moisture content. Additional parametric and ferrocyanide/organic tests will be developed and initiated at FAI. Calorimetry tests will continue on the T Plant ferrocyanide simulant. The residue from aerosol test using In Farm 1 samples will be analyzed to identify reaction products. Adiabatic calorimeter studies on ferrocyanide simulant sludges spiked with organics will continue.

- **Milestone Status.**

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

  - **January 31, 1993**. Completed pressure parametric and confined scoping aerosol/propagation tests on the most reactive flowsheet simulant at FAI. These results are reported in Fauske (1993a, 1993b).

  - **May 14, 1993**. Completed preparation and shipment of U Plant 1 simulants to FAI for calorimetric and dryout tests.

  - **July 30, 1993**. Complete report on T Plant calorimetry and propagation tests and U Plant dry out tests. This report was completed by FAI on July 28, 1993. The report will be cleared for public release next quarter.

  - **September 30, 1993**. Complete report on stoichiometric scanning calorimeter tests. This report was completed by FAI in August 1993. The report will be prepared for public release next quarter.

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

2.6 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.6 (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."

2.6.1 Action Plan for Response to Abnormal Conditions

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

Also addressed in this section are actions in response to other abnormal conditions that might be encountered with the ferrocyanide tanks, such as a leak to the environment. Of the 20 tanks currently on the Ferrocyanide Watch List, 11 are classified as assumed leakers. Four of the assumed leaker tanks have not been interim stabilized. Five tanks still require some pumping to be classified as interim stabilized. Authorization to pump these tanks must be granted by DOE because the activity involves the Ferrocyanide USQ. This authorization requires that SA and EA documentation be prepared for this activity.

- **Progress During the Reporting Period.** Both the SA and the EA for removing pumpable liquids from ferrocyanide tanks were submitted to DOE for review on September 30, 1992. Comments were received on the documents in early January and they were revised and resubmitted at the end of January. Additional comments on the EA were received from DOE-RL on March 31, 1993 and were addressed. However, several more sets of comments were received from DOE-RL in July 1993 which continue to be addressed. A request for authorization for stabilization and emergency pumping of the ferrocyanide tanks was submitted to DOE, but no response has been received.

- **Planned Work for Subsequent Months.** Comments received from DOE in July on the SA and EA will be incorporated and the document will be resubmitted to DOE. Additional analysis is required to address one issue on possible flammable gas buildup in the double contained receiver tanks. Westinghouse Hanford committed to resubmit the updated SA by November 30, 1993. The specific EA for interim stabilization has been incorporated into the generic tank farm EA to be submitted to DOE in November 1993.

  Plans for interim stabilization of the five ferrocyanide tanks remaining to be pumped will proceed as soon as authorization is received from DOE. Each tank will undergo a readiness review prior to commencing pumping operations.

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

- **Milestone Status.**

  - **August 31, 1992**. Issue a draft SA for saltwell pumping (stabilization) of ferrocyanide tanks to DOE. This SA will be applicable to tanks that may need to be pumped because of a leak. This milestone was met on September 30, 1992 with submittal of the original version of the SA.

  - **September 30, 1992**. Recommendations will be issued on the feasibility and safety of stabilizing single shell ferrocyanide tanks. These recommendations will also address actions to be taken if a tank shows evidence of a leak. The recommendation letter, together with the safety assessment on stabilization of ferrocyanide tanks, was delivered to DOE on September 30, 1992.

  - **December 31, 1992**. Incorporate comments into the SA and EA documents as appropriate and submit revised documents to DOE for review. The EA was revised and resubmitted to DOE in December and the SA was not submitted until January 25, 1993. A second revision of the EA was transmitted on January 29, 1993.

  - **February 1, 1993**. Receive authorization from DOE, based on revised SA and EA documentation, to proceed with pumping of leaking ferrocyanide tank 241-T-101. The scheduled date for initiation of pumping was changed to the first part of March 1993. Authorization was received in March and pumping was completed on April 14, 1993.

- **March 31, 1994.** Complete an evaluation report to determine which gases, if any, need to be continuously monitored on selected ferrocyanide tanks (see also Section 2.3).

