WHC-EP-0474-19

Quarterly Report on the Ferrocyanide Safety Program for the Period Ending December 31, 1995

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

Westinghouse
Hanford Company Richland, Washington

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

Approved for public release; distribution is unlimited

This report has been reproduced from the best available copy. Available in paper copy and microfiche.

Available to the U.S. Department of Energy
and its contractors from
U.S. Department of Energy
Office of Scientific and Technical Information (OSTI)
P.O. Box 62
Oak Ridge, TN 37831
(615) 576-8401

Available to the public from the U.S. Department of Commerce
National Technical Information Service (NTIS)
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4650

Printed in the United States of America

DISCLM-1.CHP (8-95)

WHC-EP-0474-19

Quarterly Report on the Ferrocyanide Safety Program for the Period Ending December 31, 1995

R. J. Cash
J. E. Meacham

Date Published
January 1996

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

Westinghouse Hanford Company P.O Box 1970 Richland, Washington

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

RELEASE AUTHORIZATION

Document Number:	WHC-EP-0474-19
Document Title:	Quarterly Report on the Ferrocyanide Safety Program for the Period Ending December 31, 1995
Release Date:	1/31/96

This document was reviewed following the procedures described in WHC-CM-3-4 and is:

APPROVED FOR PUBLIC RELEASE

WHC Information Release Administration Specialist:

Kara M. Broz January 31, 1996

A-6001-400 (07/94) WEF256

QUARTERLY REPORT ON THE FERROCYANIDE SAFETY PROGRAM FOR THE PERIOD ENDING DECEMBER 31, 1995

R. J. Cash
J. E. Meacham

ABSTRACT

This is the nineteenth quarterly report on the progress of activities addressing the Ferrocyanide Safety Issue associated with Hanford Site high-level radioactive waste tanks. Progress in the Ferrocyanide Safety Program is reviewed, including work addressing the six parts of Defense Nuclear Facilities Safety Board Recommendation 90-7 (FR 1990). All work activities are described in the revised program plan (DOE 1994b), and this report follows the same format presented there. A summary of the key events occurring this quarter is presented in Section 1.2. More detailed discussions of progress are located in Sections 2.0 through 4.0.

This page intentionally left blank.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TERMS

cal/g	calories per gram
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	data quality objectives
EA	environmental assessment
EMI	electromagnetic induction
FAI	Fauske and Associates, Inc.
FY	fiscal year
g-mole	gram-mole
GAO	U.S. General Accounting Office
IR	infrared
ISB	interim safety basis
J/g	joules per gram
kW	kilowatt
LOW	liquid observation well
NASA	National Aeronautics and Space Administration
NIR	near infrared
PNNL	Pacific Northwest National Laboratory
ppmv	parts per million by volume
Rad/h	Rad per hour
SA	safety assessment
SEM	scanning electron microscope/microscopy
SST	single-shell tank
TC	thermocouple
TMACS	Tank Monitor and Control System
TOC	total organic carbon
USQ	unreviewed safety question
wt%	weight percent

This page intentionally left blank.

1.0 INTRODUCTION

1.1 PURPOSE

This quarterly report provides a status of activities underway on the Ferrocyanide Safety Issue at the Hanford Site, including actions in response to Defense Nuclear Facilities Safety Board (DNFSB) Recommendation 90-7 (FR 1990). In March 1991, a DNFSB implementation plan (Cash 1991) responding to the six parts of Recommendation 90-7 was prepared and sent to the DNFSB. A ferrocyanide safety program plan addressing the total Ferrocyanide Safety Program, including the six parts of DNFSB Recommendation 90-7, was released in October 1994 (DOE 1994b). Activities in the program plan are underway or are completed, and the status of each is described in Sections 2.0 and 3.0 of this report.

1.2 QUARTERLY HIGHLIGHTS

- Two full-depth core samples were obtained from ferrocyanide tank 241-BY-104 this quarter, meeting the requirements specified in the Ferrocyanide Data Quality Objectives (DQO) document (Meacham et al. 1995a). Analytical analyses have started and results will be available next quarter.

- Analytical analyses of core samples from ferrocyanide tanks 241-BY-108 and 241-BY-110 continued this quarter and the final 105-day reports are due next quarter. Some samples from tank 241-BY-108 exhibited energetics greater than 480 Joules per gram (J/g). The total cyanide values in these samples were low, more than a factor of ten less than predicted from process records and ferrocyanide waste simulants.

- Flammable gas Watch List tank controls were imposed on all 177 of the Hanford Site high-level waste tanks. This action precluded core sampling of ferrocyanide tanks 241-BY-103 and 241-TY-103 planned for this quarter. A safety assessment (SA) is being prepared to address the safety requirements and controls required for rotary mode core sampling. Approval of the SA is expected next quarter.

- Because of the delays in obtaining rotary mode core samples from the scheduled ferrocyanide tanks, tank characterization report milestones will also be delayed. The tank characterization report for tank 241-BY-108 was drafted in December for review. This report will be issued in February 1996.

- A second hot cell test is planned using the modified miniature Mössbauer spectrometer developed by the National Aeronautics and Space Administration (NASA). Preparations continue for the test planned for February 1996.

- Operational deficiencies that have plagued the computer-controlled scanning electron microprobe system for the last six months were resolved this quarter during an onsite visit by vendor representatives. Preliminary tests were completed on a T-Plant ferrocyanide waste simulant; initial particulate sizes and compositional data were tabulated and plotted.

- Development work on in situ moisture determinations in the waste tanks using the neutron probe and the electromagnetic induction probe was transferred to the Organic Safety Program at the beginning of this quarter [start of fiscal year (FY) 1996]. No further results will be provided in this quarterly report.

- Moisture retention properties of sludge and saltcake in ferrocyanide tanks was completed in FY 1995. Additional work in this area is continuing with funding provided by the Organic Safety Program. Progress will not be reported in this quarterly report.

- The $Ni(CN)_4^{-2}$ anion was shown to be an intermediate species in the aging of In-Farm ferrocyanide waste simulant. The $Ni(CN)_4^{-2}$ apparently forms when free CN^- is liberated in the aging process and redissolves the $Ni(OH)_2$ that forms when $Na_2Ni(Fe(CN)_6$ is exposed to a high pH environment. Aging tests of $Ni(CN)_4^{-2}$ showed that this compound is readily degraded by hydrolysis and radiolysis as well.

- Work began this quarter at Fauske and Associates, Inc. (FAI) on a report dealing with the credibility of bulk runaway reactions. Calculations indicate that bulk runaway reactions are not possible under current storage conditions.

1.3 REPORT FORMAT

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

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

1.4 BACKGROUND

Since the mid-1940s, various high-level radioactive wastes from defense operations have accumulated at the Hanford Site in underground storage tanks. During the 1950s, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short time period, and to minimize the need for constructing additional storage tanks, Hanford Site scientists developed a process to scavenge ^{137}Cs and ^{90}Sr from tank waste liquids. In implementing this process, approximately 140 metric tons (154 tons) of ferrocyanide were added to waste that was later routed to a number of Hanford Site single-shell tanks (SSTs) (Sloat 1954, 1955).

In the presence of oxidizing material such as sodium nitrate and/or nitrite, ferrocyanide can be made to react exothermically by heating it to high temperatures or by applying an electrical spark of sufficient energy (Cady 1993). However, fuel, oxidizers, and temperature are all important parameters. If fuel, oxidizers, or high temperatures (initiators) are not present in sufficient amounts, then a runaway or propagating reaction cannot occur.

In 1990, little was known about the potential hazards of a ferrocyanide-nitrate/nitrite reaction in Hanford Site SSTs. Because the safety envelope was not adequately defined by existing analyses, an inadequacy existed in the authorization basis[1]. That is, the existing safety analysis report (Smith 1986) and subsequent analyses such as the 1987 environmental impact statement (DOE 1987) did not adequately define the conditions necessary to preclude propagating reactions in the ferrocyanide waste; therefore, an unreviewed safety question (USQ) was declared (Deaton 1990).

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

In September 1990, an ad hoc task force report (Kress et al. 1990) recommended that studies be performed to provide information on: (1) the potential for a ferrocyanide-nitrate/nitrite explosion; (2) the conditions necessary in the tanks to initiate an explosion; and (3) the potential consequences of such an occurrence. The U.S. General Accounting Office (GAO) advised the Secretary of Energy to implement these recommendations (Peach 1990).

---

[1] The U.S. Department of Energy (DOE) authorization basis characterizes the facility design basis and operational requirements for each nuclear facility. The authorization basis is described in documents such as facility safety analysis reports and other safety analyses, hazard classification documents, technical safety requirements, DOE-issued safety evaluation reports, and facility-specific commitments, such as safety assessments for specific tank operations and the Interim Safety Basis (Wagoner 1993).

A closeout report addressing all three GAO recommendations was submitted to DOE in June 1994 (Payne 1994a). The closeout report summarizes the progress made on determining the potential for ferrocyanide reactions in Hanford Site ferrocyanide tanks, and the conditions necessary to sustain an exothermic ferrocyanide reaction.

In March 1989 (Nguyen 1989), based on process knowledge, process records, transfer records, and log books, 22 Hanford Site tanks were identified as potentially containing 1,000 gram-moles (g-moles)[2] (211 kg [465 lb]) or more of ferrocyanide [as the $Fe(CN)_6^{4-}$ anion]. Two additional ferrocyanide tanks were identified in January 1991 (Borsheim and Cash 1991), increasing the number of ferrocyanide tanks to 24. To avert possible injury to personnel and damage to the facility or environment, strict controls were identified for these and other safety issue tanks in *Operating Specifications for Watch List Tanks* (WHC 1990). Tanks identified by this document (see WHC [1996] for the latest revision) have been commonly referred to as Watch List tanks. In October 1990 (Deaton 1990), the Ferrocyanide Safety Issue was declared a USQ (see Section 2.1) because the safety envelope for these tanks was no longer considered to be bounded by the existing safety analysis report (Smith 1986).

In November 1990, the Wyden Amendment (Public Law 101-510, Section 3137 [1990]) was enacted. This law required the identification of Hanford Site tanks that may have a serious potential for release of high-level waste (see Section 4.0). In February 1991 (Harmon 1991), the 24 ferrocyanide tanks were among the tanks identified, and were included in the subsequent July 1991 report to Congress (Watkins 1991) that responded to the Wyden Amendment. However, re-examination of the historical records (Borsheim and Simpson 1991) indicated that six of the 24 tanks did not contain the requisite 1,000 g-moles of ferrocyanide. Therefore, these six tanks should not have been included on the Watch List nor identified in the response to the Wyden Amendment. The six tanks were subsequently removed from the Watch List (Anttonen 1993, Sheridan 1994b).

[2]The 1,000 g-moles criterion has since been replaced with a 115 calories per gram (cal/g) fuel concentration criterion. See Section 4.1 for discussion.

2.0 FERROCYANIDE SAFETY DOCUMENTATION

The USQ process depends on an authorization basis that describes those aspects of the facility design basis and operational requirements relied on by DOE to authorize operation. The authorization basis is described in documents such as facility safety analysis reports and other safety analyses, hazard classification documents, technical safety requirements, DOE-issued safety evaluation reports, and facility-specific commitments, such as SAs, the interim safety basis (ISB), and the Final Safety Analysis Report (FSAR) scheduled for completion in December 1996. The potential hazards of a ferrocyanide-nitrate/nitrite reaction were discovered to represent an inadequacy in the authorization basis (Smith 1986). The Ferrocyanide USQ was closed on March 1, 1994 by the DOE Assistant Secretary for Environmental Restoration and Waste Management (Sheridan 1994a). Progress on the remaining safety documentation for resolving the Ferrocyanide Safety Issue is reviewed in this section.

Safety and Environmental Assessments. SAs are documents prepared to provide the technical basis to assess the safety of a proposed activity and to provide proper controls to maintain safety. The SA and the accompanying environmental assessment (EA) for that operation provide the basis for DOE authorization of the proposed activities. SAs have been approved for headspace sampling of all ferrocyanide tanks, waste surface sampling, push-mode and rotary-mode core sampling, thermocouple (TC)/instrument tree installation in sound and assumed leaker tanks, and removal of pumpable liquid (interim stabilization). A generic EA covering all proposed operations in the tank farms was approved and a Finding of No Significant Impact issued by DOE (Gerton 1994). Approval of the generic EA provides adequate National Environmental Policy Act coverage for the planned Ferrocyanide Safety Program activities.

