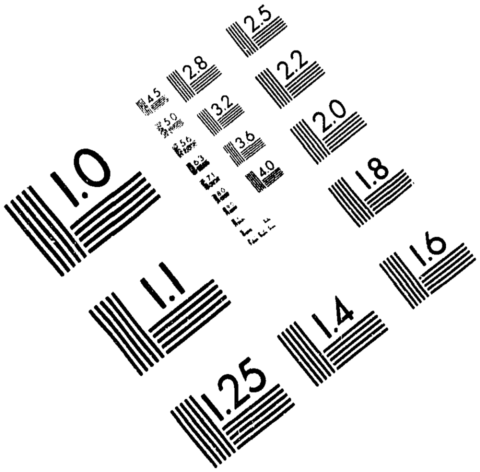

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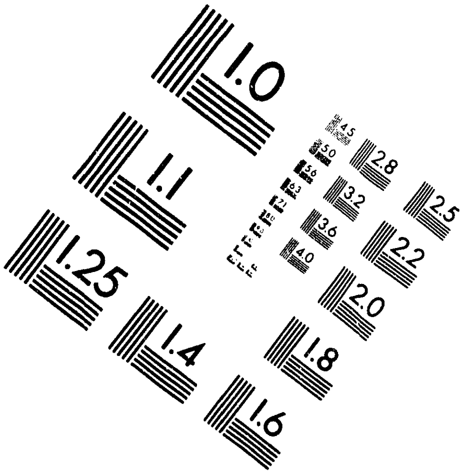

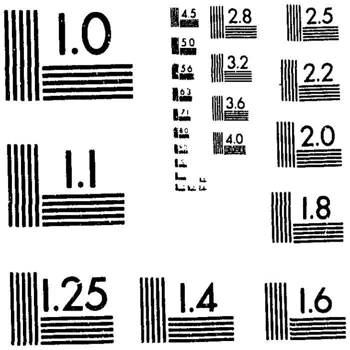

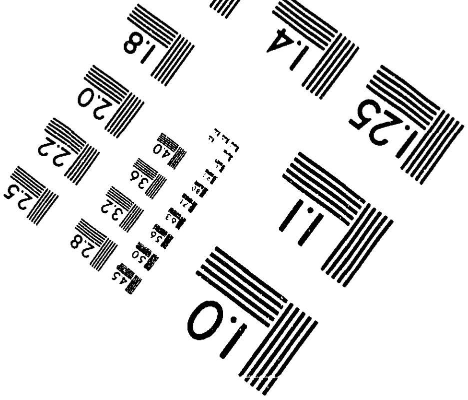

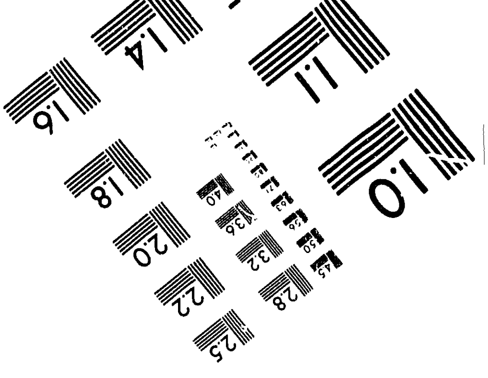

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Quarterly Report on Defense Nuclear Facilities Safety Board Recommendation 90-7 for the Period Ending December 31, 1992

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QUARTERLY REPORT ON DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7 FOR THE PERIOD ENDING DECEMBER 31, 1992

R. J. Cash
G. T. Dukelow
C. J. Forbes

ABSTRACT

This is the seventh quarterly report on the progress of activities addressing safety issues associated with Hanford Site high-level radioactive waste tanks that contain ferrocyanide compounds. In the presence of oxidizing materials, such as nitrates or nitrites, ferrocyanide can be made to explode in the laboratory by heating it to high temperatures [above 285 °C (545 °F)]. In the mid 1950s approximately 140 metric tons of ferrocyanide were added to 24 underground high-level radioactive waste tanks. An implementation plan (Cash 1991) responding to the Defense Nuclear Facilities Safety Board Recommendation 90-7 (FR 1990)* was issued in March 1991 describing the activities that were planned and underway to address each of the six parts of Recommendation 90-7. A revision to the original plan was transmitted to U.S. Department of Energy by Westinghouse Hanford Company in December 1992.*

The revised implementation plan describes the progress made on Ferrocyanide Safety Program activities since the beginning of the program in September 1990, and those continuing tasks that address or supplement the six parts of Recommendation 90-7. The plan

incorporates comments received from various reviewers after preparation of draft issues in June and September 1992. The revised plan provides an updated schedule, and includes the current status of understanding on the ferrocyanide safety issue. The document was approved for public availability and will be distributed after transmittal to the Defense Nuclear Facilities Safety Board by the U.S. Department of Energy.

Milestones completed this quarter include: (1) fabrication of the six thermocouple trees scheduled to go into the six non-leaking ferrocyanide tanks; (2) an evaluation of an ultra high pressure technique that uses minimal amounts of water to install thermocouple trees in the 14 assumed leaker ferrocyanide tanks; (3) vapor sampling of tanks 241-T-107 in preparation for core sampling, and 241-BY-104 in support of the Tank Vapor Program; (4) a report on the modeling of the vapor space of 241-C-109; (5) completion of analytical analyses of the two auger surface samples taken from tank 241-BY-104; (6) completion of analyses and receipt of the analytical data packages for tne three cores taken from tank 241-C-112; (7) additional ferrocyanide waste simulant characterization results from tests at Fauske and Associates, Inc.; (8) definition of a proposed approach for resolution of the ferrocyanide unreviewed safety question; and (9) completion of key Pacific Northwest Laboratory reports on ferrocyanide waste simulant aging studies and on analytical determination of ferrocyanide species.

Vapor sampling of 241-T-107 revealed no flammable gases present, but ammonia was detected at about 200 part per million (ppm) using Draeger tubes. Ammonia has been seen in several of the ferrocyanide tanks sampled to data, although not all tanks have had levels *above the 25 ppm Threshold Limit Value for ammonia. Core sampling of tank 241-T-107 started in November and one four-segment core was obtained before sampling operations were shut down as the result of a U.S. Department of Energy audit. Disposition of the audit findings was still in progress at the end of the quarter.*

Hot spot modeling at Fauske and Associates, Inc. shows that local dryout of the waste is not possible because of the very high capillary forces resulting from the fine particle size prevalent with the ferrocyanide precipitates. Essentially the entire contents of the tank would have to dry out before a local region could exceed the boiling point of the waste (≈ 130 °C). High capillary forces were calculated by Westinghouse Hanford and will be confirmed by special induced hot spot tests at Fauske and Associates, Inc. with Kaolin clay and U Plant flowsheet ferrocyanide simulant.

Analytical results for the 241-BY-104 auger surface samples show that the moisture content for the two samples varied from 15 to 17 wt%. Total organic carbon was about 1 wt%, which agrees with the maximum adiabatic calorimeter results of 171 Joules/gram (41 calories/gram) of as-received wet material. The level of total cyanide, and thus possible ferrocyanide, is low (approximately 40 ppm). Ferrocyanide is not expected in this saltcake waste since this type of waste was added to 241-BY-104 after the ferrocyanide scavenging runs of the 1950s.

A predecisional plan for resolving the ferrocyanide unreviewed safety question is being drafted by Westinghouse Hanford. The plan will be transmitted to the U.S. Department of

Energy and other oversight committees for review and approval. The moisture content of the waste plays a key role in demonstrating that the ferrocyanide waste in the tanks is safe and that runaway exothermic reactions are incredible.

Studies to determine the possible effects of catalysts and initiators are nearing completion at Pacific Northwest Laboratory. Various candidate initiators and catalysts were tested for their effects on lowering the onset temperature of reaction and the time to reaction using a modified Time-To-Explosion test. None of the materials tested were statistically significant below temperatures of about 300 °C. This temperature is too high to be of a safety concern.

All actions recommended by the Defense Nuclear Facilities Safety Board for emergency planning by Hanford Site Emergency Preparedness organizations have been completed. Henceforth, Tank farm emergency planning, training, and validation exercises will be accomplished as part of the normal Site emergency programs.

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

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

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ASC	Adiabatic Scanning Calorimetry
CASS	Computer Automated Surveillance System
CTMS	Continuous Temperature Monitoring System
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DSC	Differential Scanning Calorimetry
EA	Environmental Assessment
EAL	Emergency Action Level
EDTA	Ethylenediaminetetraacetic Acid
FAI	Fauske and Associates, Inc.
FFTF	Fast Flux Test Facility
FSU	Florida State University
FTIR	Fourier Transform Infrared
FY	Fiscal Year
HEDTA	Hydroxyethylenediaminetriacetic Acid
HEPA	High-Efficiency Particulate Air
HLW	High-Level Radioactive Waste
HWVP	Hanford Waste Vitrification Plant
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
JCO	Justification for Continued Operations
LANL	Los Alamos National Laboratory
LOW	Liquid Observation Well
MCNP	Monte Carlo Neutron Photon [Model]
MIT	Multifunctional Instrument Tree
NH_3	Ammonia
PNL	Pacific Northwest Laboratory
PSO	Program Secretarial Officer
RL	U.S. Department of Energy, Richland Field Office
RSST	Reactive Systems Screening Tool (Small FAI Calorimeter)
SA	Safety Assessment
SAR	Safety Analysis Report
SEM	Scanning Electron Microscopy
SST	Single-Shell Tank
STG	Scanning Thermogravimetry
TAP	Tank Advisory Panel
TC	Thermocouple
TLV	Threshold Limit Value
TMACS	Tank Monitoring and Control System
TOC	Total Organic Carbon

LIST OF TERMS (Continued)

Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*
USQ	Unreviewed Safety Question
VSP	Vent Sizing Package (Large FAI Calorimeter)
Westinghouse Hanford	Westinghouse Hanford Company
XRD	X-ray Diffraction

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QUARTERLY REPORT ON DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7 FOR THE PERIOD ENDING DECEMBER 31, 1992

1.0 INTRODUCTION

1.1 PURPOSE

This quarterly report provides a status of the activities underway at the Hanford Site on the ferrocyanide safety issues, as requested by the Defense Nuclear Facilities Safety Board (DNFSB) in their Recommendation 90-7 (FR 1990). In March 1991, a DNFSB Implementation Plan (Cash 1991) was prepared and sent to the DNFSB responding to the six parts of Recommendation 90-7. The plan was revised and forwarded to the U.S. Department of Energy (DOE) in December 1992 for transmittal to the DNFSB (Borsheim et al. 1992). All of the activities in the revised DNFSB Implementation Plan are underway, and the status of each is described in Section 2.0 of this report.

1.2 QUARTERLY HIGHLIGHTS

- Design and fabrication of thermocouple (TC) trees for installation in the last 6 of the non-leaking ferrocyanide tanks was completed. Detailed preparations are being made to complete their installation by July 30, 1993.

- A study to evaluate and identify alternative methods for installation of TC trees in assumed leaker ferrocyanide tanks was completed. The previous method used large volumes of water to wash the TC tree through the waste. An ultra high pressure concept that uses minimal quantities of water has been chosen for final testing and design. Preparation of the safety and environmental assessments are planned for the next quarter.