2.6.2 Response to an Airborne Release From a Ferrocyanide Tank

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 DOE and Westinghouse Hanford have analyzed the potential impacts of an event involving one of these tanks, and have taken additional steps so that emergency personnel can take mitigating actions in a timely fashion. These analyses resulted in development of the *Tank Farm Emergency Response Stabilization Plan* (Westinghouse Hanford 1991) in March 1991. The plan includes predetermined mitigative actions for terminating the emergency phase and providing a transition to the recovery phase. Acknowledging that an event could range from minor to major releases, the plan addresses responses in four distinct and defined steps that will cover the range of consequences. The *Stabilization Plan* provides quick, preplanned actions that can be used to stabilize an emergency event at an underground radioactive waste storage tank.

- **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.** None applicable.

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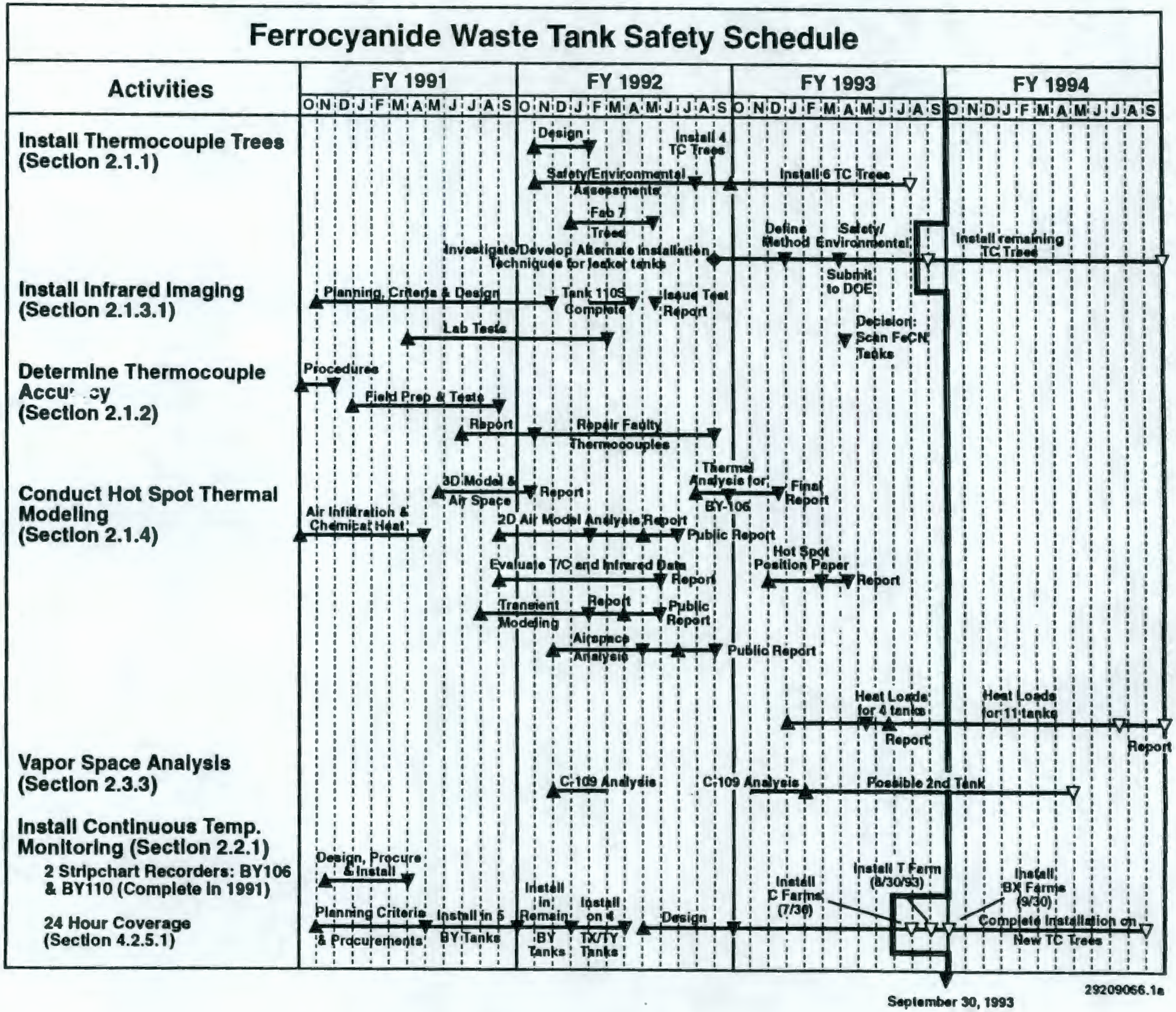
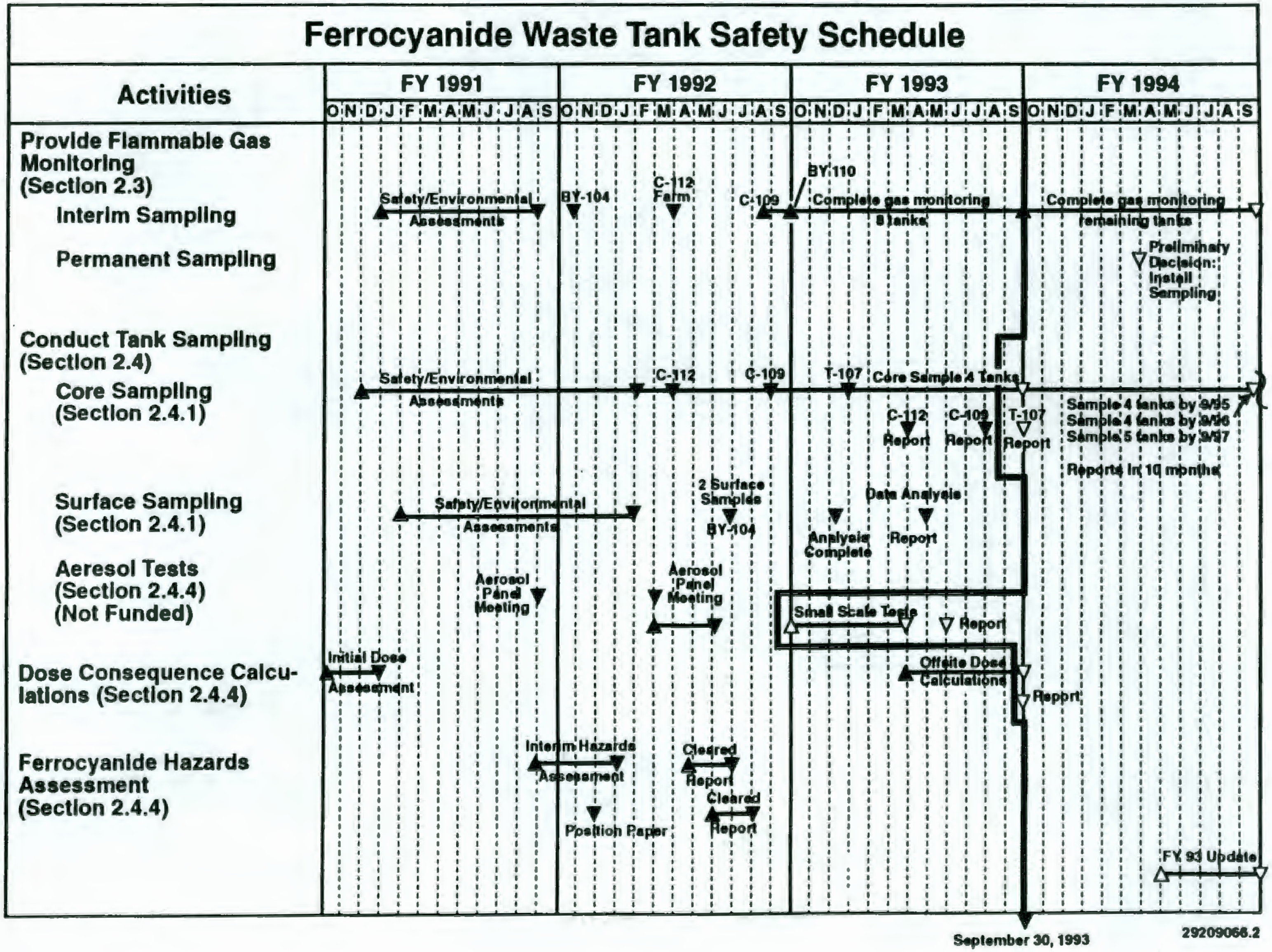
3.0 SCHEDULES

The schedules presented in this section are those provided by the revised implementation plan, WHC-EP-0415, Rev. 1 (Borsheim et al. 1992). The schedules have been statused for FY 1993, ending September 30, 1993. Work on the Ferrocyanide Safety Program is shown for FY 1991 through FY 1994. Because the scope of some of the program activities has changed over the past two years, it is appropriate that progress be tracked against this new schedule.