The authorization basis for intrusive tank operations was combined into one document, the ISB, which was approved in November 1993 (Wagoner 1993). Safety documentation concerning the ferrocyanide hazard was updated to reflect the approved ferrocyanide safety criteria and closure of the Ferrocyanide USQ. This information is also being incorporated into the FSAR that will replace the ISB when approved by DOE.

Hazard Assessment. A report assessing the ferrocyanide waste tank hazards was issued in July 1992 (Grigsby et al. 1992). The report reviewed the understanding of the ferrocyanide hazard at that time, and presented an integrated evaluation and interpretation of historical data and then-available information. Additional data are now available on the potential for exothermic ferrocyanide reactions in Hanford Site SSTs.

Work began this quarter on updating the ferrocyanide hazard assessment. Sample data from the four C Farm tanks is included in this revision and the document is scheduled for completion in January 1996. A final ferrocyanide hazard assessment will be submitted to DOE by July 31, 1996. Technical information from all Ferrocyanide Safety Program tasks will be compiled into this document, and the ISB (or FSAR) will be amended accordingly.

Ferrocyanide Program Plan. A ferrocyanide program plan was submitted to the DNFSB in December 1994 (O'Leary 1994). The program plan outlines activities planned to address DNFSB Recommendation 90-7, to meet the Wyden Amendment requirements (Public Law 101-510, Section 3137 [1990]), and to remove the remaining ferrocyanide tanks from the Watch List. All ferrocyanide program activities are scheduled to be completed by the end of FY 1997. However, an increased understanding of radiolytic and chemical degradation (aging) of ferrocyanide indicates that little ferrocyanide remains, and core sampling of all the tanks may not be required. Core sampling and analyses of only those tanks that bound aging (i.e., tanks with conditions least conducive to aging) could result in resolution of the Ferrocyanide Safety Issue much earlier and at a substantially reduced cost. As more core sample data become available, the need to sample all the ferrocyanide tanks will be reexamined.

- **Milestone Status**

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

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

  - **July 31, 1996**. Westinghouse Hanford Company prepares and submits the final ferrocyanide hazard assessment for DOE approval.

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

3.0 ACTIONS TO COMPLETE DNFSB RECOMMENDATION 90-7

This section follows the format of the program plan (DOE 1994b) and describes all work associated with the Ferrocyanide Safety Program. Where applicable, each task activity is described relative to the DNFSB Recommendation (90-7.1 through 90-7.6). The specific part of the recommendation is given, followed by a summary of activities underway to respond to that part of Recommendation 90-7 (if not already closed out).

3.1 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."

3.1.1 Instrument Trees

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

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

There are two instrument trees in all but three ferrocyanide tanks (241-BY-106, -111 and -112). The instrument trees in the ferrocyanide tanks are monitored continuously by the

Tank Monitor and Control System (TMACS). The older instrument trees are expected eventually to fail in a manner such that they cannot be repaired, and they will not be replaced.

- **Progress During Reporting Period.** All ferrocyanide tank instrument trees have been installed and are continuously monitored by TMACS. All work is complete for this task and DNFSB Recommendation 90-7.1 is closed.
- **Planned Work for Subsequent Months.** None.
- **Problem Areas and Action Taken.** None.
- **Milestone Status.** None.

3.1.2 Upgrades to Existing Temperature Monitoring Instrumentation

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

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

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

3.1.3 Hot Spot Thermal Modeling

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

Heat load analyses and thermal characteristics were completed for all ferrocyanide tanks in FY 1994 (McLaren 1994a, 1994b). The maximum heat load of any ferrocyanide tank, assuming worst-case conditions for soil moisture and thermal conductivity, was below 4.2 kilowatts (kW). Nominal heat loads calculated by McLaren (1994a, 1994b) compared very favorably with those calculated independently in 1993 (Crowe et al. 1993). A dryout analysis was also completed and released in FY 1994 (Epstein et al. 1994). The report concluded that ferrocyanide sludge could not dry sufficiently to be chemically reactive during interim storage, either globally or locally. Dryout mechanisms evaluated included global evaporation, removal of liquid by leakage or pumping, boiling as a result of hot spots, and enhanced surface evaporation from hot spots. All activities were completed for this task in FY 1994.

- **Progress During the Reporting Period.** None.
- **Planned Work for Subsequent Months.** None.
- **Problem Areas and Action Taken.** None.
- **Milestone Status.** This task is complete.

3.1.4 Infrared Scanning System

Infrared (IR) scanning systems are commercially available from numerous vendors. These systems are sensitive to changes of ±0.3 °C or less under ideal conditions and offer promise for mapping surface temperature profiles in the ferrocyanide tanks. Thermal modeling performed on ferrocyanide tank 241-BY-104 (McLaren 1993) suggested that if hot spots with temperatures of concern are possible, surface temperature differences might be great enough to be detected by IR mapping.

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

- **Progress During the Reporting Period.** None.
- **Planned Work for Subsequent Months.** None.
- **Problem Areas and Action Taken.** None.
- **Milestone Status.** This task is complete.

3.1.5 Cooling System Requirements

The program plan for resolution of the Ferrocyanide Safety Issue (DOE 1994b) provided actions that would be taken to cool the ferrocyanide tanks if such cooling were to be determined necessary. Several tentative milestones, identified below, were established for use if a cooling system(s) were to be required. The concern at the time was that increasing temperatures could lead to loss of moisture within the ferrocyanide waste matrix. Immediate emergency actions that would be taken if increased temperatures were to occur are described in the *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide* (Fowler 1994). Types of cooling systems might include, but are not limited to, the following: (1) forced ventilation of the tank, using an existing or new exhauster system; (2) air conditioning the air to the tank; (3) adding humid air or mist; and (4) adding water to the tank.

Based on the historical database, results of samples from seven ferrocyanide tanks, and results from the Pacific Northwest National Laboratory (PNNL) aging test activity, none of the 18 ferrocyanide tanks contain a high enough concentration of ferrocyanide for a propagating reaction to occur. Because dryout of the waste under the present storage conditions (Epstein et al. 1994) is not credible, a special cooling system for the ferrocyanide tanks is not considered necessary. No further work on this task is planned.

- **Progress During the Reporting Period.** None.
- **Planned Work for Subsequent Months.** None.

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

3.2 CONTINUOUS TEMPERATURE MONITORING

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

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

The TMACS system, which became operational in September 1991, has the capacity to assign alarms for a change in the value of any temperature point. Alarms, if they occur, trigger an audible annunciator and are logged immediately to hard copy. An alarm summary display provides a list of the most recent alarms in order of occurrence. Each alarm can be identified by point and time of occurrence. Operator acknowledgement of the alarm will silence the audible annunciator. Signal conditioning and multiplexing are performed locally at each tank, eliminating the need to transmit low-level signals to the tank farm boundary and reducing cable runs. Electronic noise, extension wire corrosion, and thermal gradients are also reduced.

- **Progress During Reporting Period.** Temperatures for all instrument trees in the ferrocyanide tanks are being monitored continuously by TMACS. All work is complete for this task and DNFSB Recommendation 90-7.2 is closed.
- **Planned Work For Subsequent Months.** None.
- **Problem Areas and Action Taken.** None.
- **Milestone Status.** None.

3.3 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."

3.3.1 Interim Flammable Gas Monitoring

The effort to conduct flammable and toxic gas monitoring and analyses in the ferrocyanide tanks is continuing. Most of this effort was transferred to the Tank Vapor Monitoring Program, which is coordinating interim gas monitoring of the ferrocyanide tanks and tanks involved with the tank vapor program. Tank headspaces are measured for flammability using a commercial combustible gas monitor (calibrated with pentane gas), and are monitored for potential toxic gases using an organic vapor monitor and Dräger[3] tubes. Headspace characterization of all the Hanford Site high-level waste tanks is continuing using sorbent tubes placed on the end of tubes lowered into the headspace and SUMMA[4] canisters that collect gas samples topside. The initial headspace sampling was done in several tank locations (i.e., from two widely separated risers) and at three elevations in the headspace. Reviews of sampling data and modeling (Wood 1992, Claybrook and Wood 1994, Postma et al. 1994b) indicate that the headspace is well mixed and that sampling from one riser at one elevation is adequate.

- **Progress During Reporting Period.** Headspace sampling of all 18 ferrocyanide tanks is complete. Table A-2 in the Appendix summarizes the results. Headspace sampling of the ferrocyanide tanks will continue on a periodic basis as part of the Tank Vapor Monitoring Program. DNFSB Recommendation 90-7.3 is closed.

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

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

- **Milestone Status.** None

3.3.2 Continuous Gas Monitoring

The possibility that localized concentrations or stratification of gases exist in the tanks was evaluated. A modeling study was conducted to determine airflow patterns in the headspace of tank 241-C-109 and evaluate the amount of mixing and the local gas concentrations that could occur. The study revealed that the gases in the tank are well mixed and follow Graham's law for gaseous diffusion; therefore, an analysis of a second tank was considered unnecessary (Wood 1992). Studies completed since that time (Claybrook and Wood 1994, Postma et al. 1994b) also confirm that conclusion.

---

[3]Trademark of Drägerwerk Aktiengesellschaft, Inc., Lubeck, Germany; also National Draeger, Inc., Pittsburgh, Pennsylvania.

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

The need for continuous gas monitoring was addressed in a report that also assessed the potential for cyclic venting and the possibility of accumulating flammable gases (Fowler and Graves 1994). The report concluded that continuous flammable gas monitoring in ferrocyanide tanks is not warranted based on: (1) the low concentration of flammable gases found to date; (2) anticipated low ferrocyanide concentrations because of waste aging; (3) analytical results from tanks 241-C-109 and -112 showing that the fuel concentration in the tanks is much lower than postulated by flowsheet values and operating records; and (4) calculations of hydrogen accumulation using realistic generation values and passive ventilation assumptions. Vapor sampling of all 18 ferrocyanide tanks has corroborated that flammable gas concentrations in the ferrocyanide tanks are too low to be of concern. No further activities are planned for this task.

- **Progress During Reporting Period.** None.
- **Planned Work For Subsequent Months.** This task is complete. DOE has concurred that no continuous gas monitoring is required (O'Leary 1994).
- **Problem Areas and Actions Taken.** None.
- **Milestone Status.** None

3.4 FERROCYANIDE WASTE CHARACTERIZATION

"The program of sampling the contents of these tanks should be greatly accelerated. The proposed schedule whereby analysis of two core samples from each single-shell tank is to be completed by September 1998 is seriously inadequate in light of the uncertainties as to safety of these tanks. Furthermore, additional samples are required at several radii and at a range of elevations for the tanks containing substantial amounts of ferrocyanide."

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

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

3.4.1 Ferrocyanide Tank Waste Sampling and Analyses

Tank Sampling. Rotary-mode and push-mode sampling capabilities and auger surface sampling are used to obtain waste samples from the Watch List tanks. Tanks without saltcake and with relatively soft waste solids can be sampled by the push-mode method. If a hard saltcake layer is present, rotary-mode sampling can be used. Auger sampling may also be used if the depth of waste is nominally less than 60 cm.

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

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

- **Progress During Reporting Period.** Two full-depth core samples were obtained from ferrocyanide tank 241-BY-104 this quarter, meeting the requirements specified in the Ferrocyanide DQO document (Meacham et al. 1995a). Push-mode core sampling of tank 241-BY-105 was stopped early this quarter after the downforce limit was reached and because segment recoveries were poor. Although some waste was collected, further sampling was postponed until the rotary-mode sampling method is approved for potentially flammable gas tanks. Analytical analyses of all samples obtained will be available next quarter.

  Sampling of tank 241-BY-106 using the push-mode method was partially successful this quarter. Nine of 12 segments were obtained, but the downforce limit on the sampling truck was reached and further attempts must wait for rotary-mode sampling. Analytical analyses will be completed on the nine segments of waste.

Analyses of moisture and energy (heat of reaction) concentration were completed this quarter for the 241-BY-108 and -BY-110 core samples. Results are reviewed in Tables 3-1 and 3-2. Except for water, all values are reported on a dry weight basis.

Some samples from tank 241-BY-108 exhibited energetics greater than 480 J/g. Total cyanide values in these samples were low, more than a factor of ten less than predicted from process records and ferrocyanide waste simulants (Jeppson and Wong 1993). The total organic carbon (TOC) measurements indicate that most of the energetics comes from organic salts. Historical data suggests that tank 241-BY-108 received a significant amount of organic complexants (Webb et al. 1995).