- Hot spot analysis of tank 241-BY-104 show that concentrating all the heat producing radionuclides into a layer will not produce temperatures above 220 °C unless the layer is less than 15 cm thick. As the hot spot becomes smaller, the concentrations required to reach 220 °C become larger. Information from Fauske and Associates, Inc. (FAI) indicates that local dryout would not occur because of the very high capillary forces resulting from the fine particle size of the nickel ferrocyanide precipitate. Thus, temperatures in a hot spot would not rise above about 130 °C, the boiling point of saturated sodium nitrate solution, unless the entire tank approached dryout.

- The design for the Continuous Temperature Monitoring System (CTMS) for C Farm was revised to include new TC trees recently installed as well as the new tree to be installed in C-108 in Fiscal Year (FY) 1993. Design work for the CTMS installation in the BX Farm was started. Construction planning for the C Farm installation was also started.

- Modeling of tank 241-C-109 vapor space was completed this quarter and results show that there are no significant concentrations of hydrogen gas within the tank. The airflow velocities within the tank are low but sufficient to keep the vapor space well mixed.

- Vapor sampling of tank 241-T-107 was completed in support of push-mode core sampling. Field readings for the tank showed no concentration of flammable gases above the detection limit of the combustible gas monitor. There were no detectable concentrations of HCN or CN^- using Dräger tube analysis. Vapor sampling of 241-BY-104 for flammability and toxic gases was completed on December 29, 1992. Samples collected are being analyzed by offsite laboratories.

- Push-mode core sampling of tank 241-T-107 was initiated, with one full-depth core (four 19-inch segments) obtained. One more full-depth core is planned, but sampling has been delayed pending resolution of findings of a DOE Richland Field Office (RL) audit.

- The analytical data packages for the three 241-C-112 cores taken in June 1992 were received from Pacific Northwest Laboratory (PNL) this quarter. Interpretation of the data and a report of what the results mean for the ferrocyanide safety program will be prepared next quarter.

- The three cores (one 19-inch segment each) taken from tank 241-C-109 last quarter have been extruded in the PNL hot cells and broken down into aliquots for the various analyses. Early results are expected in January 1993 and final data reports will be available by March.

- A plan for resolving the ferrocyanide unreviewed safety question (USQ) is being prepared for transmittal to DOE by January 29, 1993.

- The PNL FY 1992 annual report on ferrocyanide aging studies was issued in November 1992 as PNL-8387 (Lilga et al. 1992). Testing is continuing through FY 1993 to determine the degradation effects of radiolysis and alkaline hydrolysis on ferrocyanide originally put in the tanks.

- The PNL annual report on FY 1992 analytical work to determine various cyanide species present in ferrocyanide tank waste was issued this quarter as PNL-8399 (Bryan et al. 1992). The detection limit of the three individual cyanide species (ferrocyanide, ferricyanide, and free cyanide) using solution attenuated total reflectance infrared spectroscopy is at least 0.1 wt%.

- The presence of nickel sulfide (NiS) in some of the C Farm ferrocyanide tanks was evaluated by PNL this quarter as a possible catalyst or initiator. NiS was an added ingredient to the In Farm flowsheet for several runs during the 1950s to enhance precipitation of ^{60}Co. Sulfide compounds can react as fuels and nickel may act as a catalyst. The studies indicate that NiS can both accelerate and reduce the minimum explosion temperature for a near-stoichiometric mixture of sodium nickel ferrocyanide and an equimolar mixture of sodium nitrate and nitrite. The effect is only evident at temperatures above 300 °C and is not expected to be a safety concern.

- Results of gas analyses from Fauske and Associates, Inc. (FAI) propagation tests show that less gas is released from a ferrocyanide reaction than theoretically possible and that some metal carbonates are also produced. This means that less energy is liberated during the reaction. Two scoping aerosol/propagation tests are planned at FAI to determine what aerosols, if any, are produced during a burn of the most reactive (In Farm flowsheet) simulant.

- The environmental assessment (EA) for removing pumpable liquid from ferrocyanide tanks was revised and resubmitted to DOE this quarter. Revision of the companion safety assessment (SA) is still in progress for resubmittal in January 1993.

- All actions recommended by the DNFSB with respect to emergency planning, event recognition, protective action recommendations, and emergency response procedures were completed last quarter. Henceforth, tank farm emergency planning, training, and validation exercises will be accomplished as part of the normal Hanford Site emergency programs.

1.3 REPORT FORMAT

The quarterly report on progress of activities under each of the six parts of DNFSB Recommendation 90-7 is arranged in the same order as in the original *DNFSB Implementation Plan* (Cash 1991). The arrangement also follows the same order provided in the recommendation. To report on progress, each part of the recommendation is repeated in italics, followed by one or more paragraphs explaining the scope of work on each part or subpart of the recommendation. Subheadings for each task activity report the following items of progress:

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

1.4 BACKGROUND

Radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s. During the 1950s, additional tank storage space was required to support the Hanford Site defense mission. To obtain this additional storage volume within a short period of time, and without constructing additional storage tanks, Hanford Site scientists developed a process to scavenge radiocesium and other soluble radionuclides from tank waste liquids. In implementing this process, approximately 140 metric tons of ferrocyanide were added to 24 SSTs.

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

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

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

Using process knowledge and historical records, 24* tanks were identified at the Hanford Site as containing 1,000 g-mole or more of ferrocyanide as the $Fe(CN)_6^{-4}$ radical. In October 1990, the ferrocyanide issue was declared an Unreviewed Safety Question** because the safety envelope for these tanks may no longer be bounded by the existing safety analysis report (Bergmann 1986) and the 1987 DOE environmental impact statement. Work in and around any of the ferrocyanide tanks requires detailed planning, together with the preparation of supporting safety and environmental documentation, and approval by DOE management. These restrictions are required for safety, and significantly increase the time required to complete work or install equipment in the tanks. See also Section 2.4.6.

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*Two more tanks potentially containing ferrocyanide were identified since the DOE responded to Recommendation 90-7 (FR 1990) in November 1990.

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

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

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

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2.0 DEFENSE NUCLEAR FACILITIES SAFETY BOARD IMPLEMENTATION PLAN TASK ACTIVITIES

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

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

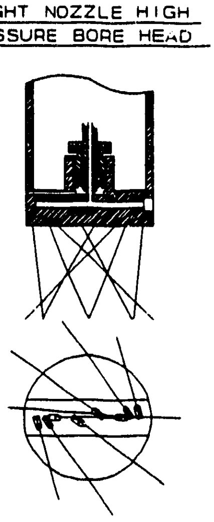
"Immediate steps should be taken to add instrumentation as necessary to the SSTs containing ferrocyanide that will establish whether hot spots exist or may develop in the future in the stored waste. The instrumentation should include, as a minimum, additional thermocouple trees. Trees should be introduced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

2.1.1 Instrument Trees

DNFSB Recommendation 90-7.1 requested that actions be taken to add instrumentation to the ferrocyanide waste tanks, in order to determine if hot spots exist or may develop.

A strategy was initially developed to provide the temperature instrumentation necessary to monitor conditions in five high concern waste tanks on an expedited basis. The strategy was to repair the existing TCs where possible; install new TC trees that would be fabricated from existing drawings; and install multifunctional instrument trees (MITs) in those tanks that have a limited number of risers available. The TC trees would provide temperature monitoring but would not provide the option to obtain any other needed data (such as gas sampling). This strategy was later revised to include installation of new TC trees and repair existing TC trees in ferrocyanide waste tanks. No MITs will be installed in these tanks at this time.

- **Progress During This Reporting Period.** Design and fabrication of thermocouple trees for installation in the last 6 of the non-leaking ferrocyanide tanks is complete. Because tank 241-T-101 was declared an assumed leaker, installation of a TC tree in that tank will now be included with the leaker tanks when safety and environmental documentation is authorized for use.



A study has been completed to evaluate alternative installation methods and identify several methods that have enough technical merit to pursue further evaluation testing. After evaluation and testing the ultra high pressure concept has been chosen for development. A full scale boring head has been tested (see diagram to the right). Testing of this bore head has demonstrated that a full scale boring head can be designed which will be installed on the bottom end of the TC tree. Test results to date on the full scale boring head indicate that it is possible to install a TC through 20 ft of hard salt cake using less than 100-gallons of water, without generating an unacceptable quantity of aerosols.

- **Planned Work for Subsequent Months.** Installations of TC trees in the last 6 non-leaking ferrocyanide tanks will be started.

  Safety and environmental documentation that will support installing TC trees into the 14 assumed leaker ferrocyanide tanks will be completed and transmitted to DOE for approval.

  Detailed design for the ultra high pressure concept will be completed and the hardware will be fabricated and tested. An acceptance test will be completed to verify that the final hardware performs as expected prior to being turned over to Tank Farm Operations for field use.

- **Problem Areas and Action Taken.** To install equipment such as TC trees into waste tanks, water is normally used to sluice in the equipment to the desired depth in the waste. Water additions to ferrocyanide tanks that are classified as assumed leakers raise an environmental issue of whether waste could leak from the tank. The first four tanks to receive new TC trees are listed as sound; however, 14 of the 24 ferrocyanide tanks are classified as assumed leakers. The study confirmed that it is feasible to reduce the amount of water used to install thermocouple trees to an acceptable amount. The alternative concept has been tested, and its design and development will completed in the next reporting period.

- **Milestone Status.**
  - **May 29, 1992**: Install first new TC tree in a ferrocyanide tank, and three additional TC trees by September 30, 1992. As a result of the issues discussed above, the first installation was delayed because the safety and environmental documentation was being reviewed by DOE and Westinghouse Hanford. The first new TC tree was installed in 241-BY-104 in September 1992.
  - **September 30, 1992:** Install additional TC trees in three ferrocyanide tanks. Three additional TC trees were installed in 241-BY-110, 241-C-109, and 241-C-112 in September 1992 (total of four new TC trees).
  - **March 30, 1993**: Submit safety and environmental documentation to DOE for installation of TC trees in assumed leaker ferrocyanide tanks.
  - **July 30, 1993**: Complete installation of an additional six TC trees in non-leaker tanks (241-BY-101, -111, and 112; 241-BX-106; 241-C-108; 241-TX-118).
  - **September 30, 1994**: Complete installation of 14 TC trees in assumed leaker tanks.

2.1.2 Upgrades to Existing Tank Temperature Monitoring Instrumentation

This task determines the operability and accuracy of presently installed TCs in the 24 ferrocyanide tanks at the Hanford Site. Until additional TC trees are installed, the existing TCs will be used to provide temperature readings for the ferrocyanide tanks.

Field measurements have been taken on each TC in the existing trees to determine the resistance and voltage across the junction and across each lead to ground. The exact condition of each TC was determined by the resistance and voltage measurements (Bussell 1991). This work was completed in FY 1991. Work in FY 1992 has focused on repair and recovery of 92 of 265 TCs that were found to be failed or marginal in performance.