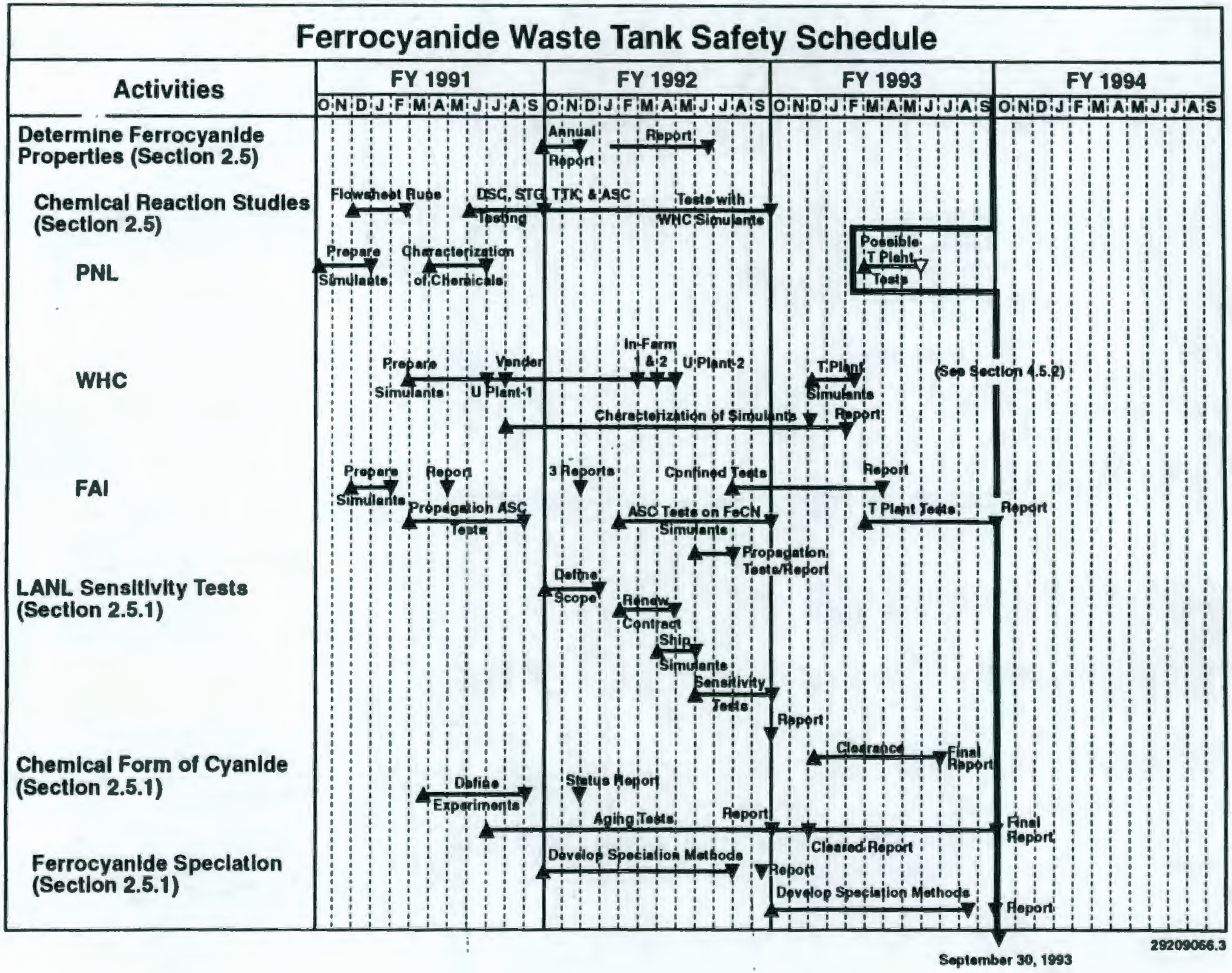
The new schedule was expanded to four pages, and is laid out in a slightly different format that is easier to read. Activities that have started or been completed are indicated by triangles that are filled in. Work indicated by open triangles has either not started or has not been completed. A status line will be drawn each quarter showing the progress completed on each activity.