No samples from tank 241-BY-110 exhibited energetics greater than 480 J/g. Total cyanide and TOC analyses for this tank are pending and should be available early next quarter.

- **Planned Work For Subsequent Months**. The next ferrocyanide tanks scheduled for sampling are 241-BY-103, -TY-103, and -TX-118. These tanks require rotary-mode sampling. The 105-day final analytical reports for tanks 241-BY-104, -BY-105, -BY-108, and -BY-110 are due next quarter.

- **Problem Areas and Actions Taken**. Monitoring of the waste height in ferrocyanide tanks 241-BY-103, -BY-105, and -BY-106 shows a positive correlation with barometric pressure indicating the waste in these tanks may contain trapped gas. Consequently, flammable gas Watch List controls were imposed on these three tanks as sound management practice. An SA is now being prepared for rotary-mode sampling of flammable gas tanks with approval by DOE expected by mid-FY 1996. Rotary-mode sampling of tanks 241-BY-103, -BY-105, and -BY-106 has been delayed until the SA is approved. (Sampling of tanks 241-BY-105 and -BY-106 this quarter using the push-mode method was not considered successful. A more detailed evaluation to determine if 241-BY-103, -BY-105, and -BY-106 are indeed flammable gas tanks is underway. Because of these problems, it will not be possible to meet the milestone dates as shown below.

- **Milestone Status**.

  - **September 30, 1995**. Westinghouse Hanford Company completes data interpretation reports, available for public release, for four ferrocyanide tanks. Three reports for tanks 241-C-108, -C-111, and -TY-104 by September 30, 1995 (Sasaki 1995, Kelly 1995a, and Kelly 1995b). Because of delays in obtaining rotary-mode core samples from tank 241-BY-108, the fourth report will not be completed until February 1996.

Table 3-1. Tank 241-BY-108 Sampling Data.

Core Number	Segment Number	Subsegment*	Water (wt%)	Energetics (J/g)	TOC (wt%)	Cyanide (wt%)
98	1	B	21	0	—	—
	2	A	15	0	—	—
		C	42	88	—	—
		D	38	0	—	—
	3	A	44	323	—	—
		C	40	116	—	—
		D	37	231	—	—
	4	A	33	343	—	—
		B	36	474	3.2	0.29
		C	39	224	—	—
		D	36	103	—	—
104	1	B	24	0	—	—
	2	A	20	0	—	—
		B	32	0	—	—
		C	13	0	—	—
	3	A	7.5	0	—	—
		C	9.4	0	—	—
		D	7.9	0	—	—
	4	A	32	30	—	—
		C	41	187	—	—
		D	9.3	0	—	—
	5	A	9.2	0	—	—
		B	37	573	2.4	<0.01
		C	36	528	2.1	0.01
		D	7.3	0	—	—

*The samples are divided into subsegments (A - D), and are in sequence with "A" being the top and "D" being the bottom quarter segment

Table 3-2. Tank 241-BY-110 Sampling Data.

Core Number	Segment Number	Subsegment*	Water (wt%)	Energetics (J/g)
		A	23	0
	1	B	14	12
		A	16	13
	2	A	18	0
	3	A	17	47
	4	B	18	57
		A	17	0
	5	A	34	136
103	6	B	28	134
		A	29	94
	7	B	32	100
		A	37	67
	8	B	15	0
		D	14	0
		A	33	93
	9	B	32	100
		C	30	349
		D	25	340
	1	A	18	8
	2	A	26	14
	3	A	16	16
	4	A	1.2	8
		C	32	31
		D	35	48
	5	A	33	67
		B	38	97
		D	31	98
	6	A	32	95
113		B	34	67
		C	38	0
		D	28	0
	7	A	33	0
		B	38	97
		C	33	0
		D	35	72
	8	A	32	0
		B	32	0
		C	31	0
		D	11	0

*The samples are divided into subsegments (A - D), and are in sequence with "A" being the top and "D" being the bottom quarter segment.

- **December 31, 1995.** Westinghouse Hanford Company obtains core samples from five additional ferrocyanide tanks. Only one ferrocyanide tank, 241-BY-104, was successfully sampled this quarter. This milestone date will not be met as planned because of the delay in sampling tanks 241-BY-103, -BY-105, and -BY-106, as mentioned above.

- **March 31, 1996.** Westinghouse Hanford Company completes data interpretation reports, available for public release, for five ferrocyanide tanks. This milestone date will not be met because of the delays encountered in rotary-mode sampling of the tanks.

- **July 31, 1996.** Westinghouse Hanford Company obtains core samples from the remaining ferrocyanide tanks. This milestone date will not be met because of the delays encountered in rotary-mode sampling of the tanks.

- **October 31, 1996.** Westinghouse Hanford Company completes data interpretation reports, available for public release, for the remaining ferrocyanide tanks. It is doubtful that this milestone date can be met because of the current delay in obtaining core samples from the tanks.

Infrared Spectroscopy Analyses. The collection of near-infrared (NIR) spectra from archived waste tank waste core samples with various chemical matrices using a Fourier transform infrared spectrometry-based fiber optics method is continuing. Calibration of the method using nonradioactive simulants that mimic the actual composition of tank waste was started.

Based on preliminary results, the fiber optic probe fabricated by the Westinghouse Savannah River Laboratory in Aiken, South Carolina, could provide sufficient throughput to perform multi-component analyses on diffusely-reflected mixed waste. The probe has a single detector fiber surrounded by six infrared source fibers beveled toward the detector fiber (six around one configuration). This cone-face design causes all fiber optic fields to cross at a fixed distance from the probe surface, forming an effective optical diameter of about 1 millimeter. The most pressing concern in performing quantitative spectral measurements with this probe is the difficulty of obtaining reproducible data because of the inhomogeneous sample surfaces. The small optical diameter of this probe makes it especially sensitive to surface inhomogeneities.

To improve sensitivity, design efforts have focused on reducing interference fringes and stray incident infrared light. Substantial improvement in sensitivity can be made through optical or experimental suppression of the interference fringes and elimination of stray light. A new diffuse-reflectance probe, consisting of a collimator, a hollow metallic light guide, focusing optics, and a sapphire window, was purchased in mid-July 1995. The probe was interfaced to a new 80-fiber bifurcated fused silica bundle (40-fiber bundle for the infrared source and 40-fiber bundle for the detector assembly in a "salt and pepper" configuration) that can be detached from the fiber bundle for cleaning or replacement.

Tests were conducted on two oven-dried simulants, 241-BY-104 and -SY-101. Results indicate that the diffuse reflectance spectra have more distinct bands for chemical structure elucidation than the photoacoustic spectra. A final report summarizing Fourier transform infrared work was issued last quarter (Rebagay et al. 1995).

- **Progress During Reporting Period.** This task was completed in FY 1995.
- **Planned Work For Subsequent Months.** None.
- **Problem Areas and Actions Taken.** None.
- **Milestone Status.** None.

Mössbauer Spectroscopy. A small task on Mössbauer spectroscopy is investigating the physical and chemical nature of iron within ferrocyanide tank waste. The NASA has developed a miniaturized Mössbauer spectrometer that is small enough to perform elevation scans in the liquid observation wells (LOWs). Iron is a major constituent of ferrocyanide waste, and information about its location and composition in the tanks supports safe interim storage and eventual retrieval of the waste.

Mössbauer spectroscopy can provide the valence state of iron as well as specific coordination chemistry for the iron atom. That is, Mössbauer spectroscopy can see differences in anions surrounding the iron cation in a stable crystalline structure and distinguish between different iron-based minerals. A recent development in this type of spectroscopy is the use of reflectance rather than transmission spectroscopy, thus allowing information to be gained in situ. Mössbauer spectroscopy can distinguish between ferrocyanide and ferricyanide complexes and almost any iron compound that might exist within tank waste. By knowing the iron concentration and species as a function of elevation in a given tank, it should be possible to determine how much aging has occurred within the waste.

The Mössbauer program represents a cooperative venture between Westinghouse Hanford Company, DOE, and NASA. The contact at NASA is Dr. Richard Morris at the Johnson Space Center in Houston, Texas.

- **Progress During Reporting Period.** Although last quarter's report stated that the Mössbauer spectrometer task was completed, a small amount of funding was allocated in FY 1996 to complete another hot cell test using actual tank waste from a ferrocyanide tank after modifications are made by NASA to the existing Mössbauer spectrometer. The hand-wired electronics in the miniaturized spectrometer are being replaced by circuit boards to minimize the overall noise level of the signal. The viewing window of the detector was also made narrower in order to minimize the interference caused by yttrium or strontium peaks that hampered resolution during the first hot cell test.

  Samples from several ferrocyanide waste tanks will be analyzed by the Mössbauer spectrometer. The amount of yttrium and strontium in samples available for analysis are now being calculated based on total beta analysis so that any interference can be correlated back to the specific yttrium and strontium activities. If possible, samples with a range of total yttrium/strontium activities will be selected.

- **Planned Work for Subsequent Months.** A second hot cell test is planned for February 1996. If sufficient funding is available, the Mössbauer spectrometer will be used to complete at least one scan in a liquid observation well, probably in tank 241-BY-104, to determine the applicability of the spectrometer for detecting various iron species present. Tank 241-BY-104 originally received the largest inventory of ferrocyanide sludge during the 1950s.

- **Problem Areas and Actions Taken.** Initial results obtained in the hot cell in FY 1995 indicated the need for better signal discrimination within the spectrometer. Hardware improvements to the detector are underway in Houston, Texas. The detector is being cooled and the viewing window is being narrowed. The hand-wired electronics are now being replaced with printed circuit boards. The unit is close to being cold tested in Houston. When the testing is completed the second hot cell test will be performed at Hanford.

- **Milestone Status.**

  - **September 30, 1995.** Westinghouse Hanford Company issues a report, available for public distribution, on the Mössbauer spectroscopy program results for FY 1995. This milestone was completed on schedule (Riedel 1995).

- **May 31, 1996.** Westinghouse Hanford Company completes a second hot cell test and at least one scan in an LOW using the improved Mössbauer spectrometer, if sufficient funding is available; and issues a final report, available for public distribution, on the Mössbauer spectroscopy program.

Scanning Electron Microscopy. Chemical and physical properties of ferrocyanide tank waste are being determined to accurately assess the waste for safety and inventory purposes. Analyses indicating the presence or absence of key chemical components--including CN^-, Na, Fe, Ni, and Cs--can be used to characterize the tank waste and to assess whether the waste can be stored safely until retrieval for final disposal. Measurements that allow examination of possible correlations of chemical composition and physical properties, such as particle and crystallite size, may provide additional information on how the waste may have changed with time and facilitate comparisons of real waste properties with those determined earlier for waste simulants.

Scanning electron microscopy (SEM), coupled with backscattered electron detection and energy dispersive X-ray spectroscopy, provides a method uniquely capable of providing particle size, chemical composition, and particle morphology information in a single measurement. Recent developments in instrumentation computer control, digital data acquisition, and light element X-ray detection have significantly enhanced the utility of this technology for particle characterization applications. Further refinements in integrated computer software and firmware now enable rapid collection, processing, and storage of large volumes of chemical and numerical data. Through these instrumentation and data processing enhancements, SEM micro-characterization has evolved into a new and potentially powerful methodology for the characterization of ferrocyanide and organic tank waste.

- **Progress During Reporting Period.** Operational deficiencies with the R. J. Lee Personal SEM™[5] were resolved during an onsite visit of vendor representatives during December 4-13, 1995. Without this resolution the quality of analytical data obtained in the computer-controlled analysis of ferrocyanide tank waste would have been adversely affected. During the past quarter, both the manual and motorized specimen stage systems were repaired, column electronics modules were replaced, and updated versions of several software programs were installed in order to correct operational deficiencies in column beam control and specimen positioning functions. Vendor representatives successfully demonstrated that remaining problems with raster positioning and magnification calibration did not severely affect the quality or validity of data obtained using the automated analysis feature.

  Design and layout of a 2.5 meter x 6.5 meter trailer to house the SEM instrument and support analysis of radioactive ferrocyanide tank waste samples is continuing. This trailer will be a posted radiological zone located at the

[5]Trademark of R. J. Lee Instruments Ltd., Trafford, Pennsylvania.

600 Area Weather Station. Acquisition of special equipment required for installation of a radioactive specimen preparation station within a 222-S building hood was completed this quarter.