- **Progress During the Reporting Period**. As a result of the overall ferrocyanide TC repair campaign, a total of 26 TC elements were successfully repaired and the measurement procedure for 6 TCs in the T farm was revised to obtain temperature readings where none were taken before. TMACS will be installed in the T farm during the next fiscal year, and these 6 TCs will be permanently repaired. Thus, the failed TC count was reduced from 41 to 9. The marginal TC count increased from 51 to 82 as failed thermocouples were repaired.

TC elements are still classified as marginal since (1) the repairs have not yet been fully evaluated; and (2) temperatures can be off by as much as 10 °F because the steel pipe is used as a reference, rather than the failed iron lead. The acceptable TC count increased from 96 to 97. There was no change in the good TC count, which is 77. All of the ferrocyanide tanks now have one or more functional TCs in the waste zone, except for tanks 241-BY-111 and -BY-112, which have one dedicated TC element each in the respective liquid observation wells (LOWs).

- **Planned Work for Subsequent Months.** Additional repairs will be performed during the next fiscal year when the TMACS is installed in other tank farms. Repairs of new failures will be made as required.

- **Problem Areas and Actions Taken.** See paragraph above.

- **Milestone Status.** This task is considered to be complete and no further reporting will be performed.

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

2.1.3 Alternate Monitoring Technologies

2.1.3.1 Infrared Scanning System. Infrared systems are commercially available from numerous vendors. Because these systems are sensitive to changes of ±0.28°C (0.50 °F) or less under ideal conditions, they may prove to be beneficial for mapping surface temperature profiles in the ferrocyanide tanks. Thermal modeling performed on ferrocyanide tank 241-BY-104 shows that, if hot spots with temperatures of concern are possible, surface temperature differences might be great enough to be detected by infrared mapping. More modeling is required to determine expected surface temperatures in each tank as a function of the hot spot conditions (location, size, and temperature). Transient modeling to predict how fast the waste surface temperature would change was conducted earlier in FY 1992 (see Section 2.1.4 and Cash et al. 1992b).

One drawback of an infrared camera is the limited life caused by gamma radiation exposure to the semiconductor components within the scanner. Based upon an average radiation level within the SSTs of 150 R/h, the useful life of an infrared camera may be limited to approximately 100 hours. Therefore, deployment for surface monitoring would have to be done periodically, perhaps monthly, unless tank anomalies dictate otherwise. Another concern, which seems to have been dispelled by the scan of tank 241-S-110, is the dependence of measuring a surface temperature on the emissivity of the surface and its ability to emit infrared radiation. This property changes with variations in surface composition, texture, moisture content, and angle of incidence. Because the waste surface in most of the tanks is not uniform, accurate temperature measurement may not be possible; however, temperature mapping may be used for potential hot spot detection and for historical comparisons when scans are examined.

- **Progress During Report Period.** The comments received from DOE requiring changes to the infrared scanning report (Efferding et al. 1992) were incorporated into a new report (WHC-EP-0593). This report is currently being reviewed by Westinghouse Hanford. The conclusions in this report remain the same.

- **Planned Work For Subsequent Months.** The new report will be reviewed by Westinghouse Hanford program management prior to review by the DOE. The predecisional report will be issued by January 15, 1993.

- **Problem Areas and Action Taken.** The December 31, 1992, milestone was missed due to other safety issues requiring immediate attention.

- **Milestone Status.**

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

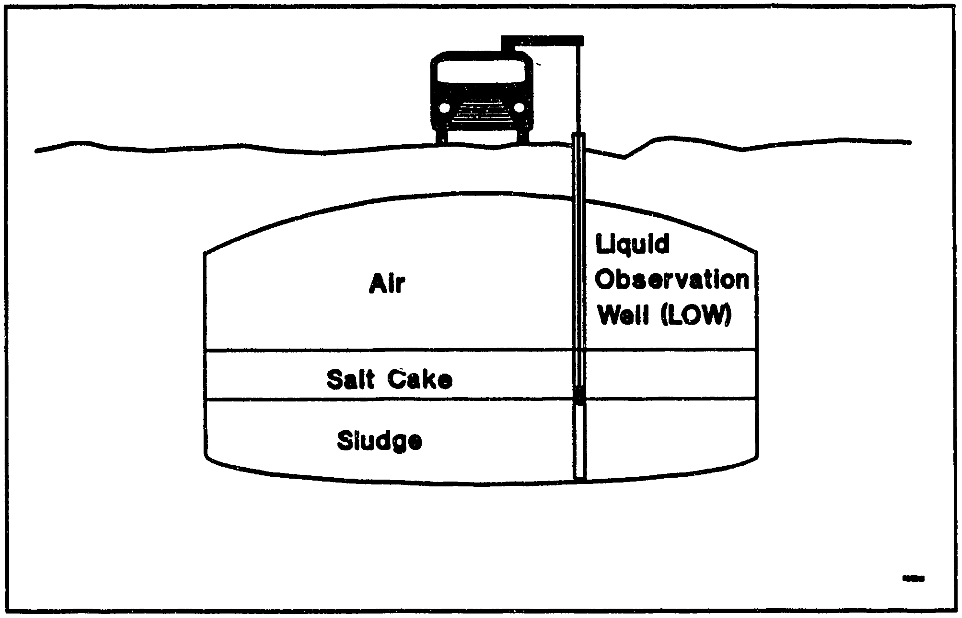
    - **May 29, 1992**: Complete a report on the infrared scan of a non-Watch List tank. The report was completed on schedule. Comments have been received from DOE and the report will be revised.

    - **December 31, 1992**: The December 31, 1992, milestone was missed due to other safety issues requiring immediate attention. The report will be issued to RL as a predecisional document on January 15, 1993.

    - **April 15, 1993**: Make decision on whether infrared scans will be performed in selected ferrocyanide tanks.

2.1.3.2 In Situ Tank Moisture Monitoring. Determination of moisture concentrations in the ferrocyanide waste tanks is being pursued using data analysis and available surveillance techniques. Application of an existing neutron probe, and improved well-logging techniques coupled with computer modeling are being developed and applied to determine new and useful information about moisture levels, material interfaces, and other waste characteristics using the existing neutron probe or, if warranted, a newly designed probe. The improved technique may be used to determine the axial moisture concentration profile within the ferrocyanide tanks.

Figure 2-1. Neutron Surveillance Scan Configuration.

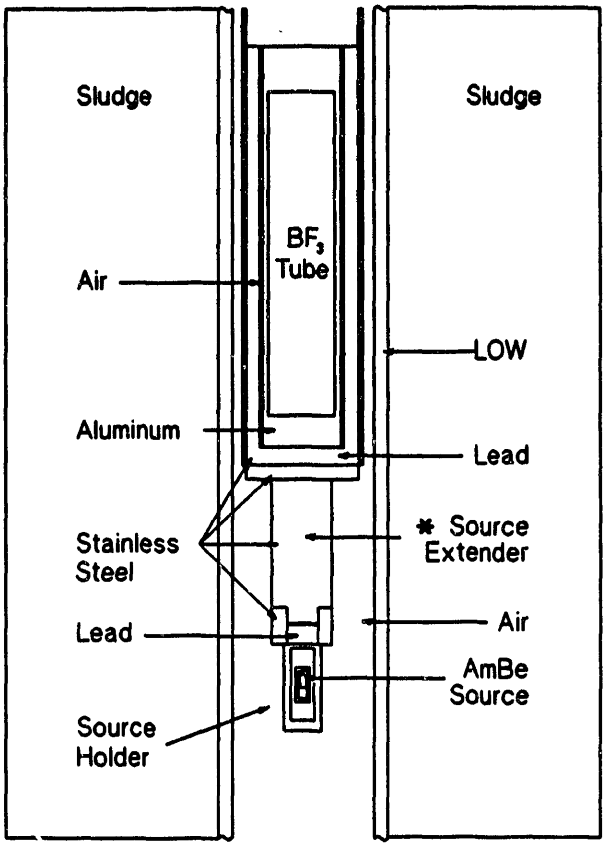


The existing neutron probe used routinely to determine liquid levels utilizes closed-bottom, liquid observation wells (LOWs) for access to the tank contents, see Figure 2-1.

This probe, as presently configured, is sensitive to thermalized neutrons, less sensitive to the epithermal neutrons, and insensitive to the fast neutrons produced by the americium-beryllium (AmBe) source and to gamma rays. Thermal neutrons originate as fast neutrons that are slowed primarily by the hydrogen in the volume surrounding the detector. Therefore, the observed countrate from the neutron detector is a strong function of the moisture present in the surrounding media.

The response of an active neutron probe to variations in the moisture content of the surrounding material depends primarily upon the distance between the detector and the neutron source. For short separation distances (near field), the observed countrate increases with increasing moisture content. For longer separation distances (far field), the observed countrate decreases for the same conditions. In the well-logging industry, the ratio of near field to far field countrate is used to determine moisture concentrations. The existing neutron probe was designed to permit adjustment of source-to-detector separation distance.
A computer model was used to investigate the change in detector countrate to moisture variations as a function of the moisture content of the waste for the present neutron probe, (see Figure 2-2).

Figure 2-2. Simplified Monte Carlo Neutron Photon Computer Model Geometry.

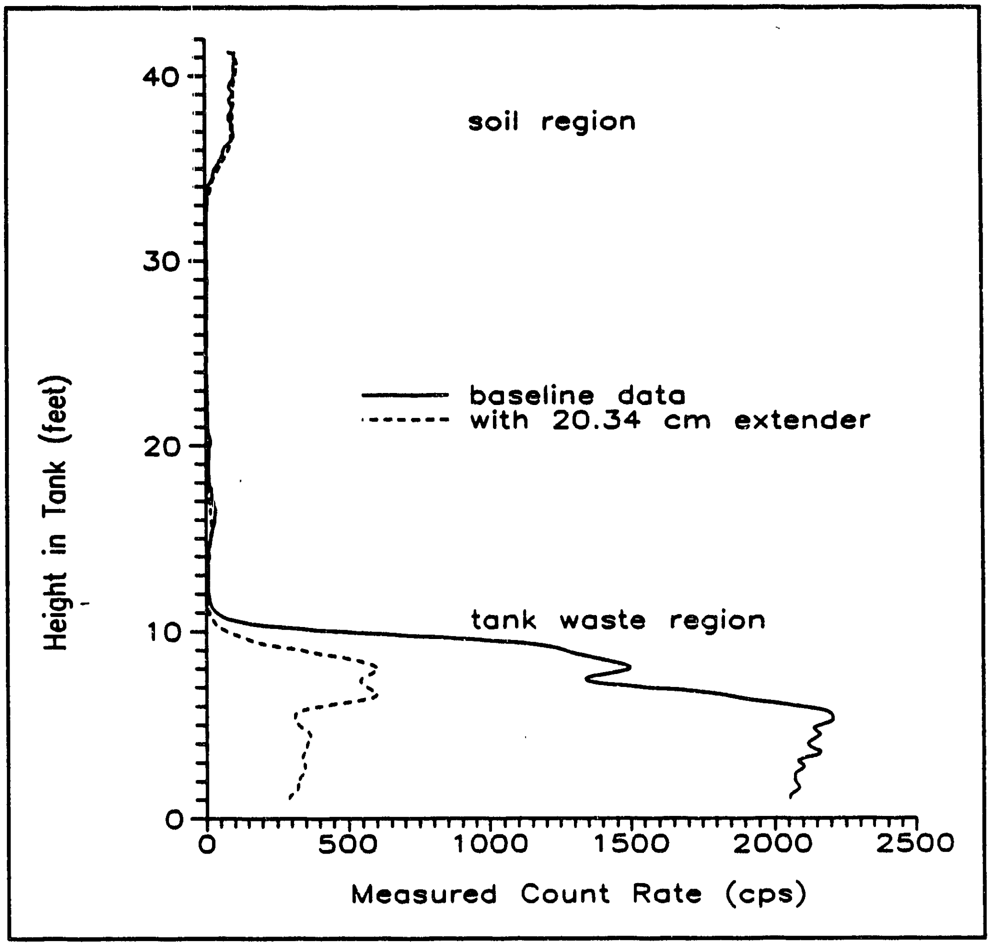


* Source extenders not included in present probe configuration

The calculations suggest that all of the acquired scans for liquid level measurement have always been performed with an intermediate distance which limited the moisture concentration measurement capabilities of past neutron scans.