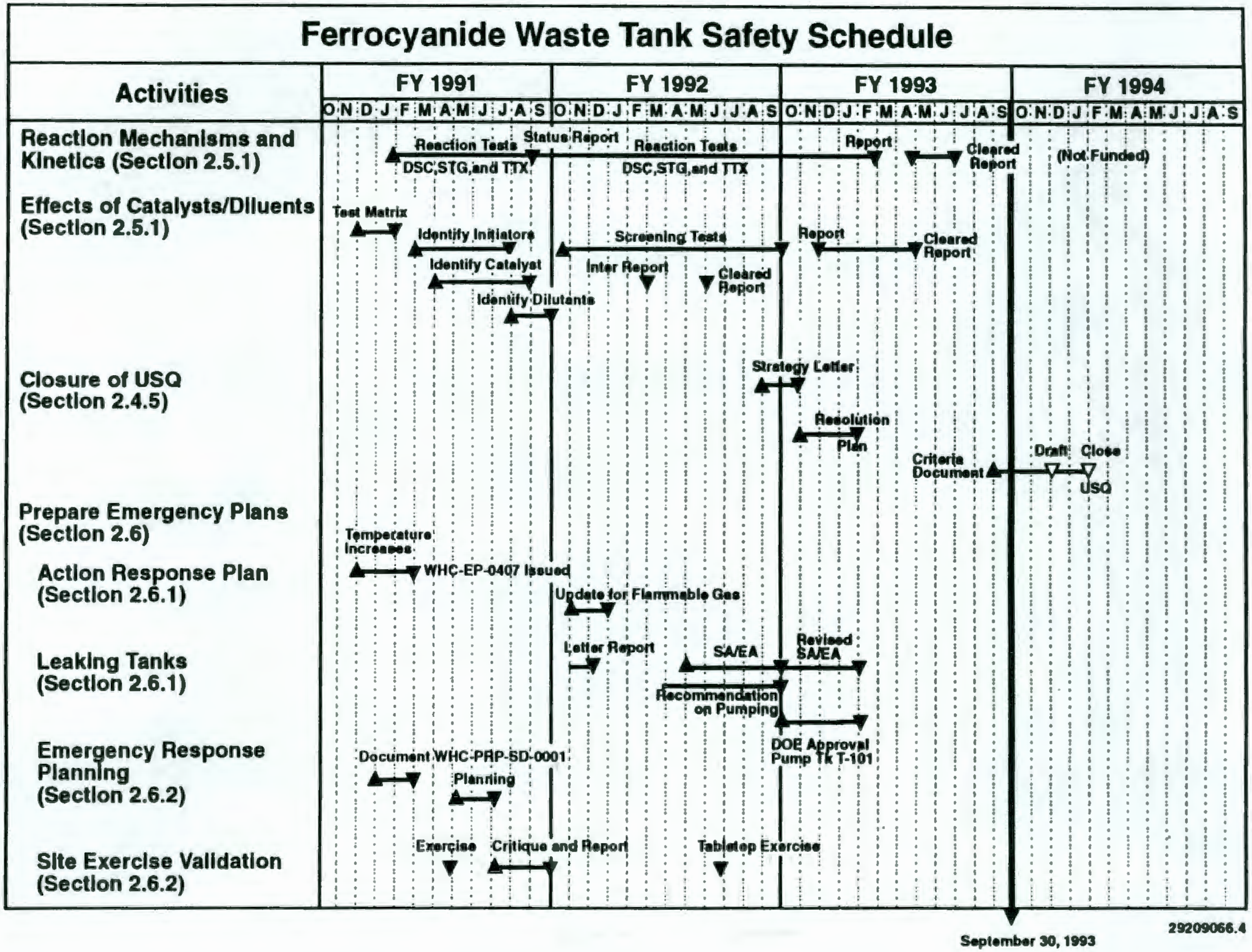
Schedule 3-1. (Sheet 1 of 4)



Schedule 3-1. (Sheet 2 of 4)



Schedule 3-1. (Sheet 3 of 4)