Preliminary Test Results. A vendor representative specializing in particle characterization using the proprietary R. J. Lee Group computer-controlled SEM (CCSEM) protocols was onsite December 7-12. The vendor representative (1) verified the proper installation and operation of the particle characterization software packages delivered with the SEM system; (2) reviewed specimen preparation developmental activities performed to date and recommended modifications; (3) validated the capability of the CCSEM protocols to generate reproducible, particulate population and characterization data in repetitive analyses; and (4) monitored initial data collection activities and suggested parameter optimization strategies for analysis of ferrocyanide waste simulants.

Test results for an analysis of T-Plant T-23 simulant by the CCSEM are shown in Tables 3-3 and 3-4. Figures 3-1 and 3-2 present the data in ternary diagrams generated using a vendor proprietary software package.

In Tables 3-3 (A) and 3-3 (B) the initial particulate characterization data are sorted into classes identified by combinations of up to four elemental components. Within any class, the elements are listed in order of decreasing analytical X-ray signal intensity. Table 3-3 (A) indicates that 49.6% of the population of 911 particles measured in this run are a bismuth (Bi)/phosphorus (P)/sulfur (S) phase. The majority of the remaining particles represent a sodium (Na)/silicon (Si)/phosphorus/iron (Fe) phase. In Table 3-3 (B) the data are sorted further according to average particle diameter. The larger, 1.0 - 20.0 micrometers, particles in this sample are dominated by the Bi/P/S composition. The sub-micrometer-sized particles are primarily of the Na/Si/P/Fe phase.

In Tables 3-4 and 3-5 the CCSEM data are sorted by classes generated through application of user generated rule tables. The average percent relative intensities of analytical X-ray signals associated with each class are shown in Table 3-5. Through examination of Table 3-5 and the percent particle size distribution sorting in Table 3-4 it can be inferred for this specimen that (1) a Bi/P phase dominates the particulate population of average diameter exceeding 1.0 micrometer; (2) the sub-micrometer-sized population is dominated by an extensive, secondary Na/Si/P/Fe phase; (3) the Bi/P phase is found in discretelarge particles and as smaller diameter inclusions embedded in the Na/Si/P/Fe matrix material; (4) strontium (Sr) is associated with the Bi/P based particles of 1.0 to 10.0 micrometers average diameter; and (5) cesium (Cs) is found primarily in sub-micrometer particles with a composition resembling the Na/Si/P/Fe secondary matrix material.

Table 3-3. CCSEM Analysis of T-Plant Simulant Sample T-23: (A) Summary Data Table and (B) Number Distribution of Particles Measured by Average Diameter. [Sorting in each table is by computer generated, 4-Element classes.]

(A)

Mag	Fields	Grid
400	176.9476	0.868
1000	42.0160	0.347
2000	11.9105	0.174

Classes	#	Number %	Area %	Area Fr.
Bi- P- S	452	49.62	88.61	0.0011530
Si- P-Na-Fe	95	10.43	2.29	0.0000298
P-Si-Na-Bi	93	10.21	2.19	0.0000285
Si	1	0.11	1.16	0.0000151
Si- O-Ca-Na	14	1.54	0.84	0.0000109
P-Bi-Si-Na	7	0.77	0.75	0.0000097
Si-Mg- O-Na	1	0.11	0.73	0.0000095
Si-Ca- O-Na	1	0.11	0.60	0.0000077
Si- S-Al-Ca	1	0.11	0.42	0.0000055
P-Na-Si-Fe	76	8.34	0.41	0.0000054
Si-Na- P-Bi	77	8.45	0.41	0.0000053
Na- P-Si- O	72	7.90	0.35	0.0000045
Si-Fe- K-Ca	4	0.44	0.34	0.0000044
Bi-Si- P-Na	5	0.55	0.33	0.0000042
Ti	1	0.11	0.31	0.0000040
Ca-Si- O- P	4	0.44	0.17	0.0000022
Fe- P-Na-Si	2	0.22	0.04	0.0000005
Ca- O- P	2	0.22	0.03	0.0000004
Na-Al-Si- P	1	0.11	0.03	0.0000003
O-Na-Si-Fe	2	0.22	0.00	0.0000000
Totals	911	100.00	100.00	0.0013012

(B)

Number Distribution by Average Diameter (microns)

Classes	Number	0.1 - 1.0	1.0 - 10.0	10.0 - 20.0	>>>
Bi- P- S	452	17	427	8	0
Si- P-Na-Fe	95	49	46	0	0
P-Si-Na-Bi	93	55	37	1	0
Si	1	0	0	1	0
Si- O-Ca-Na	14	10	4	0	0
P-Bi-Si-Na	7	1	6	0	0
Si-Mg- O-Na	1	0	1	0	0
Si-Ca- O-Na	1	0	1	0	0
Si- S-Al-Ca	1	0	1	0	0
P-Na-Si-Fe	76	52	24	0	0
Si-Na- P-Bi	77	50	27	0	0
Na- P-Si- O	72	51	21	0	0
Si-Fe- K-Ca	4	0	4	0	0
Bi-Si- P-Na	5	3	2	0	0
Ti	1	0	1	0	0
Ca-Si- O- P	4	0	4	0	0
Fe- P-Na-Si	2	0	2	0	0
Ca- O- P	2	0	2	0	0
Na-Al-Si- P	1	0	1	0	0
O-Na-Si-Fe	2	2	0	0	0
Totals	911	290	611	10	0

The ternary plot of Figure 3-1 confirms the major occurrence of the Na/Si/P/Fe phase in the measured particle population. The particles are seen to cluster around a central locus in the Na/P/Si phase space with the exception of a cluster of particles near the P vertex representing the Bi/P particles.

The two ternary plots of Figure 3-2 (A) and (B) illustrate the size partitioning of the Bi/P phase by particle diameter. In Figure 3-2 (A) it is seen that the 290, sub-micrometer Bi/P particles are strongly associated with particles containing high Na + Si contents. In Figure 3-2 (B) the domination of the 1.0 to 20.0 micrometer-sized particles by the BI/P phase is emphasized by the clustering of particle points on the diagram axis near the Bi vertex.

- **Planned Work For Subsequent Months**. Work on the SEM program has been carried forward into FY 1996. The target date for the completion of SEM-based micro-characterization of a ferrocyanide tank core sample is February 29, 1996. A Westinghouse Hanford Company SEM program report, available for public release, is to be issued by March 31, 1995. Because of the problems discussed above and the delay these have caused in moving the SEM equipment to the radiologically-controlled trailer, these dates are expected to slip by approximately two months.

  Over the ensuing quarter, preparation of the radiological sample, SEM analysis trailer will be completed; specimen preparation procedures will be finalized; computer-controlled SEM analysis protocols will be finalized; arrangements for ferrocyanide tank specimen acquisition, handling, preparation, transport and disposal will be finalized; base analyses of ferrocyanide tank waste simulants will be completed; analysis of ferrocyanide tank core samples will be initiated; and a final SEM activity report will be generated.

- **Problem Areas and Actions Taken**. Hardware and software deficiencies with major impact on the quality and collection of computer-controlled SEM data were addressed and resolved during a vendor site visit of December 4-13, 1995. Progress during this period has been closely monitored by Dr. R. J. Lee, President of R. J. Lee Group, Inc. and D. A. Crawford, President of R. J. Lee Instruments, Ltd. Remaining hardware and software issues are currently being addressed at the vendor's facility.

  Personnel qualified to replace those lost in the FY 1995 Hanford Site reduction-in-force activities have not been identified. SEM program activities have been adjusted to accommodate both minimum project targets and available personnel, but the hardware problems and the subsequent delay in moving the SEM to the radiologically-controlled trailer will delay completion of SEM scans using radioactive ferrocyanide tank waste samples by approximately two months.

Table 3-4. CCSEM Analysis of T-Plant Simulant Sample T-23: Percent Particle Size Distribution by Average Diameter. [Sorting by user-generated, rule-based classed.]

Size Distribution by Average Diameter (microns)

Classes	Number %	0.0 - 1.0	1.0 - 10.0	10.0 - 20.0	>>>
Sr Bearing	6.0	5.5	94.5	0.0	0.0
Cs Bearing	3.1	85.7	14.3	0.0	0.0
Bi\P	39.3	1.4	96.4	2.2	0.0
Bi Rich	4.7	16.3	83.7	0.0	0.0
Ni\Bi	7.4	65.7	34.3	0.0	0.0
Ni Bearing	5.2	53.2	46.8	0.0	0.0
Bi Bearing	24.3	54.8	44.8	0.5	0.0
Ca Silicate	0.9	0.0	100.0	0.0	0.0
Ca Rich	0.2	0.0	100.0	0.0	0.0
Fe Silicate	0.2	0.0	100.0	0.0	0.0
Na\Si\Fe\P	8.2	80.0	20.0	0.0	0.0
Na Silicate	0.2	0.0	100.0	0.0	0.0
Si	0.1	0.0	0.0	100.0	0.0
Ti	0.1	0.0	100.0	0.0	0.0
Na	0.1	100.0	0.0	0.0	0.0
Totals	100.0	31.8	67.1	1.1	0.0

Table 3-5. CCSEM Analysis of T-Plant Simulant Sample T-23: Average Percent Relative X-Ray Signals Associated with Rule-Based Classes.

Average Composition

Classes	#	O	Na	Al	Si	P	S	K	Ca	Ti	Fe	Ni	Sr	Cs	Bi
Sr Bearing	55	2	1	0	1	21	0	0	0	0	1	0	7	0	67
Cs Bearing	28	15	17	1	20	18	3	0	1	1	12	1	0	4	6
Bi\P	358	1	0	0	0	23	1	0	0	0	0	0	0	0	74
Bi Rich	43	8	6	0	7	23	2	0	0	0	5	0	0	0	49
Ni\Bi	67	14	19	1	20	19	3	0	0	0	12	4	0	0	8
Ni Bearing	47	15	20	1	22	22	0	0	0	0	14	4	0	0	0
Bi Bearing	221	14	18	1	21	21	2	0	0	0	13	0	0	0	10
Ca Silicate	8	10	4	9	34	5	2	2	32	0	1	0	0	0	0
Ca Rich	2	9	0	0	2	6	0	0	85	0	0	0	0	0	0
Fe Silicate	2	7	9	4	30	13	4	5	5	0	21	0	0	0	0
Na\Si\Fe\P	75	16	21	1	24	23	0	1	0	0	14	0	0	0	0
Na Silicate	2	6	35	16	34	5	0	2	2	0	0	0	0	0	0
Si	1	0	0	0	100	0	0	0	0	0	0	0	0	0	0
Ti	1	0	0	0	0	0	0	0	0	100	0	0	0	0	0
Na	1	0	100	0	0	0	0	0	0	0	0	0	0	0	0
Totals	911	8	10	0	11	21	2	0	1	0	7	1	0	0	39

Figure 3-1. Ternary Plat of T-Plant Simulant Sample T-23 CCSEM Analysis Data: Distribution of Major Sodium-Silicon-Phosphorus Phase by Average Particle Diameter.