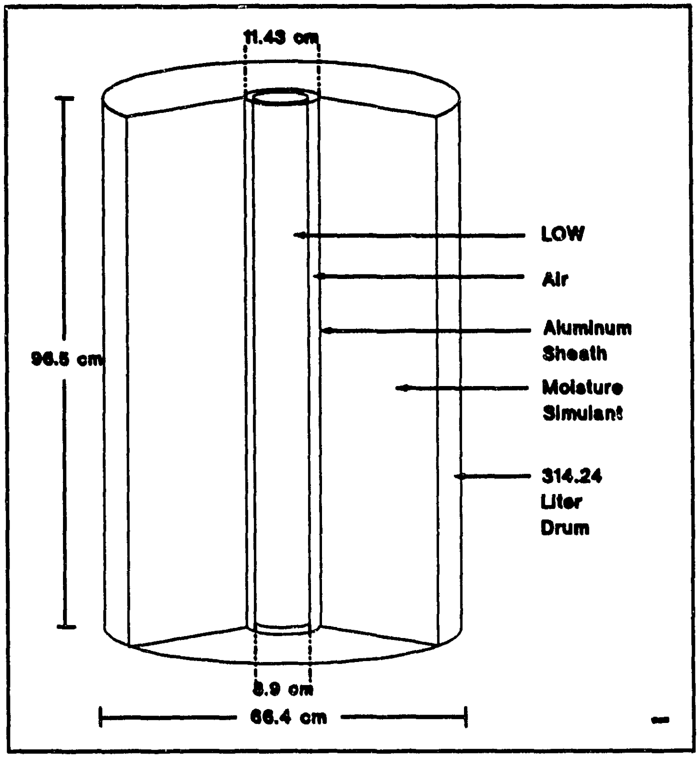
- **Progress During Reporting Period.** Eight successful neutron test scans were performed in ferrocyanide tanks BY-101, BY-104, BY-105, and BY-106 on November 30 and December 1, 1992. Two scans for each tank were performed with neutron probes fitted with a 20.34 cm extender. Previous data with no extender served as the baseline information. Figure 2-3 shows the test scan for tank 241-BY-104 compared to the baseline data. Previous test scans showed the reduced countrates due to the longer source-to-detector distance results in significant statistical error. This was overcome by decreasing the probe scanning rate which consequently increases the sampling time at each data point. Interpretation of this scan will be provided at a later date when more tank scans are available, as well as scans made of the simulated moisture standards.

Figure 2-3. Tank 241-BY-104 Neutron Probe Test Scans With 20.34 cm Source Extender and Without Source Extender.



To validate the accuracy of the computer model and verify its functionality as a calibration tool requires benchmarking measurements in a controlled environment. A controlled system must be fabricated and precisely represented by the computer model. With the completion of preliminary limited moisture calibration standards, efforts to validate and verify the model are underway. The standards are 314.24 liter (83 gallon) overpack drums filled with a moisture absorbing material with a controlled moisture concentration (within 1 wt% water accuracy) throughout the drum. To represent tank conditions, the probe will be deployed into the standards through an unused length of typical fiberglass LOW. Due to the shortage of available LOW material, the standards are equipped with a 1/8-inch-thick aluminum pipe and the LOW can be interchanged from drum to drum. Aluminum is relatively transparent to neutrons. Five standards were fabricated. Three standards contain controlled moisture concentrations of 6, 15, and 30 wt% water. Two standards contain pure water where one of the drums does not have an aluminum sheath. This will benchmark the effect of the aluminum sheath and small air region around the LOW (see Figure 2-4).

Figure 2-4. Geometry of Limited Moisture Standards Containing an Aluminum Sheath.



The computer model has been modified to represent the probe-barrel system. Countrate data from the limited moisture standards will benchmark the computer model.

Computer analyses were performed to evaluate the effect of the hydrogen bound in normal paraffin hydrocarbons (NPH) present in tank wastes on the probe response. It was concluded that 0.7 wt% NPH would appear to the probe as 1.0 wt% water and that the relationship is linear. Since NPH exists in tank wastes in small quantities, less than 1 wt%, the effect of NPH on the probe response is negligible.

On November 23 and 24, a meeting was held to review the LANL technology development workscope in support of the Hanford TWRS program. The use of a polyethylene shield wrapped around the detector tube region of the probe was suggested during discussions with LANL personnel. The desired effect is to increase the probe response by slowing down higher energy neutrons to energies which are more readily detected by the BF_3 tube. To explore this possibility, a polyethylene shield was added to the MCNP probe computer model. Preliminary calculations show a substantial increase in countrate and changes in the probe's response to moisture variations.

Another outcome of the meeting was an understanding that facilities at LANL would help to optimize a neutron detector for future probe designs. Additional discussions on neutron probes followed at Los Alamos.

The application of a data fitting technique to the neutron scans helps identify material regions and interfaces. This eliminates the necessity to investigate countless material interfaces with the neutron probe computer model. This technique has been applied to the neutron test scans obtained during the period ending September 30, 1992, from non-Watch List tank 241-B-104 and appears to reveal features that are visible in tank waste photographs.

- **Planned Work for Subsequent Months.** Data will be collected from the preliminary limited moisture standards using the neutron probe and the dry well van surveillance system. Countrates will be acquired with several source-to-detector separation distances and compared to a precise computer model of the probe-barrel system. This should provide a much needed validation of the computer model.

  The neutron test scans will be studied for trends which are reproducible with the computer model and theoretical moisture profiles will be determined.

  Funds have been appropriated to design, procure, and fabricate necessary components for a dual detector neutron probe. This work will commence in the subsequent months. The final dual detector probe, a probe which simultaneously measures the near field and far field, would be assembled in Fiscal Year 1994.

- **Problem Areas and Action Taken.** The preliminary limited moisture standards represent a well known geometry and controlled moisture concentrations. Benchmark data from these standards will validate the computer model's ability to accurately represent these conditions. However, the limited moisture standards do not model the neutron absorption properties of tank waste. To further validate the computer model's ability to represent tank materials, neutronically similar material will be tested in the barrels. Calculations show that the limited addition of boron, a strong neutron absorber, would be a suitable addition to the moisture standards to simulate tank material. Similar benchmarking work will be performed with existing ferrocyanide simulants when they become available.

  Knowledge of the density of materials surrounding the probe is important to the determination of moisture levels. In the recent discussions with LANL, the development of a gamma ray density measuring tool was discussed. It would be useful if LANL included in their workscope in support of the Hanford TWRS program the development of the gamma ray density measuring device.

- **Milestone Status.**
  - **July 31, 1992:** Completed fabrication of four neutron source extenders.
  - **August 29, 1992:** Completed preliminary neutron probe scans of non-Watch List tank 241-B-104 using the modified neutron probe.
  - **September 30, 1992:** A letter report documenting the current status of Monte Carlo calculations, tank 241-B-104 test scans, and the increased understanding of the neutron probe was completed. The report also included a description of recommended tasks to be performed, including field activities.
  - **December 1, 1992:** Completed neutron probe test scans of tanks 241-BY-101, -104, -105, and -106 using the modified neutron probe.
  - **March 29, 1993:** Deliver limited moisture simulant drums.
  - **June 25, 1993:** Complete limited calibration using special simulant-filled drums as standards.
  - **September 27, 1993:** Transmittal of comprehensive proof of principle final report.

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

Screening studies are being conducted to identify possible sources of interferences to and limitations of the Raman method. Possible interference could come from the presence of organic and inorganic decomposition products in the waste matrix. The fluorescence of the products caused by the excitation from the incident laser light could possibly overwhelm the Raman backscatter under certain conditions. The effect of pH >8, in addition to the effect of other ions and organics on ferrocyanide signal strength and frequency position is being studied. Tests to establish detection limits and levels of accuracy and precision for ferrocyanide in the presence of other components are underway.

- **Progress During Reporting Period.** Testing and operation of the Raman system at the Hanford Site continues to be on hold pending the repair of the laser diode. The laser is expected by the middle of January and spectra of real material are expected to be taken in the hot cell by the end of February. This data addresses assumptions that have been made to date based on simulants. The Florida State University (FSU) final report of their FY-92 contracted work was received and will be cleared for public release. The report contains archive spectra of pure materials (ferro/ferricyanides, nitrates/nitrites, sulphates) of concern to Waste Tank Safety. It also shows that Raman spectra are not strongly impacted by pH and fluorescence interference. The report documents positive feasibility for using Raman spectroscopy for characterization. Cyanide species and nitrate compounds all have unique, well defined Raman spectra.

  The Westinghouse Hanford Raman system is being set up and calibrated in preparation for system testing. These first tests will baseline the performance of the-Raman System, including the fiber optic probe, with pure, surrogate, and some real materials.

  The FY-94 Technology Development (TD) Technical Task Plan (TTP) guidance included the preparation of a requirements document for a Hanford hot cell deployable Raman system. This document has been prepared and delivered to LLNL to produce a rugged system per their TTP guidance. The LLNL Raman system is expected to be delivered to Hanford in the July time frame.

  A Raman technology workshop will be held at Hanford January 13-15, 1993. Raman and spectroscopy experts from LLNL, LANL, SRL, FSU, and Westinghouse Hanford will be in attendance. The objective of the workshop is to assemble the team members contributing to the Raman technology that will be used and to work through the technical issues related to Raman systems. Five topic areas have been identified specifically for discussion at the workshop: (1) chemical speciation; (2) qualification plan; (3) probe analysis; (4) irradiation data; (5) Raman system optimization.

  Initial data indicate that Raman technology will be useful for multiple applications, including homogeneity and speciation. Activities that remain to be completed include comparisons with other analytical methods, as well as the effects of high radiation fields on system components and abilities.

- **Planned Work For Subsequent Months.** Conclude the process of extending the contract with FSU. The proposed workscope includes speciation analysis on surrogates, investigation of salt cake water with Raman, and archival of Raman spectra on potential waste tank organic species. This work will establish the basis for applying Raman spectroscopy instrumentation in (1) Hanford Site hot cells as a waste tank sample screening tool; and (2) in situ waste tank materials characterization.