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APPENDIX A

FERROCYANIDE TANKS

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

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g mol)	Heat load (1,000 Btu/h)[c]	Maximum temp. (°C)	(°F)	Status of tanks[e]
BX-102	96	< 1	< 10	19	66	IS; AL
BX-106	46	< 1	< 10	18	64	NS; Sound
BY-103	400	66	8.6	27	81	NS; AL
BY-104	406	83	5.5 - 11.0[d]	53 46[f]	128 115	IS; Sound
BY-105	503	36	4.0 - 8.0[d]	46 49	114 121	NS; AL
BY-106	642	70	5.5 - 11.0[d]	54	129	NS; AL
BY-107	266	42	14.5	36	97	IS; AL
BY-108	228	58	4.4 - 8.8[d]	43	109	IS; AL
BY-110	398	71	4.0 - 8.0[d]	49 42[f]	120 108	IS; Sound
BY-111	459	6	2.4 - 4.8[d]	31 29[f]	88 85	IS; Sound
BY-112	291	2	< 10	28 32[f]	83 89	IS; Sound
C-108	66	25	< 10	24	76	IS; Sound
C-109	66	30	3.5 - 7.0[d]	27 27[f]	80 80	IS; Sound
C-111	57	33	< 10	24	76	IS; AL
C-112	104	31	< 10	27 27[f]	81 81	IS; Sound
T-107	180	5	< 10	18	65	NS; AL
TX-118	347	< 3	4.9	24	76	IS; Sound

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

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g mol)	Heat load (1,000 Btu/h)[c]	Maximum temp. (°C) (°F)		Status of tanks[e]
TY-101	118	23	< 10	19	66	IS; AL
TY-103	162	28	< 10	21	70	IS; AL
TY-104	46	12	< 10	19	66	IS; AL
Totals	4,881,000 gal	624K g-mol.				

[a] Reflects removal of four ferrocyanide tanks from Watch List in July 1993. Tank information and temperature data as of August 1993 (Hanlon 1993).

[b] Inventories from Borsheim and Simpson, 1991.

[c] Heat load values are conservatively high. New values will be calculated.

[d] New heat load data as of September 1992, showing low and high end of range based on variances in thermal conductivities for waste and soil.

[e] IS - Interim Stabilized Tank; NS - Not Stabilized; AL - Assumed Leaker Tank; Sound - Non-Leaking Tank.

[f] Temperatures recorded for new thermocouple trees.

Table A-2. Ferrocyanide Tank Vapor Sampling Summary

Tank[1]	Date Sampled	Flamm (% LFL)	Org. Vapor (ppm)	Ammonia (ppm)	HCN/CN (ppm)	Hydrazine (ppm)	Nitrous Gas (ppm)
241-BY-104	10/16/91 - 10/30/91	1.0	37.2	250	<2	>3.0[2]	>10
241-C-112	03/09/92 - 03/18/92	<1.0	<0.2	<5	<2	<0.2	<2
241-C-109	08/26/92	<1.0	---	<5	<2	<0.2	<0.5
241-BY-110	09/27/92	<1.0	350	612[3]	<2	<0.2	<0.5
241-T-107	10/22/92	<1.0	24	203	<2	<0.2	<0.5
241-T-101	02/24/93	1.0	2.1	20.5	<2	<0.2	<0.5
241-BY-111	03/25/93	<1.0	6.3	10.2	<2	<0.2	<0.5
241-BY-112	03/26/93	<1.0	5.9	10.0	<2	<0.2	<0.5
241-BX-111	06/08/93	<1.0	3.5	69.9	<2	<0.2	<0.5
241-BX-110	06/09/93	<1.0	7.0	80.3	<2	<0.2	<0.5
241-BX-106	06/17/93	<1.0	12	17.9	<2	<0.2	<0.5
241-BY-101	06/30/93	<1.0	20	40.0	<2	<0.2	<0.5
241-C-108	07/23/93	<1.0	1.2	<2	<2	<0.2	<0.5
241-TX-118	07/28/93	<1.0	0.3	10.1	<2	<0.2	0.5
241-C-111	08/11/93	<1.0	<0.2	<2	<2	<0.2	<0.5

[1]Maximum reported values for sampling effort
[2]High reading due to ammonia interference
[3]Approximation due to concentration exceeding Dräger tube range

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APPENDIX B

METRIC CONVERSION CHART

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Table B-1. Metric Conversion Chart.

Into Metric			Out of Metric		
If You Know	Multiply By	To Get	If You Know	Multiply By	To Get
Length			Length		
in.	2.54	cm	mm	0.04	in.
ft	30.48	cm	cm	0.4	in.
Mass (weight)			Mass (weight)		
lb	0.453515	kg	kg	2.2	lb
Volume			Volume		
gal	3.78541	L	L	0.264172	gal
Temperature			Temperature		
Fahrenheit (°F)	Subtract 32 then multiply by 0.55555...	Celsius (°C)	Celsius (°C)	Multiply by 1.8, then add 32	Fahrenheit (°F)

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