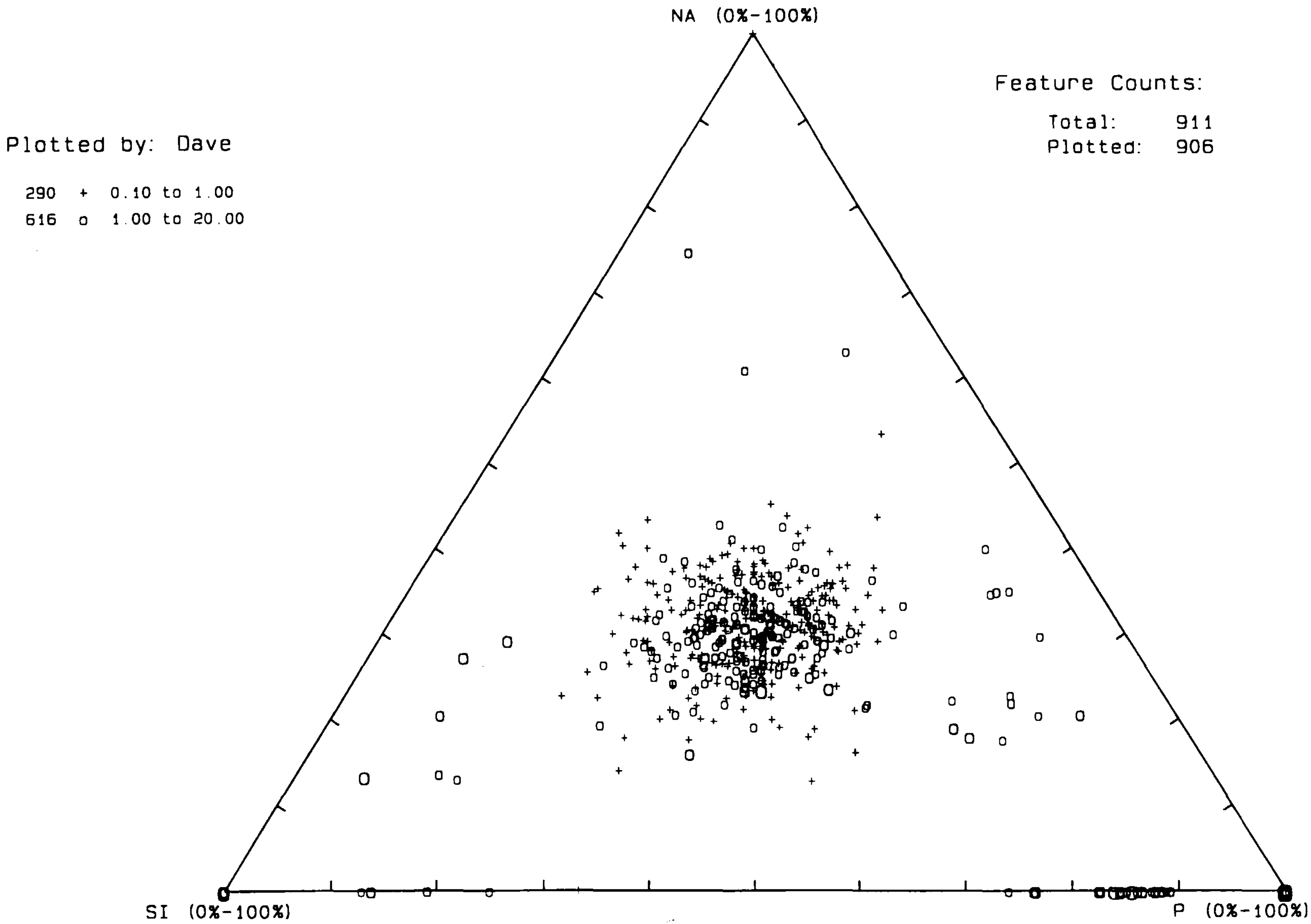
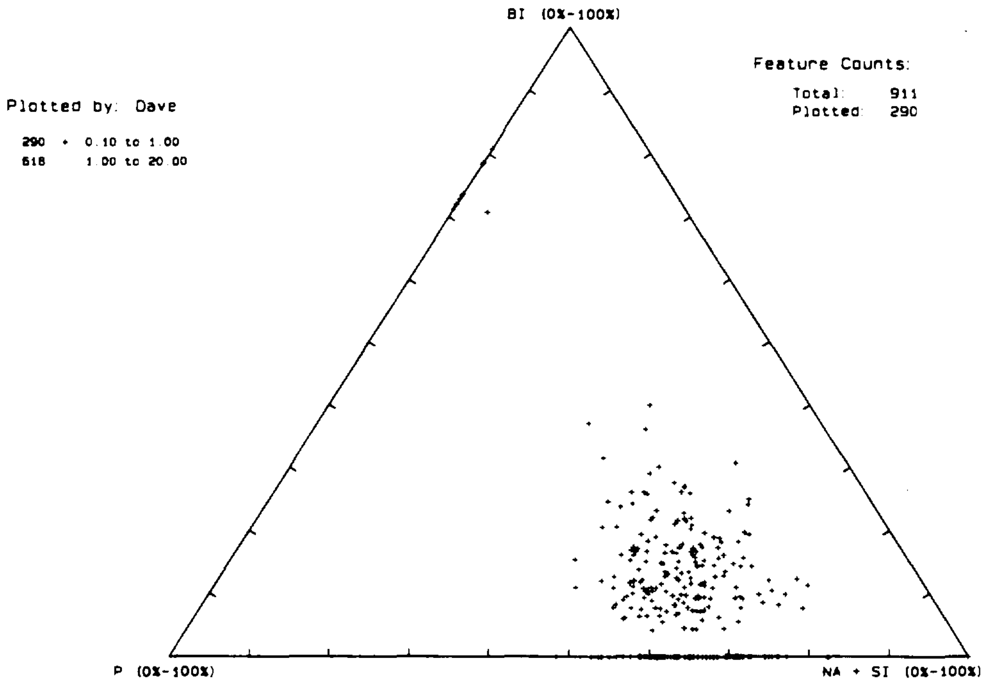
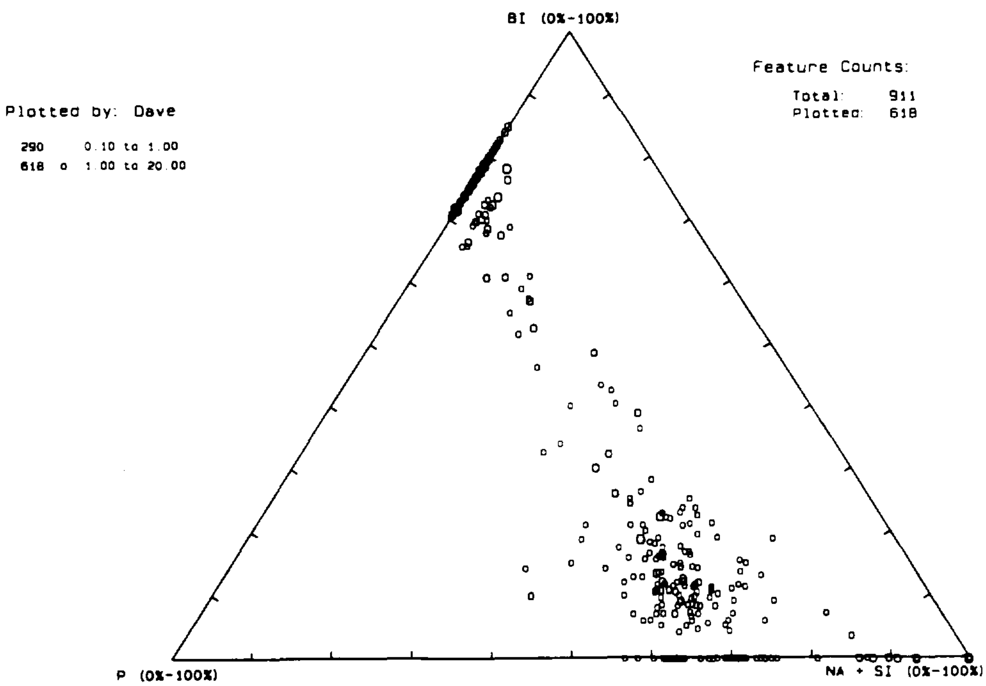


Figure 3-2. Ternary Plots of T-Plant Simulant Sample T-23 CCSEM Analysis Data: Size Distribution of Bismuth-Phosphorus Phase by Average Diameter. (A) 0.1 Through 1.0 Micrometer Particles and (B) 1.0 Through 20.0 Micrometer Particles.

(A)



(B)



The Special Analytical Studies group (direct ferrocyanide program SEM activity support) was transferred from the Hanford Technical Services organization to the TWRS Analytical Services organization on November 6, 1995. This transfer will provide better working relationships with 222-S building personnel and allow for higher priorities in completing this work.

- **Milestone Status.**

  - **May 31, 1995**. Westinghouse Hanford Company installs and completes operational acceptance tests on SEM system. Personal SEM™ operational problems were resolved this quarter and the milestone was completed December 29, 1995.

  - **September 29, 1995**. Westinghouse Hanford Company issues a report, available for public release, on SEM program results for FY 1995. A report was issued on schedule (Callaway 1995).

  - **March 29, 1996**. Westinghouse Hanford Company issues a final report on SEM technology development. This milestone is expected to be delayed until May 31, 1996 because the radiologically-controlled facility for doing SEM scans on radioactive materials will not be ready in time to meet the March milestone date.

3.4.2 Estimation of Moisture Content

Methods for determining moisture concentrations in ferrocyanide waste tanks are being developed using sample data analyses and available surveillance systems. This work is an increase in scope from the original implementation plan (Cash 1991), which did not examine moisture monitoring. Two in situ moisture monitoring technologies are currently being investigated by the Ferrocyanide Safety Program, neutron diffusion and electromagnetic induction (EMI). Initial development of NIR spectroscopy was completed in FY 1994 (Reich et al. 1994) at the University of Washington Center for Process Analytical Chemistry. This surface moisture monitoring technology will not be developed further by the Ferrocyanide Safety Program. Additional moisture monitoring technologies, such as copper foil activation and fission chamber in a cone penetrometer, are being evaluated by other programs. A report examining moisture monitoring technologies was completed in April 1993 (Meacham et al. 1993).

Neutron Diffusion. Well-logging techniques, coupled with computer modeling, were developed and applied to an existing neutron probe to determine information about moisture levels, material interfaces, and other waste characteristics in the ferrocyanide tanks. Using the knowledge gained from computer modeling, in situ measurements, and experimental calibration data with the current in-tank liquid level neutron probe (Watson 1993), prototype moisture measurement neutron probes were developed. This system consists of three neutron probes: a near-field thermal neutron probe, a far-field thermal neutron probe, and a far-field epithermal neutron probe. This improved system would primarily be used to determine the axial moisture concentration profile within the ferrocyanide tanks.

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

Two methods are generally used in the measurement of moisture concentration around wells using neutron diffusion. The first method, the moisture gauge, has a short source-to-detector spacing (near field) on the order of 0 to 10 cm. The response of a moisture gauge is characterized by an increase in detector response with increasing moisture concentration of the surrounding medium. The second method, the neutron log, often has two detectors with longer source-to-detector spacings: 20 to 50 cm (far field). The detectors in a neutron log arrangement exhibit a decreased response to increased moisture concentrations. The detector placed at the shorter spacing is used to correct the response of the longer-spaced detector for borehole effects.

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

The initial design and prototype tests were completed for a new surface moisture measurement neutron probe in FY 1995. This effort was transferred to the Organic Safety Program, and no additional development work will be conducted for the Ferrocyanide Safety Program.

- **Progress During Reporting Period.** This task was transferred to the Organic Safety Program at the end of FY 1995, and progress on this ongoing task will no longer be reported in this document.

- **Planned Work for Subsequent Months**. Not applicable.

- **Milestone Status.** Not applicable.

Electromagnetic Induction Probe. The purpose of this task is to deploy the EMI probe in the LOWs and possibly near the waste surface to measure moisture concentration. EMI probes operate by creating a magnetic field that induces current in a conductive medium. This induced current can be measured and is related to the media conductivity. The higher the electrical conductivity, the higher the free moisture content in the tank waste.

The EMI probe is designed with four separate coils of wire that can be either exciting coils or sensing coils. The present configuration uses one coil as the exciting coil and three coils as the sensing coils. This configuration allows three different depths of penetration during one scan. The electronics can be programmed to use four frequencies during one scan, so the information acquired will be four frequencies at three different coil spacings. This information will be useful in separating the environment near the LOW from the environment far from the LOW. Two different EMI probes have been built, with different coil spacing and turns per coil, to determine in-tank responses.

Two areas of engineering activity apply to measurement of free moisture in the high-level waste tanks: (1) EMI measurement of absolute conductivity of the waste medium; and (2) determination of the electrical conductivity as a function of free moisture content of ferrocyanide or organic waste. Measurement of absolute conductivity is being studied using finite-element modeling of the EMI probe geometry. The modeling is being performed by Washington State University using ET Analysis[6], a proprietary code, and in-house using EMIP, an electromagnetic induction program developed at Oak Ridge National Laboratory during the early 1970's.

EMI probes were deployed in tanks 241-BY-104, -BY-106, -BY-107, -BY-111, -BY-112, -TY-103, -TX-118, -TX-114 (3 LOWs), -S-105, and -S-106. Observations of the in-tank acquired data allowed some conclusions about EMI to be made: (1) the system is sensitive to loss of hydraulic conductivity, which occurs about 0.08 to 0.12 volume fraction of liquid, depending on porosity; (2) the scan can interrogate multiple depths simultaneously; (3) EMI is sensitive to small changes in material properties; (4) EMI method measures conductivity directly, while moisture interpretation requires some assumptions; (5) EMI results are affected by temperature, so compensation is required; and (6) EMI method is strongly affected by ferromagnetic items. A report was issued in September 1995 (Crowe and Wittekind 1995). The remaining development effort was transferred to the Organic Safety Program at the end of FY 1995.