The Westinghouse Hanford Tank Characterization function is to coordinate these Raman spectroscopy development efforts with funding from the DOE Office of Technology Development.

Complementary work on Raman systems and spectroscopy is also being funded at SRL and LLNL by the DOE Office of Technology Development. These tasks will be integrated to provide the best synergetic effects for all involved.

- **Problem Areas and Actions Taken.** None.
- **Milestone Status.**
  - **May 1, 1992**: Receive initial experimental data from FSU on tests using In Farm and U Plant simulants provided by Westinghouse Hanford. Data from FSU on these simulants was received on schedule.
  - **September 30, 1992**: Receive interim report on initial data collection and validation methods for ferro/ferricyanides. This report was received October 27, 1992.
  - **December 31, 1992**: The final report on initial collection and validation methods for remainder of the simulant constituents (e.g., nitrates, phosphates, sulfates, etc.) has been received.
  - **January 31, 1993**: Complete the renewal of the FSU contract.
  - **December 31, 1993**: Complete the requirement document for a rugged deployable Raman system.
  - **August 31, 1993**: Obtain Raman system performance data with real (waste tank) materials.
  - **September 15, 1993**: Demonstrate hot cell Raman spectroscopy.

2.1.4 Hot Spot Thermal Modeling

The decay of radioactive materials in the waste tanks generates heat. A rapid chemical reaction within the ferrocyanide waste could occur if the ferrocyanide is sufficiently concentrated and a high enough temperature is present in the tank to cause an exothermic excursion and local propagation. Because most of the ferrocyanide tanks have only one

TC tree* and the trees are not always at the same location, there is concern that heat generation could exist in these tanks and not be detected. This task models and analyzes available temperature data from the ferrocyanide tanks in order to determine heat loads and temperatures as a function of vertical and horizontal distances within the waste from the tank centerline. Sensitivity and parametric analyses are included to determine the magnitude of allowable hot spots that might exist within the waste and still not cause a propagating reaction to occur.

State-of-the-art validated computer codes are used in the modeling. They are benchmarked with existing data and employ two- and three-dimensional capabilities. Both steady-state and transient models will be used.

- **Progress During the Reporting Period.** Additional analyses of hot spot growth in tank 241-BY-104 have been conducted. These analyses were done to support the hot spot position paper. The analyses show that concentrating all the heat-producing radionuclides into a layer will not produce temperatures above 220 °C unless the layer is less than 15 cm (3 inches) thick. A parametric study showed that, as the size of the hot spot becomes smaller, the radionuclide concentrations required to reach 220 °C become larger. A study approximating a hot spot formed from convection currents and growing in size required unreasonable concentrations of the heat source (about 12,000 times the bulk average heat source) in order to form. These studies all assume that dryout would occur as the temperature in the hot spot exceeds 100 °C. Recent information from Fauske and Associates, Inc. (FAI) indicates that local dryout would most probably not occur because of the very high capillary forces resulting from the fine particle size of the nickel ferrocyanide precipitates. As a result, temperatures in the hot spot would not rise above 130 °C until essentially the entire tank approached dryout. Consequently, it is doubtful that any deep hot spot would be discernable by an infrared scan. However, with such a temperature limitation, it now appears that there can be no hot spot of concern, as long as the ferrocyanide in the tanks is kept wet.

  Additional testing and analyses are being planned in order to verify that the high capillary forces calculated for the nickel ferrocyanide precipitates do exist.

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* Exceptions are tanks 241-BY-111 and -112, which have only a single dedicated TC element in the LOW, and tanks 241-BY-104, -105, -110, -C-109, and -C-112, which have two TC trees. See Table A-1.

- **Planned Work for Subsequent Months.** The following items will be completed during FY 1993.
    - Conduct an analysis to determine the concentrations required to form a hypothetical hot spot if convection currents are credible. This effort will include microconvection modeling to ascertain whether this mechanism could create hot spots that might reach 220 °C. Results of this analysis will feed into the hot spot position paper and the decision on whether infrared scans of selected higher interest ferrocyanide tanks should be conducted. See Section 2.1.3.1.
    - Conduct an analysis of selected tanks to determine their heat loads and the thermal conductivities of the waste within the tanks using the latest temperature data and soil conductivity values; issue a report of the analysis.
    - Complete hot spot thermal modeling analysis of a worst case ferrocyanide tank, taking into account the transpiration of moisture away from the hot spot, using the latest temperature data and soil conductivity values.
- **Problem Areas and Action Taken.** None.
- **Milestone Status.**
    - **July 31, 1992**: Determined the heat loads and calculated thermal conductivities of the contents for tanks 241-BY-105, -106, -108, -110, -111, and -C-109. The upper and lower bounds of these parameters were calculated. The report on this work was delayed to September 30, 1992, to include additional work with thermal conductivities more representative of actual waste. A predecisional report on this work was completed.
    - **September 30, 1992**: Performed a detailed thermal analysis of tank 241-BY-106 to determine the response of the tank contents to a hot spot of varying intensities. This analysis included both steady-state and transient analyses. A predecisional report was issued September 30, 1992.
    - **April 15, 1993**: Perform detailed thermal modeling studies to (1) determine if there is enough likelihood for forming hot spots to warrant infrared scans of selected ferrocyanide tanks; and (2) issue a position paper on whether hot spots of concern are credible.
    - **June 25, 1993**: Complete thermal hydraulic analyses of four ferrocyanide tanks to determine heat loads and conductivities of the waste contents and issue a report that is approved for public release.

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

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

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

2.2.1 Continuous Temperature Monitoring

This task will provide continuous monitoring of presently installed (and operable) TCs for the 24 ferrocyanide-tanks. New TC trees, as they are added to each tank, will be connected to the system, resulting in continuous monitoring. All data are collected automatically at the continuously manned Computer Automated Surveillance System (CASS) Operator Control Station in the 2750E Building, 200 East Area. The monitoring system is independent of the CASS and capable of displaying data to an operator on request. Trend data on selected points is available for display in numeric or graphic form.

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

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

Five BY Farm tanks were connected to the system in September 1991, and an additional five in December 1991. These include tanks 241-BY-101, -103, -104, -105, -106, -107, -108, -110, -111, and -112. Tank 241-BY-105 has two operating TC trees; both have been connected to the continuous temperature monitoring system (CTMS). In April 1992, tanks 241-TY-101, -103, -104, and 241-TX-118 were connected to the system and are now operational. This makes a total of 14 ferrocyanide tanks now being monitored by the CTMS. Temperature readings from the working TCs in these tanks are being recorded continuously.

- **Progress During Reporting Period.** The design for connection of two tanks in T Farm and four tanks in C Farm was completed. Two new temperature trees recently installed (BY-104 and BY-110) were connected to the CTMS in November 1992.

- **Planned Work For Subsequent Months.** The design for connection of four tanks in BX Farm will be initiated. Construction will begin in C and T Farms to complete the CTMS for those tank farms.

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

- **Milestone Status.**

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

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

    - **April 29, 1992**: Completed installation of continuous monitoring for three tanks in TY Farm and one tank in TX Farm.

    - **September 30, 1992**: Completed design of continuous monitoring systems for C and T farms.

    - **July 30, 1993**: Complete installation of continuous monitoring for the four ferrocyanide tanks in C Farm.

    - **August 30, 1993**: Complete installation of continuous monitoring for the two ferrocyanide tanks in T Farm.

    - **September 30, 1993**: Complete design and installation of continuous monitoring for the four ferrocyanide tanks in BX Farm.

    - **September 30, 1993**: Complete installation of continuous monitoring for new TC trees installed during FY 1993.

    - **September 30, 1994**: Incorporate continuous monitoring on new TC trees installed during FY 1994.

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

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

2.3.1 On-Line Gas Monitoring

Options for installing a gas monitoring capability on new TC trees will be reviewed. The use of a separate riser, possibly in conjunction with other equipment, to achieve an installed capability may be necessary. However, a definite decision to monitor continuously or have the installed capability for grab samples has not been made. The frequency of gas monitoring and/or the need for continuous monitoring will be determined after a significant number of the ferrocyanide tanks have been vapor sampled, or if a concern is detected during the sampling program. Evaluation of gas samples secured to date for tanks 241-BY-104 and -110, 241-C-112 and -109, and 241-T-107 has not indicated the need to continuously monitor for specific gases.

2.3.2 Interim Flammable Gas Monitoring

The effort to conduct flammable and toxic gas monitoring and analyses in the 24 ferrocyanide tanks is continuing. This effort has been transferred to the waste tank Toxic Vapor Program, which will coordinate interim gas monitoring of the ferrocyanide tanks. There is presently no plan to develop the cryogenic technique for vapor sample analysis. Therefore, Westinghouse Hanford ceased taking cryogenic samples from the ferrocyanide tanks. Tank vapor spaces are only measured for flammability, and are monitored using the organic vapor monitor (OVM) and Dräger tubes for detection and measurement of toxic gases as required by the safety assessments for a particular activity. Development and validation of alternative technologies for vapor space characterization is in progress using Summa canisters and specific absorption tubes.

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

All 24 ferrocyanide tanks are passively ventilated through individual high-efficiency particulate air (HEPA) filters. The "breathing" is dependent upon changes in barometric pressure and differences in temperature between the waste tank and the outside air. The pressure change causes a small volume of stagnant air to be replaced with fresh air, which helps control the concentration of chemical vapors inside the tanks.

Initial vapor space gas samples were taken through two different risers and at three elevations for the first two ferrocyanide tanks (241-BY-104 and 241-C-112). The lowest elevation sample was about 25 cm (1 ft) above the waste surface, with one sample in the middle and one near the top of the dome space. Gas sampling criteria were defined and included identification of the chemicals to be monitored, detection limits, accuracy and precision of the analytical methods, and sample positions inside the tank. Vapor space gas samples were taken from one riser at three elevations in tanks 241-C-109 and 241-BY-110. Mobile Analytical Laboratory Testing (MALT) samples were also taken from tank 241-C-109 and archived for future analysis (if warranted).

- **Progress During Reporting Period**: Sampling of vapor space gases in ferrocyanide tank 241-T-107 was completed on October 22, 1992. The tank was sampled through one riser at three elevations. Analytical methods used included the combustible gas monitor for flammable gases, an organic vapor monitor (OVM) for organics, and Dräger tubes for hydrazine, ammonia, cyanides, hydrogen cyanide, and nitrous fumes, Field readings for the tank showed no concentrations of flammable gases above the detection limit of the combustible gas monitor. The only compound detected by the Dräger tubes was ammonia at approximately 200 ppm at each elevation. The OVM field readings were 34 ppm at the highest sample elevation, and 39 and 42 ppm in the middle of the vapor space and nearest the waste surface (respectively).

  Tank 241-BY-104 was successfully vapor sampled on December 28-29, 1992. Analytical results from offsite laboratories are expected in January 1993. This sampling effort represents the first vapor sampling specifically targeted at decreasing or eliminating the respiratory protection zones around tanks with a history of vapor exposure. No flammable gases above the detection limit of the portable combustible gas monitor were observed in the field.

  The Vapor Space Sampling Criteria for Single-Shell Tanks Containing Ferrocyanide Wastes, (WHC-EP-0424), was revised via a record of revision (ROR). The ROR changes the criteria to allow vapor sampling from only one riser to test for vapor flammability prior to intrusive tank activities such as thermocouple tree information and core sampling.

- **Planned Work for Subsequent Months**. Flammable gas sampling will be done, as required, to support planned core sampling and thermocouple installation. Once the Vapor Program validates a method for characterization of tank vapors, more extensive sampling will resume.

- **Problem Areas and Action Taken.** Since the validity of the toxic gas results obtained from the cryogenic gas sampler has been questioned, standardized but less sensitive methods will have to be used, such as Dräger tubes. However, they are adequate for worker safety. Gas sampling for potential gases of interest to the ferrocyanide program will be performed after improvement and validation of the sampling method is completed.

- **Milestone Status.**

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

  - **September 30, 1993:** Complete flammable gas sampling of eight additional ferrocyanide tanks to support push mode core sampling and TC tree installation.

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

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

2.3.3 Vapor Space Gas Modeling

The possibility that localized concentrations or stratification of gases exist in the waste tanks continues to be evaluated. Radiolysis of water generates hydrogen, and the possible interaction of various chemicals in the tanks may release hydrogen and other gases. Some of these gases may have the potential to be explosive or otherwise hazardous, if their concentrations become large enough and are mixed properly with air. This concern is being addressed through the sampling effort described above. A modeling effort that was partially completed in FY 92 had determined airflow patterns in the tank vapor space of 241-C-109 to evaluate the amount of mixing and local gas concentrations that could occur. The results of this analysis will be used to evaluate the hazards and risks involved in sampling and other intrusive activities within the tanks. This work will aid in developing a methodology for performing future vapor space analysis for all ferrocyanide tanks.

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

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

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

- **Progress During the Reporting Period.** The 241-C-109 vapor space analysis was completed during this period and a report was prepared and approved for limited release. The results of the analysis show that there are no significant concentrations of hydrogen gas within the tank. The airflow velocities within the tank are low, but are sufficient to keep the vapor space well mixed. There is a transfer of gas to the atmosphere through the breather filter due to barometric pressure changes in the atmosphere over time. This breathing is sufficient to prevent any gas build-up within the tank.

- **Planned Work for Subsequent Months.** The report of the analysis will be cleared for public release and distributed. No further gas modeling studies are planned since this work has shown that the tank gases are well mixed even for tanks with waste temperatures near ambient.

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

- **Milestone Status.**

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

    - **April 30 1993.** Complete an analysis, if warranted, of a second tank with greater differential temperatures within the tank. Issue a report approved for public release. This activity is not required because the gases in the tanks are well mixed.

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

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

2.4.1 Ferrocyanide Tank Waste Sampling and Characterization

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

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 (phosphates, aluminates, sulfates, carbonates, oxides, hydroxides, et al.). The location of fission products such as ^{137}Cs and ^{90}Sr is important because these products are heat sources that can raise and maintain the temperature of the tank contents, and because they are potential source terms in postulated radiological releases from an exothermic ferrocyanide reaction. The water content of the waste is very important because the high heat capacity and the heat of vaporization of water make it an effective inerting material; this water content can prevent a sustained combustion or an explosion. Also, wet ferrocyanide material should not react nor propagate; it would have to be dried out first. Other materials (e.g., nickel, copper, lead, and the rare earths) may be important as potential catalysts.

The push-mode core sampling technique is presently the only viable Hanford Site method for waste tank core sampling, until it is demonstrated that rotary-drill core sampling will not produce excessive temperatures in the waste. Seven ferrocyanide tanks suitable for push-mode core sampling were placed on the list of SSTs to be core sampled in FY 1992 and FY 1993. Tank 241-C-112 was core sampled through three risers (two segments per core) in March 1992, and tank 241-C-109 was core sampled through three risers (one segment per core) in September 1992. Core sampling of tank 241-T-107 started in November; two risers will be used and four segments per core will be obtained.

Development and design work required to demonstrate that rotary-drill core sampling of a "harder" waste can be done without producing unacceptably high bit temperatures has now been completed and the system is going through acceptance testing. It is now anticipated that the system will be approved for field use by September 30, 1993.

- **Progress During the Reporting Period.** The analytical data packages for the three 241-C-112 core samples have been received from PNL, although they have not yet been released by the Westinghouse Hanford Office of Sample Management (OSM). The packages are being reviewed and a data interpretation report is being prepared. This report will be completed next quarter, and the report results and conclusions will be summarized in the next quarterly report.

  The three 241-C-109 core segments have been extruded and prepared for analysis at the PNL laboratories. Poor sample recovery (approximately 35 %) was obtained in one of the one-segment cores. The first preliminary analytical results are expected by the end of January 1993.

  The next ferrocyanide tank being push-mode core sampled is 241-T-107. The first of two four-segment cores scheduled was secured on November 10, 1992, from riser 2. Core sampling operations were shut down by Westinghouse Hanford as a result of a DOE-RL audit of the vapor space sampling and core sampling operations. Securing the second core from 241-T-107 has been delayed until next quarter in order to respond to the audit findings. A response letter was forwarded to DOE on December 18, 1992, but additional actions must be completed before core sampling and vapor space sampling of tanks can continue.

  The hard saltcake sampling system, the new hydrostatic balance system, and the purge gas system for universal sampling system are now complete. Installation of the equipment on the rotary-mode core sample truck was completed on December 2, 1992; the nitrogen purge gas trailer was completed November 20, 1992. These systems are now undergoing acceptance testing. The only sampling equipment component remaining is the portable exhauster. The conceptual design for the exhauster is complete and has been reviewed; the final design is scheduled for completion next quarter. The Washington state air quality agencies reviewed and gave preliminary approval for the exhauster design and construction approach.

  The analysis report for the two surface samples taken from ferrocyanide tank 241-BY-104 in June 1992 using the auger sampling technique was completed and cleared for public release (Beck 1992). These samples were analyzed at the Westinghouse Hanford 222-S Analytical Laboratory. The report states that the reactivity of the tank surface waste (saltcake) is generally mild. The maximum exotherm seen was 171 Joules/gram (41 calories/gram) of as-received wet material. The material has the ability to self-heat at approximately 180 °C, but showed no tendency to propagate. This is consistent with the sample analysis of one weight percent total organic carbon. The samples contained 15 - 17 weight percent water, which further decreases the reactivity of the waste.

The level of total cyanide, and thus possible ferrocyanide, is low (approximately 40 parts per million). Ferrocyanide is not expected in this saltcake waste since this type of waste was added to 241-BY-104 after the ferrocyanide scavenging runs of the 1950s. The surface samples showed considerable inhomogeneity, particularly in the horizontal direction, but the concentrations for most constituents are within the expected range for saltcake in this tank. Additional detail will be provided in a data interpretation report for these samples (scheduled for completion in April 1993).

- **Planned Work For Subsequent Months.** The data interpretation report for the 241-C-112 core samples will be completed and issued. Analysis of the 241-C-109 core samples at the PNL 325 Analytical Laboratory will continue, and a data interpretation report for the 241-BY-104 auger surface samples will be prepared. The first core from 241-T-107 (five segments were extruded in December) will be analyzed, and the second core will be taken when corrective actions responsive to the DOE audit findings are completed and the weather permits.

  Testing of the universal core sampling system is complete. Core sampling of ferrocyanide tanks with saltcake will likely be deferred until the rotary-mode core sample truck is available for field use. However, possible push-mode core sampling of tank 241-BY-104 is currently being evaluated. This effort was started because installation of the new thermocouple tree into this tank showed the waste to be softer than expected.

- **Problem Areas and Actions Taken.** Core sample recovery continues to be a problem for push-mode core sampling of tanks. Although the sampler valve has been changed to incorporate a spring-loaded mechanism to close the sampler tightly when the sampling operation for that segment is complete, one of the three 241-C-109 core sample segments had poor recovery. Two of the five segments from 241-T-107 also had poor recovery. It may be necessary to take another core from tank 241-C-109 in the future.

  A validated laboratory procedure for total cyanide is not yet available. This, along with the fact that an analytical procedure for ferrocyanide speciation is not yet available, will greatly impact the analytical data interpretation reports. Laboratory development work is underway to address both of these procedures.

  It is expected that the majority of the ferrocyanide tanks, particularly those with a saltcake surface, will require rotary drilling to obtain core samples.

- **Milestone Status.**

  - **August 30, 1992**: Obtain three full-length push-mode core samples from 241-C-109. This sampling was completed on September 7, 1992.
  - **September 30, 1992**: Obtain two full-length push-mode core samples from 241-T-107. This milestone is now scheduled for completion in January 1993. One of the two core samples was secured on November 10, 1992.
  - **March 31, 1993**: Complete interpretation of ferrocyanide tank 241-C-112 analytical data and issue a report that is cleared for public release.
  - **April 30, 1993**: Complete interpretation of ferrocyanide tank 241-BY-104 auger surface sample analytical data and issue a report that is cleared for public release.
  - **July 31, 1993**: Complete interpretation of ferrocyanide tank 241-C-109 analytical data and issue a report that is cleared for public release.
  - **September 30, 1993**: Complete interpretation of ferrocyanide tank 241-T-107 analytical data and issue a report that is cleared for public release.
  - **September 30, 1993**: Obtain two full-length push-mode core samples from four additional ferrocyanide tanks in FY 1993. The following order for sampling in the tanks is planned: 241-C-111, -C-108, -T-101, and -BX-102 or -BX-106.
  - **September 30, 1994**: Secure core samples from four ferrocyanide tanks (tanks 241-BY-104, -110, -107, and -105).
  - **September 30, 1995**: Obtain Core samples from four ferrocyanide tanks (tanks 241-BY-103, -112, -TY-103, and -BY-106).
  - **September 30, 1996**: Obtain core samples from four ferrocyanide tanks (tanks 241-BY-101, -TY-101, -104, and -BY-110).
  - **September 30, 1997**: Obtain core samples from the remaining five ferrocyanide tanks (tanks 241-BX-106, -111, -BY-111, -TX-118, and -BY-108).

2.4.2 Simulated Ferrocyanide Waste Preparation and Characterization

Ferrocyanide waste precipitates have been and are being prepared and analyzed to determine their composition and chemical and physical properties. These simulants are representative of ferrocyanide waste placed in the SSTs, based upon flowsheets used during the scavenging campaigns. Analytical results obtained from these simulants, combined with analysis of actual tank waste samples and data from tank monitoring and modeling, provide information to address the safety concerns in each of the ferrocyanide tanks. The results also provide a technical basis for (1) safety measures to be taken; (2) decisions leading to resolution of the ferrocyanide USQ; and (3) eventual remediation of the waste.