- **Progress During Reporting Period.** None. This task was transferred to the Organic Safety Program at the end of FY 1995.

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

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

- **Milestone Status.** None.

[6]Trademark of Zetech, Inc., Issaquah, Washington.

3.4.3 Moisture Retention Properties of Ferrocyanide Sludge and Saltcake Simulants

The moisture content of ferrocyanide sludge is critical in preventing exothermic ferrocyanide/nitrate-nitrite reactions. Studies are underway to evaluate the moisture retention properties of ferrocyanide tank sludge and saltcake simulants as they relate to possible waste tank leaks, tank stabilization by pumping, and possible evaporation from exposed surfaces. Previous work (Epstein et al. 1994) has shown that ferrocyanide sludge cannot dry sufficiently to be chemically reactive during interim storage, either globally or locally. Dryout mechanisms evaluated included global evaporation, removal of liquid by leakage or pumping, boiling as a result of hot spots, and enhanced surface evaporation from hot spots. Current work is focusing on moisture retention in saltcake material, especially after a tank has been interim stabilized.

Modeling calculations are being performed to estimate the moisture-retaining capability of ferrocyanide waste in typical Hanford Site tank systems. The effort focuses on evaluating the impact of consolidation and surface evaporation processes. Computer models are employed to estimate the moisture retention within the matrix and to determine surface drying of sludge and saltcake waste. To accomplish these objectives, the hydraulic properties of actual sludges and saltcake porous media must be compared with tested waste simulants, and their physical properties must be correlated.

Modeling work is being performed to examine the resistance of saltcake waste to gravity drainage and surface evaporation. Under gravity's influence, saturated saltcake will drain when liquid is pumped out and when a tank is stabilized. In contrast, sludge does not readily drain and the interstitial liquid must be expelled by consolidation, usually caused by an overburden. Because saltcake drains when stabilized, it is more subject to potential drying at the surface as a result of moisture evaporation.

Modeling of the moisture retention properties of saltcake and sludge waste was completed and documented in September 1995 (Simmons 1995). Moisture retention modeling for the Ferrocyanide Safety Program has been completed. However, additional saltcake modeling continues for the Organic Safety Program.

- **Progress During Reporting Period**. None.
- **Planned Work for Subsequent Months**. None.
- **Problem Areas and Actions Taken**. None.
- **Milestone Status**. None.

3.5 CHEMICAL REACTION STUDIES

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

Chemical reaction studies on ferrocyanide waste simulants are being conducted by Westinghouse Hanford Company, FAI, PNNL, and Los Alamos National Laboratory. Westinghouse Hanford Company and PNNL have produced flowsheet simulant materials for testing and characterization. FAI is conducting adiabatic calorimetry and propagation tests on these same flowsheet materials and on stoichiometric mixtures of pure sodium nickel ferrocyanide and sodium nitrate/nitrite. The test program at Los Alamos National Laboratory was completed in FY 1993.

3.5.1 Chemical Reaction Studies at Pacific Northwest National Laboratory

Chemical reaction studies are continuing at PNNL using flowsheet simulant materials. Waste studies addressing DNFSB Recommendation 90-7.5 are being conducted to determine the following: (1) the aging effects (hydrolysis and radiolysis) from more than 35 years of storage in the tanks; (2) the correlation of waste simulant and actual waste properties; and (3) modeling calculations to predict the moisture-retaining capability of ferrocyanide waste in a typical tank system (this work is reported in Section 3.4.3).

- **Progress During Reporting Period.**

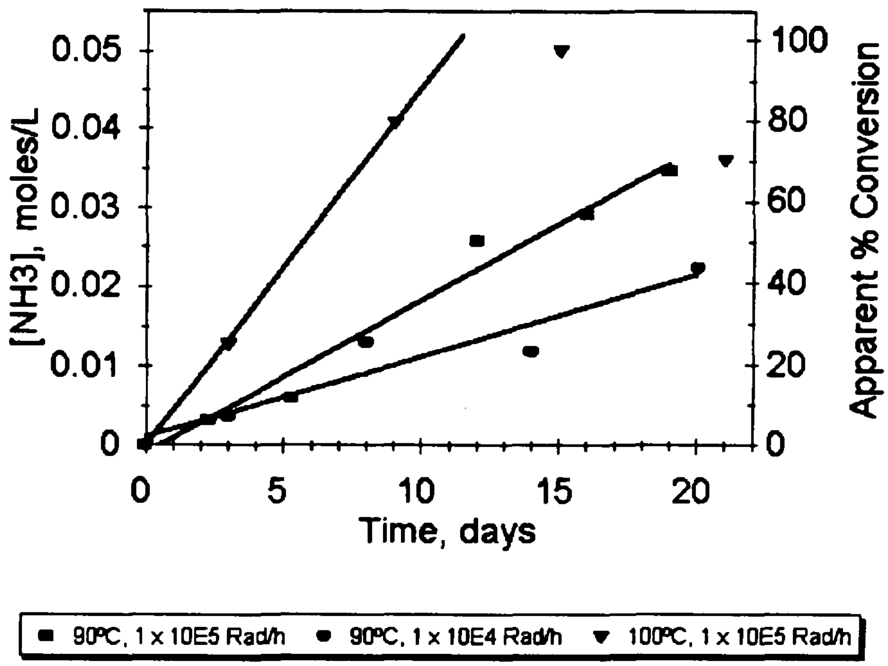
  Aging Studies. The $Ni(CN)_4^{-2}$ anion was shown to be an intermediate in the aging of In-Farm ferrocyanide waste simulant. The presence of this anion was indicated first by the increase in solution nickel concentrations during aging, and later identified with use of Fourier transform infrared spectroscopy. $Ni(CN)_4^{-2}$ apparently forms when free CN^- is liberated in the $Fe(CN)_6^{-4}$ aging process and redissolves $Ni(OH)_2$.

  The aging of $Ni(CN)_4^{-2}$ in 2 *M* NaOH as a function of temperature and applied gamma dose rate was investigated. Experiments were conducted at 90 °C with applied dose rates of either 1 x 10^5 Rad/h (Ni1) or 1 x 10^4 Rad/h (Ni3), and at 100 °C with 1 x 10^5 Rad/h (Ni4) applied gamma dose rate. Control experiments were prepared identically and run under the same conditions except that they were not exposed to gamma radiation. The appropriate amount of $K_2Ni(CN)_4$ was used to give the same amount of nickel as in In-Farm waste simulant aging experiments. Experiments Ni3 and Ni4 were conducted in the presence of the same concentrations of nitrate and nitrite that would be present in the comparable

In-Farm waste simulant experiments, while Ni1 contained no added nitrate or nitrite.

The results of the aging experiments are shown in Figure 3-3, in which the solution concentration of ammonia is plotted as a function of time. As in In-Farm waste simulant aging, ammonia production increased with increasing temperature and gamma dose rate. Hydrolysis was complete in the 100 °C experiment (Ni4) after about 12 days, after which time the ammonia concentration decreased. The decrease is due to the radiolysis of ammonia, as described previously. The percent conversion (% hydrolysis of cyanide ion) scale, therefore, is labeled "apparent" because no attempt has been made to account for the extent of ammonia radiolysis.

Figure 3-3. Production of Ammonia During the Aging of $Ni(CN)_4^{-2}$.



- **Planned Work For Subsequent Months.** Aging experiments will be completed next quarter.

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

- **Milestone Status.**

  - **June 28, 1996.** PNNL revises aging report to include the results of experiments carried over into FY 1996.

3.5.2 Preparation and Characterization of Ferrocyanide Simulants

Pure sodium nickel ferrocyanide is being prepared and analyzed to determine its chemical reaction properties with stoichiometric mixtures of sodium nitrate/nitrite as a function of water content. These tests are being conducted by FAI to clearly define the margin of safety between the theoretical and experimental propagation limits for ferrocyanide. These tests are run in the FAI reactive systems screening tool. These tests and previous tests with simulants--along with analyses of actual tank waste samples, waste tank monitoring, and waste modeling--provide information to characterize with a great deal of assurance safety concerns relating to the sludge in the ferrocyanide tanks.

- **Progress During Reporting Period.** Work began this quarter on a FAI report discussing the credibility of bulk runaway reactions. Calculations indicate that bulk runaway reactions are not possible under current storage conditions. This conclusion is best understood by comparing the tank cooling response times with the current storage time. For a bulk runaway to occur, chemical heating must exceed tank cooling. Calculations show that the tank cooling response times range from a few hours to 3.1 years. Some waste has been stored for more than 40 years, and there has been no transfer of waste into the single-shell tanks for about 15 years. Several cooling response times have passed over the last 15 years of storage; consequently, bulk runaway reactions are not a hazard under current storage conditions. This report will be finalized next quarter.

- **Planned Work for Subsequent Months.** Issue final FAI report.

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

- **Milestone Status.**

  - **September 30, 1996.** Complete FAI support for Ferrocyanide Safety Issue resolution and conclude chemical reactivity studies of chemical waste. This will close DNFSB Recommendation 90-7.5.

3.6 EMERGENCY RESPONSE PLANNING

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

The original *Action Plan for Response to Abnormal Conditions in Hanford Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991) was prepared in response to DNFSB Recommendation 90-7.6. The 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 (Cash and Thurman 1992) to include the monitoring criteria and responses for abnormal levels of flammable and toxic gases, as well as the reporting requirements, if established criteria are exceeded. The second revision of the plan was released in June 1994 (Fowler 1994).

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

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

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

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

4.0 IMPLEMENTATION OF THE WYDEN AMENDMENT

The Wyden Amendment (Public Law 101-510, Section 3137 [1990]) requires that:

"...the Secretary of Energy shall identify which single-shelled or double-shelled high-level nuclear waste tanks at the Hanford Nuclear Reservation, Richland, Washington, may have a serious potential for release of high-level waste due to uncontrolled increases of temperature or pressure. After completing such identification, the Secretary shall determine whether continuous monitoring is being carried out to detect a release or excessive temperature or pressure at each tank so identified. If such monitoring is not being carried out, as soon as practicable the Secretary shall install such monitoring, but only if a type of monitoring that does not itself increase the danger of a release can be installed."

4.1 THE WATCH LIST

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

In November 1990, the Wyden Amendment (Public Law 101-510, Section 3137 [1990]) was enacted. This law required the identification of Hanford Site tanks that may have a serious potential for release of high-level waste. In February 1991 (Harmon 1991), the 24 ferrocyanide tanks were among the tanks identified, and were included in the subsequent July 1991 report to Congress (Watkins 1991) that responded to the Wyden Amendment. However, re-examination of the historical records (Borsheim and Simpson 1991) indicated that six of the 24 tanks did not contain the requisite 1,000 g-moles of ferrocyanide. Therefore, these six tanks should not have been included on the Watch List nor been identified in the response to the Wyden Amendment. The six tanks were subsequently removed from the Watch List (Anttonen 1993, Sheridan 1994b) (Note: these tanks do not contain greater than 8 wt% $Na_2NiFe(CN)_6$ and should not be on the Watch List for this reason also).

As part of the overall safety screening module being conducted by Westinghouse Hanford Company Tank Waste Remediation System, all of the Hanford Site SSTs will be core sampled and characterized. Eighteen ferrocyanide tanks are currently on the Watch List, and no more ferrocyanide tanks are expected to be added to the Watch List.

Work conducted since 1991 on ferrocyanide reactions has resulted in a change of the criterion used for placing ferrocyanide tanks on the Watch List. The 1,000 g-mole inventory criterion has now been replaced with a fuel concentration criterion of 115 calories per gram (cal/g) of dry sample (this is an energy equivalent to a concentration of 8 wt% $Na_2NiFe(CN)_6$ in the waste). This fuel concentration criterion more accurately reflects the risk associated with ferrocyanide tanks. Ferrocyanide tanks with concentrations less than an energy equivalent of 8 wt% $Na_2NiFe(CN)_6$ cannot support a propagating reaction, and are categorized as *safe*. Detailed rationale for the 115 cal/g of dry fuel concentration criterion is presented in Postma et al. (1994a).

Core sampling and characterization efforts will determine the ferrocyanide concentration for those tanks that bound aging (see Sections 2.2 and 3.4). After adequate characterization, if these tanks contain concentrations less than 8 wt% $Na_2NiFe(CN)_6$ (i.e., the fuel value of the maximum concentration is less than 115 cal/g); then a request will be made by Westinghouse Hanford Company for DOE concurrence to remove all the ferrocyanide tanks from the Watch List.