Five waste simulants (without radioactive species) are being used to represent the variety of waste that was produced in the mid-1950s and which is currently stored in SSTs. The wastes produced at the Hanford U Plant are represented by U Plant 1 and U Plant 2 test mixtures. The U Plant 1 waste simulant represents 41 of 59 batches; the U Plant 2 simulant represents 9 of 59 batches of U Plant waste. Most U Plant batches were about 2,300,000 L (600,000 gal). The other nine batches of U Plant waste are expected to have a ferrocyanide concentration between that of U Plant 1 and U Plant 2, and a test mixture representing these batches will not be prepared and tested.

The In Farm flowsheet waste (in four C Farm tanks) is represented by In Farm 1 and In Farm 2 simulants. In Farm 1 is representative of one batch (expected to have the greatest ferrocyanide concentration) of the 29 In Farm batches processed in the 1950s. In Farm 2 is representative of 11 intermediate ferrocyanide concentration batches of the 29 In Farm batches. An average-size In Farm batch was approximately 1,500,000 L (400,000 gal). It should also be noted that six of these 29 scavenging batches did not contain any ferrocyanide; however, they did contain nickel sulfide to enhance precipitation of ^{60}Co as cobalt sulfide. Calcium nitrate was occasionally added to enhance ^{90}Sr decontamination. A T Plant mixture representing the six T Plant batches produced will also be prepared for testing.

Three main adjustments from the actual processes used in the 1950s are made in the laboratory scavenging preparation method to provide waste simulants thought to closely represent present sludges. These changes are (1) the solution concentrations are adjusted to include nitrite at a 1:3 mole ratio of nitrite/nitrate to account for nitrite buildup over time in the wastes by radiolysis of nitrate; (2) the waste simulants do not contain radioactive isotopes present in actual waste because of the difficulty of working with radioactive materials; and (3) the settled waste simulants from the laboratory scavenging process are centrifuged at approximately 2,500 g to mimic an equivalent 30 gravity year settling period.

- **Progress During the Reporting Period.** Three of the five simulated wastes (In Farm 1 and 2, and U Plant 2) were further characterized this quarter. Ion chromatography (IC) analysis on the 5% EDTA and 5% ethylene diamine solution soluble dry simulants was completed on the top and bottom fractions of each. The anion analysis of the supernatant from the three simulants were completed. Particle size measurements were also completed for these three simulants. The T Plant waste will be produced for characterization and testing next quarter.

Table 2-1 shows the ion chromatography results of analysis of the dry top and bottom fraction of In Farm 1 and 2 and U Plant 2 simulants. The results for the IC analysis of the soluble anions in 5% EDTA and 5% ethylene diamine solution are shown in Table 2-2 for comparison to the results of the IC analysis of the water soluble anions. The nitrate results are in good agreement by the two methods. The water soluble results for the nitrite are expected to be more reliable than the EDTA/ethylene diamine soluble results, because the latter was analyzed at a later date and some oxidation of nitrite may have occurred during the holding period. The sulfate and phosphate results of the EDTA/ethylene diamine soluble anions are considered correct since not all sulfates or phosphates are soluble in water. There were no uncharacterized peaks observed in the chromatograms. The results are reported on a mass fraction basis in grams of anion per gram of dry solid.

Table 2-1. Anion Analysis by Ion Chromatography of Soluble Dry Simulant.

	mass fraction by water solubility			
Sample	Nitrate	Nitrite	Sulfate	Phosphate
In Farm 1 top	0.291	0.0821	0.0248	0.0192
In Farm 1 bottom	0.290	0.0758	0.0255	0.0241
In Farm 2 top	0.271	0.0726	0.0222	0.0197
In Farm 2 bottom	0.247	0.0628	0.0200	0.0233
U Plant 2 top	0.350	0.0802	0.0470	0.0287
U Plant 2 bottom	0.319	0.0729	0.0430	0.0321

Table 2-2. Mass Fraction by 5% EDTA and 5% Ethylene Diamine Solution Solubility.

Sample	Nitrate	Nitrite	Sulfate	Phosphate
In Farm 1 top	0.34	0.016	0.033	0.024
In Farm 1 bottom	0.29	0.0038	0.033	0.024
In Farm 2 top	0.25	0.0041	0.024	0.058
In Farm 2 bottom	0.27	0.0045	0.023	0.076
U Plant 2 top	0.39	0.073	0.048	0.080
U Plant 2 bottom	0.34	0.067	0.044	0.089

The supernatant solutions associated with each simulant were analyzed for anion content by ion chromatography analysis. Results are listed in Table 2-3 below. Previously reported results of U Plant 1 supernatant are included for comparison. These results indicate that the pH results for the In Farm 1, In Farm 2, U Plant 2, and U Plant 1 supernatants were measured to be 8.71, 9.42, 9.12, and 9.60, respectively. The specific gravity of each of the supernatants were measured to be 1.32, 1.27, 1.21, and 1.21, respectively.

Table 2-3. Ion Chromatography Analysis Results of Simulant Supernatants.

	Molarity			
Sample	In Farm-1	In Farm-2	U Plant-2	U Plant-1
Nitrate	4.46	3.82	2.5	3.34
Nitrite	1.46	1.29	0.85	0.00
Sulfate	0.24	0.17	0.21	0.23
Phosphate	0.12	0.14	0.12	0.14
Ammonium	NA	NA	0.014	0.04
Cyanide (CN^-)				0.00032

The particle size measurements for the top and bottom fractions of each of the simulants are listed in Table 2-4 below.

Table 2-4. Particle Size Measurements of Simulants.

	Median diameter (μm)		
Simulant	Number	Area	Cell
In Farm-1 Top Fraction Acquisition Range 0.5-60 μm 0.5-150 μm	 0.68 0.76	 0.80 0.81	 10.9 21.3
In Farm-1 Bottom Fraction Acquisition Range 0.5-60 μm 0.5-150 μm	 0.69 0.77	 0.90 0.91	 5.1 7.8
In Farm-2 Top Fraction Acquisition Range 0.5-60 μm 0.5-150 μm	 0.69 0.76	 0.82 0.84	 19.5 14.3
In Farm-2 Bottom Fraction Acquisition Range 0.5-60 μm 0.5-150 μm	 0.70 0.76	 0.85 0.83	 16.1 16.8
U Plant-2 Top Fraction Acquisition Range 0.5-60 μm 0.5-150 μm	 0.66 0.82	 0.80 1.58	 1.4 4.4
U Plant-2 Bottom Fraction Acquisition Range 0.5-60 μm 0.5-150 μm	 0.73 0.77	 1.56 0.95	 4.1 3.9

- **Planned Work for Subsequent Months.** The following activities are planned:
    - Quantitative anion and ferrocyanide speciation measurements of the ferrocyanide simulants will be made by FTIR photoacoustic methods.
    - Complete final report on the preparation and characterization of the ferrocyanide simulants.

  - Prepare the T Plant flowsheet waste simulant next quarter for characterization and testing.

- **Problem Areas and Actions Taken.** Characterization of the simulants were not completed as originally scheduled because laboratory analyses took longer than anticipated. Higher priority core samples have preempted many routine chemical analyses. This delayed final preparation of the ferrocyanide simulant characterization report until this quarter.

- **Milestone Status.**

  - **July 17, 1992**: Characterize In Farm 1, In Farm 2, and U Plant 2 waste simulants. This milestone was delayed to December 31, 1992, because laboratory analyses were not completed as originally scheduled.

  - **September 30, 1992**: Issue a report, approved for public release, on the flowsheet waste simulant compositions and ferrocyanide species characterization. This milestone is delayed to January 29, 1993, because laboratory analyses were not completed as stated above. The draft report was issued for review on December 31, 1992, as rescheduled.

  - **December 31, 1992**: Define parametric and aerosol sampling tests to be conducted at FAI using In Farm and U Plant flowsheet ferrocyanide waste simulants. Parametric tests and the scope of aerosol tests to be conducted at FAI were defined with Dr. H. K. Fauske of FAI on December 10, 1992. The letter to FAI authorizing these tests was issued January 12, 1993.

  - **January 15, 1993**: Complete production of T Plant ferrocyanide waste simulant and ship samples to PNL, FAI, and Westinghouse Hanford for characterization. This task has been delayed to February 15, 1993.

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

  - **September 30, 1993**: Complete characterization tests of T Plant ferrocyanide waste simulants at PNL, FAI, and Westinghouse Hanford. Incorporate results in the second update of the hazards assessment document (scheduled for July 1994).

2.4.3 Position Paper on Safety of Ferrocyanide Tanks

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

The ferrocyanide position paper, and subsequent revisions, represents a snapshot in time of (1) what is known about ferrocyanide wastes stored in underground tanks at the Hanford Site; (2) what this information means in terms of storage safety; (3) what key uncertainties exist; and (4) what must be done to resolve the USQ.

A predecisional position paper (report) was issued November 27, 1991, for DOE and TAP review. Comments were received by May 1992 and the document was revised and cleared for public release as WHC-EP-0531, Rev. 1 (Postma et al. 1992) on July 24, 1992. Updates of the position paper will be issued as significant new information becomes available, and as results of core sample analyses are reported.

- **Progress During the Reporting Period.** The position paper is an overview document with technical backup provided by the ferrocyanide hazards assessment document discussed in Section 2.4.4 (Grigsby et al. 1992). Although the contents of each tank are different, studies completed to date indicate that an uncontrolled, exothermic reaction in any ferrocyanide tank is a highly unlikely event, given the current conditions of temperature and moisture in the tanks. Key actions required to maintain the tanks in a safe condition are surveillance and control of the waste temperature and moisture levels. Characterization of the waste by obtaining and analyzing core samples is a necessary action required to validate the current conclusions.

- **Planned Work for Subsequent Months.** Because moisture and temperature surveillance and control will be key to keeping the ferrocyanide waste in a safe condition, activities are underway for determining the hydrophilic properties of the waste and providing improved temperature monitoring of the highest-concern ferrocyanide tanks. Tank waste sampling and analysis, providing one or more methods for measuring the moisture content, and improving the temperature monitoring capabilities within the ferrocyanide tanks are top priority items for the near term (see Sections 2.1.3.2, 2.4.1, and 2.4.2). An update of the parent ferrocyanide hazards assessment document is described in Section 2.4.4.

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

- **Milestone Status.**

  - **November 27, 1991**: Issue position paper on current understanding of ferrocyanide safety issue. Completed on schedule.

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

  - **December 31, 1993**: Issue a ferrocyanide position document, approved for public release, that updates the current understanding of the ferrocyanide safety issue. This will be a revision of WHC-EP-0531 (Postma et al. 1992).

2.4.4 Ferrocyanide Waste Tanks Hazards Assessment

The scope of the ferrocyanide hazards assessment task is to provide a technical assessment (and periodic updates) of the ferrocyanide waste tank safety concerns and progress towards resolution of the USQ. These assessments are based upon information as it becomes available from the Ferrocyanide Safety Program. Contributions are included from FAI, LANL, PNL, Westinghouse Hanford, and other sources.

A predecisional interim report assessing the ferrocyanide waste tank hazards was issued on December 3, 1991, for review and comment by TAP, DOE-HQ, and RL. Comments were incorporated into a new revision, approved for public release, and the document was issued on July 24, 1992 as WHC-SD-WM-RPT-032, Rev. 1 (Grigsby et al. 1992).