Some sample bias and analytical error are unavoidable; therefore, confidence intervals have been established to specify when it is appropriate to conclude that a ferrocyanide tank contains concentrations less than an energy equivalent of 8 wt% $Na_2NiFe(CN)_6$. An 80% confidence interval was chosen for tanks with a fuel concentration of 8 wt% $Na_2NiFe(CN)_6$. That is, if five ferrocyanide tanks contain exactly an energy equivalent of 8 wt% $Na_2NiFe(CN)_6$, statistically, four tanks would remain on the Watch List and one tank would be removed. The possibility of removing a ferrocyanide tank from the Watch List decreases substantially as the fuel concentration increases. The confidence intervals increase to 95% and 99% at $Na_2NiFe(CN)_6$ concentrations of 12% and 15 wt%, respectively. Detailed discussions on how sample bias and analytical error are factored into determining the actual fuel concentrations in a ferrocyanide tank are given in the Ferrocyanide DQO document (Meacham et al. 1995a).

- **Planned Work To Complete Program.** An increased understanding of ferrocyanide aging indicates that little ferrocyanide remains, and the assumption that it is necessary to core sample all ferrocyanide tanks may not be valid. By characterizing the waste in only those tanks that bound aging (i.e., tanks with conditions least conducive to aging), the Ferrocyanide Safety Issue could be resolved much earlier and at a substantially reduced cost. As more core sample data become available, the need to sample all the ferrocyanide tanks will be reexamined.

- **Milestones.**

  - **January 31, 1996.** Westinghouse Hanford Company issues documentation supporting resolution of the Ferrocyanide Safety Issue for the four C Farm tanks, and recommends resolution of the Ferrocyanide Safety Issue for C Farm tanks. All four C Farm tanks have been sampled and data interpretation reports have been completed for the tanks.

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

  - **March 31, 1997.** Westinghouse Hanford Company prepares documentation to support resolution of the Ferrocyanide Safety Issue for the last 14 ferrocyanide tanks, and recommends Ferrocyanide Safety Issue resolution.

  - **September 30, 1997.** Westinghouse Hanford Company receives DOE approval to resolve the Ferrocyanide Safety Issue. This completes the Ferrocyanide Safety Program.

4.2 TEMPERATURE MONITORING

The installation of temperature monitoring capabilities is discussed in Sections 3.1.2.1 and 3.2.2. Installation of instrument trees and continuous temperature monitoring are considered prudent waste management practices. Therefore, new instrument trees will be installed in ferrocyanide tanks, even though the ferrocyanide waste has aged and little fuel value remains. Instrument trees have been installed in all ferrocyanide tanks and are continuously monitored by TMACS.

- **Planned Work To Complete Program.** None. This task is complete.

- **Milestones.** None.

4.3 PRESSURE MONITORING

The ferrocyanide tanks were initially identified as having "a serious potential for release" and were placed on the Watch List because insufficient data were available on the probability for ferrocyanide-nitrate/nitrite reactions. Pressure monitoring instrumentation is not presently installed on the ferrocyanide tanks. It would take several years to install pressure monitoring instrumentation because of the capital project time cycle. Ferrocyanide waste has probably degraded (aged) significantly, and all of the tanks may now contain less than the 8 wt% $Na_2NiFe(CN)_6$ fuel concentration specified for the *safe* category (see also

Postma et al. 1994a). This eliminates the need for continuous pressure monitoring for offgases from a ferrocyanide reaction.

The rationale for not installing pressure monitors in ferrocyanide tanks was prepared and submitted to DOE in July 1994 (Payne 1994b). Low gas generation rates (Fowler and Graves 1994) and the low potential for exothermic ferrocyanide reactions (Postma et al. 1994a) indicated that continuous pressure monitoring is not warranted.

- **Planned Work For Subsequent Months.** No additional work is planned in this area, because DOE has concurred that pressure monitoring is not required as stated in the revised Ferrocyanide Safety Issue Program Plan (O'Leary 1994).

- **Milestones.** None.

5.0 PROGRAM SCHEDULES AND MILESTONES

Schedules (Figure 5-1) are presented in this section. The schedules review milestones for FY 1994 through the expected end of the program in FY 1997. The sequence and anticipated completion dates of the major milestones leading to resolution of the Ferrocyanide Safety Issue are presented. Closure of DNFSB recommendations are indicated on the schedule as diamonds, and completion of interim milestones are indicated as triangles. The schedules are statused through December 31, 1995.

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

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

This page intentionally left blank.

6.0 REFERENCES

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

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

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

Bussell, J. H., 1992, *Engineering Evaluation of Thermocouples in Ferrocyanide Watch List Tanks*, WHC-SD-WM-ER-134, Rev. 0 and Rev. 0A, Westinghouse Hanford Company, Richland, Washington.

Cady, H. H., 1993, *Evaluation of Ferrocyanide/Nitrate Explosive Hazard*, LA-12589-MS, Los Alamos National Laboratory, Los Alamos, New Mexico.

Callaway, W. S., 1995, *Scanning Electron Microscopic Analyses of Ferrocyanide Tank Wastes for the Ferrocyanide Safety Program - FY 1995 Report*, WHC-SD-WM-RPT-194, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

Cash, R. J., and J. M. Thurman, 1991, *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide*, EP-0407, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Cash, R. J., and J. M. Thurman, 1992, *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide*, EP-0407, Rev. 1, Westinghouse Hanford Company, Richland, Washington.

Claybrook, S. W., and S. A. Wood, 1994, *Organic Evaporation in Waste Tank C-103*, WHC-SD-WM-ER-344, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0709, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Crowe, R. D., and W. D. Wittekind, 1995, *Ferrocyanide Safety Program: In-Tank Application of Electromagnetic Induction (EMI) Moisture Measurements - FY 1995 Report*, WHC-SD-WM-ER-520, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Deaton, D. E., 1990, *Unusual Occurrence - Unreviewed Safety Questions Regarding Tanks Containing Ferrocyanide*, WHC-90-B003-R1 (Update 10-22-90), Westinghouse Hanford Company, Richland, Washington.

Dickinson, D. R., J. M. McLaren, G. L. Borsheim, and M. D. Crippen, 1993, *Ferrocyanide Safety Program: Credibility of Drying Out Ferrocyanide Tank Waste by Hot Spots*, WHC-EP-0648, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

DOE, 1994a, *Recommendation 93-5 Implementation Plan*, DOE/RL 94-0001, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

DOE, 1994b, *Program Plan for Resolution of the Ferrocyanide Waste Tank Safety Issue at the Hanford Site*, DOE/RL-94-110, Rev. 1, U.S. Department of Energy, Richland Operations Office, Richland, Washington.

Epstein, M., H. K. Fauske, M. D. Crippen, D. R. Dickinson, J. D. McCormack, R. J. Cash, J. E. Meacham, and C. S. Simmons, 1994, *Ferrocyanide Safety Program: An Assessment of the Possibility of Ferrocyanide Sludge Dryout*, WHC-EP-0816, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

Fowler, K. D., 1994, *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide*, WHC-EP-0407, Rev. 2, Westinghouse Hanford Company, Richland, Washington.

Fowler, K. D., and R. D. Graves, 1994, *Decision Analysis for Continuous Cover Gas Monitoring of Ferrocyanide Watch List Tanks*, WHC-EP-0743, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

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

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

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

Kelly, S. E., 1995b, *Tank Characterization Report for Single Shell Tank 241-TY-104*, WHC-SD-WM-ER-481, Rev. 0-A, Westinghouse Hanford Company, Richland, Washington.

Kress, T., K. Bandyopadhyay, P. d'Entremont, S. Slezak, and M. Reich, 1990, *Risk of a Ferrocyanide Explosion in the Hanford Waste Tank Farm*, (memorandum to John Tseng, DOE-HQ, September 20), Ad Hoc Task Force formed by U.S. Department of Energy to evaluate the ferrocyanide safety concerns at the Hanford Site, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

McLaren, J. M., 1993, *Ferrocyanide Safety Program: Updated Thermal Analysis Model for Ferrocyanide Tanks with Application to Tank 241-BY-104*, WHC-EP-0669, Rev. 0, Westinghouse Hanford Company, Richland Washington.

McLaren, J. M., 1994a, *Ferrocyanide Safety Program: Thermal Analysis of Ferrocyanide Tanks, Group I*, WHC-EP-0729, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

McLaren, J. M., 1994b, *Ferrocyanide Safety Program: Thermal Analysis of Ferrocyanide Watch List Tanks, Group II*, WHC-EP-0794, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Meacham, J. E., H. Babad, and H. Toffer, 1993, *Moisture Monitoring of Ferrocyanide Tanks: An Evaluation of Methods and Tools*, WHC-EP-0658, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

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

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

Payne, M. A., 1994a, *Ferrocyanide Safety Program: Transmittal of General Accounting Office Closeout Report*, (letter 9454280 to R. E. Gerton, DOE-RL, June 16), Westinghouse Hanford Company, Richland, Washington.

Payne, M. A., 1994b, *Ferrocyanide Safety Program: Continuous Pressure Monitoring in Ferrocyanide Watch List Tanks*, (letter 9455175 to R. E. Gerton, DOE-RL, July 29), Westinghouse Hanford Company, Richland, Washington.

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

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

Postma, A. K., D. B. Bechtold, G. L. Borsheim, J. M. Grigsby, R. L. Guthrie, M. Kummerer, M. G. Plys, and D. A. Turner, 1994b, *Safety Analysis of Exothermic Reaction Hazards Associated with the Organic Liquid Layer in Tank 241-C-103*, WHC-SD-WM-SARR-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

Rebagay, T. V., R. J. Cash, D. A. Dodd, C. T. Narquis, F. R. Reich, and W. D. Winkelman, 1995, *Remote Characterization of Mixed Waste by Fourier Transform Infrared Spectroscopy*, WHC-SD-WM-RPT-192, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Reich, F. R., R. E. Johnson, B. L. Philipp, J. B. Duncan, and G. L. Schutzenhofer, 1994, *Summary of Fiscal Year 1994 Near-Infrared Spectroscopy Moisture Sensing Activities*, WHC-EP-0839, Westinghouse Hanford Company, Richland, Washington.

Riedel, E. F., 1995, *Ferrocyanide Safety Program: FY 1995 Report on Mössbauer Spectroscopy Task Activities*, WHC-SD-WM-RPT-195, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

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

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

Simmons, C. S., 1995, *Modeling Water Retention of Tank Waste*, PNL-10831, Pacific Northwest Laboratory, Richland, Washington.

Sloat, R. J., 1954, *TBP Plant Nickel Ferrocyanide Scavenging Flowsheet*, HW-30399, General Electric Company, Richland, Washington.

Sloat, R. J., 1955, *In-Farm Scavenging Operating Procedure and Control Data*, HW-38955, General electric Company, Richland, Washington.

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

Wagoner, J. D., 1993, *Approval of Hanford Site Tank Farm Facilities Interim Safety Basis*, (letter 93-TOB-209 to T. M. Anderson, President, Westinghouse Hanford Company, November 18), U.S. Department of Energy, Richland Operations Office, Richland, Washington.

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

Watson, W. T., 1993, *Proof of Principle Report for In-Tank Moisture Monitoring Using an Active Neutron Probe*, WHC-EP-0695, Westinghouse Hanford Company, Richland, Washington.

Webb, A. B., J. L. Stewart, D. A. Turner, M. G. Plys, B. Malinovic, J. M. Grigsby, D. M. Camaioni, P. G. Heasler, W. D. Samuels, and J. J. Toth, 1995, *Preliminary Safety Criteria for Organic Watch List Tanks at the Hanford Site*, WHC-SD-WM-SARR-033, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

WHC, 1991, *Tank Farm Stabilization Plan for Emergency Response*, WHC-SD-PRP-TI-001, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

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

Wood, S. A., 1992, *Gas Space Analysis For Tank C-109*, WHC-SD-WM-ER-183, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

FERROCYANIDE TANK INFORMATION SUMMARY

This page intentionally left blank.

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

Tank	Total waste volume (1,000 L)	FeCN[b] (1,000 g-mole)	Heat load (kW)[c]	Maximum temp. (°C)	(°F)	Riser No.	Status of tanks[d]
BY-103	1510	66	1.6	27 27[e]	81 81	1 5	NS; AL
BY-104	1540	83	3.3[f]	52[e] 44	125 112	1 10B	IS; Sound
BY-105	1900	36	4.9[f]	48 44	118 112	1 10C	NS; AL
BY-106	2430	70	4.7[f]	50	121	1	NS; AL
BY-107	1010	42	2.6	35 37[e]	96 99	1 5	IS; AL
BY-108	863	58	2.7	42[e] 42	108 108	3 8	IS; AL
BY-110	1510	71	3.3[f]	47 41[e]	117 107	1 10A	IS; Sound
BY-111	1690	6	2.1[f]	29[e]	84	14	IS; Sound
BY-112	1100	2	2.4[f]	32[e]	90	2	IS; Sound
C-108	250	25	2.9[f]	27[e] 26	80 78	1 5	IS; Sound
C-109	250	6.8[g]	3.0[f]	29[e] 28	83 82	3 8	IS; Sound
C-111	216	33	2.5[f]	26 26[e]	79 78	5 6	IS; AL
C-112	394	11.5[g]	3.3[f]	30 30[e]	85 85	1 8	IS; Sound
T-107	681	5	1.2[f]	20 22[e]	67 72	4 5	NS; AL
TX-118	1310	<3	1.4	24[e] 25	75 77	1 3	IS; Sound
TY-101	447	23	1.1[f]	19[e] 19	66 67	3 4	IS; AL

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

Tank	Total waste volume (1,000 L)	FeCN[b] (1,000 g-mole)	Heat load (kW)[c]	Maximum temp. (°C)	(°F)	Riser No.	Status of tanks[d]
TY-103	613	28	1.5	22 21[e]	71 71	4 7	IS; AL
TY-104	174	12	0.9	21[e] 20	71 68	3 4	IS; AL

Notes:

[a]Reflects removal of four ferrocyanide tanks from the Watch List in July 1993 and two additional tanks in October 1994. Tank information and temperature data as of December 1995.
[b]Original tank inventories (Borsheim and Simpson 1991).
[c]Heat load values from Table 7-1 in Crowe et al. (1993).
[d]IS - Interim Stabilized Tank; NS - Not Stabilized; AL - Assumed Leaker Tank; Sound - Non-Leaking Tank.
[e]Readings from new instrument trees; tank 241-BY-105 already had two trees.
[f]New data taken from Crowe et al. (1995).
[g]Calculated as ferrocyanide $[Fe(CN)_6^{-4}]$ based on the total cyanide values reported in Simpson et al. (1993a, 1993b).

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

Tank	Date Sampled (Type)[a]	Flamm. (% LEL)[b]	Organic Vapor (ppmv)[c]	NH_3 (ppmv)[d]	NH_3 (ppmv)[e]	HCN (ppmv)[d]	$NO+NO_2$ (ppmv)[d,g]	TNMOC (mg/m^3)[f]	H_2 (ppmv)[g]	N_2O (ppmv)[g]	CO (ppmv)[g]	CO_2 (ppmv)[g]	Water Content %RH (°C)[h]
BY-103	05/05/94 (2)	<1	1.2	25	30.7	<0.005[i]	<0.3	5.2	21.4	49.2	<1	--	--
	11/01/94 (3)	--	--	--	26	--	<0.2	--	<99	16.5	<12	126	49 (25.5°C)
BY-104	04/22/94 (2)	<1	26	200	285	<0.005[i]	<0.3	56	204	305	<1	--	--
	06/24/94 (3)	--	--	--	248	--	<0.4	61	295	201	1	10.5	58 (26 °C)
BY-105	05/09/94 (2)	<1	4.9	40	57	<0.005[i]	<0.1	17.8	85	122	0.5	--	--
	07/07/94 (3)	--	--	--	43	--	<0.2	12.7	48	50	0.4	94	61 (26 °C)
BY-106	05/04/94 (2)	<1	5.7	60	87	<0.01--	<0.2	6.3	46	94	--	--	--
	07/08/94 (3)	--	--	--	74		<0.2	9.9	46	71	0.5	47.6	57 (27 °C)
BY-107	03/25/94 (2)	3 - 4	67	97	--	--	--	173	692	802	<5	--	--
	10/26/94 (3)	--	--	--	972	--	<0.2	150	267	621	<20	94	36 (33.1°C)
BY-108	03/28/94 (2)	1	97	700	--	--	<0.5	594	644	757	<5	--	--
	10/27/94 (3)	--	--	--	1040	--	<0.1	510	400	641	<76	224	56 (25.7°C)
BY-110	09/27/92 (1)	<1	350	612	--	<2	<0.5	--	--	--	--	--	--
	11/11/94 (3)	--	--	--	401	--	<0.2	29	<160	103	<76	229	31 (27 °C)
BY-111	05/11/94 (2)	<1	8.9	60	--	--	--	--	--	--	<1	--	--
	11/16/94 (3)	--	--	--	59	--	<0.2	9.6	67	99	<1	219	27 (27 °C)
BY-112	03/26/93 (1)	<1	5.9	10	--	<2	<0.5	--	--	--	--	--	--
	11/18/94 (3)	--	--	--	63	--	<0.2	5.8	<94	40	<12	121	53 (23.3°C)
C-108	07/23/93 (**)	<1	1.2	<2	--	<2	<0.5	--	--	--	1	--	--
	07/07/94 (2)	--	--	--	--	<0.0002[i]	--	<0.4	--	--	--	--	--
	08/05/94 (3)	--	--	--	2.7	--	<0.3	<1.4	15.3	344	0.1	16.3	76 (25 °C)
C-109	06/23/94 (2)	<1	1	4	--	--	--	--	--	--	--	--	--
	08/09/94 (3)	--	--	--	10.1	--	<0.6	0.65	125	369	0.4	3	79 (27 °C)
C-111	08/10/93 (**)	<1	<0.2	<2	--	<0.04[k]	<0.5	<0.3	16	39	0.1	--	--
	06/20/94 (2)	<1	<0.2	<2	0.1	<0.01[i]	<0.2	0.18	--	--	--	--	--
	09/13/94 (3)	--	--	--	5.6	--	≤0.7	<0.6	12.4	99	0.1	198	86 (27 °C)
C-112	06/24/94 (2)	<1	<0.2	4	--	--	--	--	--	--	--	--	--
	08/11/94 (3)	--	--	--	22.7	--	<0.7	3.4	204	544	0.9	102	82 (28 °C)
T-107	10/22/92 (1)	<1	24	203	--	<2	<0.5	--	--	--	--	--	--
	01/18/95 (3)	--	--	--	125	--	<0.1	1.4	<94	42	<12	75	82 (17.2°C)

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

Tank	Date Sampled (Type)[a]	Flamm. (% LEL)[b]	Organic Vapor (ppmv)[c]	NH_3 (ppmv)[d]	NH_3 (ppmv)[e]	HCN (ppmv)[d]	$NO+NO_2$ (ppmv)[d,g]	TNMOC (mg/m^3)[f]	H_2 (ppmv)[g]	N_2O (ppmv)[g]	CO (ppmv)[g]	CO_2 (ppmv)[g]	Water Content %RH (°C)[h]
TX-118	07/28/93 (**)	<1	0.3	10	--	<2	<0.5	--	--	--	--	--	--
	09/07/94 (2)	<1	7.8	28	--	<0.02	<0.5	9.3	97	17	2.5	54	--
	12/16/94 (3)	--	--	--	33	--	--	--	<94	29	<12	98	42 (21.5°C)
TY-101	08/04/94 (2)	<1	4	12	16	<0.01	<0.2	--	--	--	--	--	--
	04/06/95 (3)	--	--	--	16	--	<0.2	1.0	<93	98	<12	83	77 (15.6°C)
TY-103	08/04/94 (2)	<1	5	30	31	<0.01	<0.1	--	--	--	--	--	--
	04/11/95 (3)	--	--	--	49	--	<0.2	60	<93	159	<12	121	85 (15.9°C)
TY-104	08/05/94 (2)	<1	2.5	24	50	--	<0.2	--	--	--	--	--	--
	04/27/95 (3)	--	--	--	61	--	≤0.2	3	<49	98	<23	<23	88 (15.6°C)

[a]Sample Type:

**Vapor samples taken from in-tank, non-heated tubes using a vapor sampling cart (SUMMA™ only - no NH_3).

1 Monitoring performed by Industrial Hygiene technicians using three varying length, non-heated sampling tubes into the tank headspace to evaluate for flammability and toxic vapors; this method is no longer used.

2 In Situ Sampling (ISS) - Sampling is performed by lowering special sorbent traps into the tank headspace that are connected topside to a portable handcart.

3 Sampling involves the mobile vapor sampling system, heated transfer lines, and installation of a water-heated sampling probe into the tank headspace. All ferrocyanide tanks are scheduled for resampling using this method.

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

[c]Measured using an Organic Vapor Monitor (OVM). OVM readings are affected by ammonia; OVM ammonia response is about 13:1, so that 13 ppmv of ammonia is indicated as 1 ppmv of organic vapors (ppmv = parts per million by volume).

[d]For Type 1 sampling only; value is measured using colorimetric (Dräger™) tubes (values are estimated, and not quantitative).

[e]Analyses of ammonia sorbent trap samples.

[f]Total non-methane organic compound (TNMOC) concentrations measured for SUMMA™ canister samples.

[g]Analyses of SUMMA™ canister samples from Type **, and 3 sampling methods.

[h]% RH is the percent relative humidity calculated from measured headspace water content (mg/L), temperature and atmospheric pressure. Temperature of headspace gas in °C is listed in parentheses.

[i]HCN determinations obtained in selected tanks using a special sorbent trap; values shown are below detection limit of the measurement technique.

[j] -- Data not yet available or not obtained by this type of sampling.

[k]This HCN number was < 0.04 parts per billion vapor as determined by a special sodium hydroxide bubbler.

APPENDIX REFERENCES

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

Crowe, R. D., M. Kummerer, and A. K. Postma, 1993, *Estimation of Heat Load in Waste Tanks Using Average Vapor Space Temperatures*, WHC-EP-0709, Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Crowe, R. D., D. P. Maassen, and S. A. Parra, 1995, *Calculated Heat Load for Watchlist Single-Shell Waste Tanks Using the Average Vapor Space Temperatures*, (letter report attached to internal memorandum from H. Toffer to R. J. Cash, September 29), Westinghouse Hanford Company, Richland, Washington.

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

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

This page intentionally left blank.

DISTRIBUTION

Number of copies

OFFSITE

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

DISTRIBUTION (Continued)

Number of copies

OFFSITE

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

DISTRIBUTION (Continued)

Number of copies

OFFSITE

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

DISTRIBUTION (Continued)

Number of copies

OFFSITE

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

DISTRIBUTION (Continued)

ONSITE

10	U.S. Department of Energy, Richland Operations Office	
	R. G. Harwood	S7-54
	W. F. Hendrickson (2)	S7-54
	M. F. Jarvis	S7-54
	A. G. Krasopoulos	A4-81
	J. K. McClusky	S7-53
	J. C. Peschong	S7-53
	Public Reading Room	H2-53
	RL Docket File (2)	B1-17
5	Pacific Northwest Laboratory	
	J. W. Brothers	K5-22
	R. T. Hallen	P8-38
	M. A. Lilga	P8-38
	C. S. Simmons	K9-33
	Hanford Technical Library	P8-55
37	Westinghouse Hanford Company	
	H. Babad	S7-30
	J. B. Billetdeaux	S7-16
	W. S. Callaway	S3-90
	R. J. Cash (5)	S7-14
	M. D. Crippen	L5-31
	R. D. Crowe	H0-38
	M. L. Dexter	R1-51
	D. R. Dickinson	L5-31
	G. T. Dukelow	S7-14
	J. M. Grigsby	A3-37
	M. N. Islam	R3-08
	D. W. Jeppson	L5-31
	N. W. Kirch	R2-11
	C. A. Kuhlman	B3-30
	L. L. Lockrem	S3-90

DISTRIBUTION (Continued)

Westinghouse Hanford Company (Continued)

J. M. McLaren	H0-34
J. E. Meacham (2)	S7-14
N. J. Milliken	H4-65
S. R. Moreno	B3-06
T. V. Rebagay	T6-30
F. R. Reich	L5-55
E. F. Riedel	S3-90
B. C. Simpson	R2-12
W. T. Watson	H0-38
W. D. Winkelman	L5-55
W. D. Wittekind	H0-38
Central Files	A3-88
Correspondence Processing	A3-01
EDMC	H6-08
OSTI (2)	A3-36