The assessment is a snapshot of the understanding of the ferrocyanide hazard, at the time the report was prepared. It presents an integrated evaluation and interpretation of (1) historical data; and (2) recently- acquired information. These interim reports will continue to be revised and expanded as additional information becomes available through ongoing work.

Several review comments received on the predecisional document could not be resolved in the July 1992 release, because sufficient information was not available at the time the report was written. These comments will be incorporated into the next revision of the document, which is scheduled for completion in May 1993.

- **Progress During the Reporting Period.** No work was specifically planned this quarter on preparation of the updated ferrocyanide hazards assessment document.

- **Planned Work For Subsequent Months.** Technical information from all the ferrocyanide safety program tasks will be gathered into the next revision of the hazards assessment document. This effort will start next quarter. The planned approach and key safety criteria that must be met for resolving the ferrocyanide USQ (Section 4.2.6) will be addressed in detail. The technical basis for each safety criterion and how each can be met will be presented in the document. The objective of the technical data presented will be to prove that in situ storage of the waste is safe. This document will provide the technical basis for resolution of the USQ.

  Analytical results obtained from core sampling of tanks 241-C-112 and -C-109 will be used to reassess the ferrocyanide safety issue. Results from other ferrocyanide core samples (tank 241-T-107 and others yet to be obtained) will not be ready in time for the May 1993 issue date.

- **Problem Areas and Action Taken.** When the Aerosol Experts Panel met in March 1992, they reviewed available data on the ferrocyanide safety issue and recommended that small-scale aerosol tests be conducted. These tests were originally planned for the second half of FY 1992, but were deferred to FY 1993. Present planning for FY 1993 does not provide for these tests (as originally scoped) because of resource constraints. Westinghouse Hanford is currently evaluating the possibility of a reduced aerosol testing program.

  To aid in this decision the ferrocyanide waste simulants tested at Fauske and Associates, Inc. (FAI) are being analyzed to determine how much cesium was lost during the propagation tests. The In Farm 1 simulant had cesium added to the flowsheet for this purpose. Additional aerosol sampling tests are also being conducted at FAI (Section 2.5.2). If considerable cesium was lost during the dry simulant burn tests, and this result is confirmed in the new tests planned at FAI, then a small-scale aerosol test(s) may be conducted to determine a more accurate source term and particle size distribution than possible with the FAI tests. If less than 10% of the cesium was lost, then testing may not be warranted.

- **Milestone Status.**

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

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

- **July 31, 1993**: Complete parametric and aerosol tests on the most reactive (In Farm) flowsheet simulant at FAI and issue a test report that is approved for public release. This will allow time to complete dose consequence recalculations.

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

- **July 1994**: Issue second update of the ferrocyanide hazards assessment document.

2.4.5 Concepts for Resolution of the Ferrocyanide Safety Issue

A predecisional report on three approaches evaluated for resolution of the ferrocyanide safety issue was issued by Westinghouse Hanford in November 1991. The concepts were evaluated by selected working groups, as requested by DOE-HQ, as an action item from the June 1991 TAP meeting.

The conclusions supported by this evaluation at the time were as follows:

- The In Situ Safe Storage Option should be continued on a tank by tank basis until the ferrocyanide USQ is satisfied or waste mitigation or remediation can be implemented, if necessary.

- Remediation should be implemented, if needed, on a tank by tank basis when sufficient characterization is completed and an acceptable remediation process is ready for implementation.

- Mitigation approaches should be considered on a tank by tank basis where characterization is complete without resolution of the USQ, and only if a remediation process is not ready for implementation.

- **Progress During the Reporting Period**. Comments were received on the predecisional report from TAP, DOE-HQ, and RL in May 1992. Work on this task since then has been directed to revising the report to reflect the latest information available on the ferrocyanide safety issue. Based upon this information, Westinghouse Hanford has taken the position that in situ safe storage is a safe and viable choice for all 24 tanks on the ferrocyanide Watch List.

Mitigation approaches are not recommended as a separate undertaking, because the condition of the ferrocyanide waste in the tanks poses no imminent threat to the safety of workers and the public or the environment. Mitigation is not required based upon the current understanding of the ferrocyanide safety issue (Cash et al. 1992a; Cash and Dukelow 1992).

The ferrocyanide safe storage report will also recommend that remediation approaches be considered as part of the pretreatment studies underway in Hanford's Tank Waste Remediation System for single-shell tank waste retrieval and final disposal. Thus, engineering studies to provide specific technical details for design, development, and implementation, as recommended in the predecisional report, will not be conducted on selected mitigation and remediation options. Instead, studies are focusing on in situ safe storage of the ferrocyanide waste. The report is nearly complete and should be issued next quarter.

- **Planned Work for Subsequent Months.** Final inputs to the ferrocyanide safe storage report are scheduled for January and February 1993. The document will be submitted for clearance and released for public availability during the next quarter.

- **Problem Areas and Action Taken.** Final preparation of the report was delayed this quarter because the authors have not had enough time to complete a major revision of the document. The scope of the document was changed to incorporate the latest knowledge on the ferrocyanide safety issue and reflect the selection of in situ safe storage as the defensible option of choice.

- **Milestone Status.**

  - **November 30, 1992**: Issue a report, approved for public release on selected concepts and recommendations for resolution of the ferrocyanide safety issue. This milestone has been delayed to April 30, 1993.

2.4.6 Resolution of the Ferrocyanide Unreviewed Safety Question

Since inception of the Ferrocyanide Safety Program at Westinghouse Hanford, the ultimate objective of the program has been to resolve the safety issue. To accomplish that goal the USQ must be resolved and the waste ultimately removed and disposed in the Hanford Waste Vitrification Plant. A new activity was started during the last quarter of FY 1992 to (1) devise a strategy that would be acceptable to DOE and oversight panels; and (2) follow with a detailed USQ resolution plan.

The DOE order on USQs establishes the process for USQ identification and resolution (DOE 1991). The steps in the USQ process include the following.

- Identify a situation that may be a potential USQ.
- Take action to place the facility in a safe condition while a safety evaluation is being prepared, so as to determine if an actual USQ exists.
- If a USQ is identified, establish the interim-operating conditions for safe operation of the facility while a safety analysis is being performed.
- Perform a safety analysis to resolve the USQ by establishing a new safety envelope relative to the USQ issue.
- Incorporate into the existing Safety Analysis Report (SAR) or authorization basis any changes that are needed as a result of the safety evaluation, safety analyses, or other action taken.

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

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

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

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

In the past, issues have arisen regarding the scope of work to be addressed in SAs, the level of detail, and the consistency between SAs. These issues are being satisfactorily resolved by using guidelines issued by DOE. The entire review and approval process needs to be streamlined for cost effectiveness.

A Justification for Continued Operations (JCO) of selected activities in ferrocyanide tanks that have previously been addressed in safety documents is being prepared for submittal to the DOE. Approval of the JCO will then allow Westinghouse Hanford to complete the specified activities in accordance with established company policies and procedures without having to obtain DOE approval for each operation.

- **Progress During the Reporting Period.** A strategy letter outlining a proposed approach for resolving the ferrocyanide USQ was transmitted to DOE on October 28, 1992. The approach was to classify the 24 individual ferrocyanide tanks as belonging to one of three categories: Inherent Safety, Passive Safety, or Controlled Safety as discussed in Kazimi 1992. Tanks that are inherently safe do not contain ferrocyanide or oxidizers so that a reaction is impossible. Passive safety is assured when fuel and oxidizer are present but their concentrations are not-sufficient for a reaction to occur. Controlled safety is assured when moisture in the tank is above a minimum level that prevents propagation even if ferrocyanide concentrations are sufficient to burn (as a dry mixture); or if the temperature of the waste is maintained below a value that would cause exothermic reactions to begin (greater than 220 °C).

  To show that ferrocyanide safety issue is no longer an USQ, key tank safety criteria must be demonstrated such that a ferrocyanide reaction is incredible. Westinghouse Hanford believes this to be the case, and the USQ resolution plan will outline the approach and key criteria that need to be met to assure in situ safe storage of the waste. A listing and description of the key safety criteria will be provided in the next quarterly report.

  As reported in the last quarterly, the SA and the EA for removal of pumpable liquid (interim stabilization) from ferrocyanide tanks were submitted to DOE on September 30, 1992. Comments were received from DOE and the SA is currently in the process of being revised for a planned resubmittal in January 1993. The EA was revised and returned to DOE during the quarter.

  A decision was made to revise the existing SA for installing TC trees in sound (non-leaking) ferrocyanide tanks so the document includes installation in leaker tanks as well. A study to evaluate and identify alternative methods for installation of TC trees in assumed leaker ferrocyanide tanks was completed. The previous method used large volumes of water to wash the TC tree through the waste. An ultra high pressure concept that uses minimal quantities of water has been chosen for final testing and design. Revision of the SA and EA will start next quarter.

Preparation of a limited SAR for core sampling of ferrocyanide and other Watch List tanks that contain hard waste (e.g., saltcake) has started. This type of sampling will be performed with a rotary drill system. The rotary sampling rig is not expected to be ready for deployment in the field until September 1993.

On October 4, 1992, tank 241-T-101 was declared an assumed leaker tank based upon liquid level changes in the tank that had occurred over several months. This is one of eight ferrocyanide tanks that still contains pumpable liquid. Approval of the SA and EA documents for pumping ferrocyanide tanks has now become a high priority task to allow pumping of 241-T-101. This documentation, along with other safety evaluations of accompanying activities, such as in-tank photography and approval to use a submersible pump, must be approved prior to pumping.

A JCO for selected activities in ferrocyanide tanks was drafted in December and is currently undergoing peer review within Westinghouse Hanford. Comments received will be incorporated and the JCO will be forwarded to DOE for approval in January 1993. The following activities are covered in this JCO: vapor sampling or monitoring; small additions of water for special flushes and from intrusion of rainwater and snow melt; non-intrusive activities such as surveillance, LOW scans, instrument calibration and repair, utility installations, and grinding and welding in the vicinity of the tanks; manual surface level monitoring, in-tank photography, installation/removal of instrumentation, HEPA filter testing, and other activities that break tank containment that have already been addressed in safety assessments; waste intrusive operations such as liquid sampling, TC tree installations [in sound tanks], LOW installations, saltwell pump installations, push-mode core sampling, and auger sampling; and interim stabilization from the eight ferrocyanide tank that still contain pumpable liquids.

- **Planned Work for Subsequent Months.** The Ferrocyanide USQ Resolution Plan will be completed and transmitted to DOE as a predecisional document. This milestone is due on January 29, 1993. The approach to be taken and the key safety criteria that must be proven will be presented and discussed in the plan. Review of the plan by several oversight panels, including the TAP and the Waste Management External Advisory Committee, will be requested by Westinghouse Hanford. This review is expected to take one to two months. Comments will be incorporated and a final plan, approved for public release, will be issued during the third quarter of FY 1993. A technical report documenting resolution of the USQ will be prepared during the first half of FY 1994; a schedule for USQ resolution will not be set until the USQ resolution plan is accepted and released.

  The SA for pumping non-stabilized ferrocyanide tanks will be revised and forwarded to DOE for concurrence by January 29, 1993.

The revised SA and new EA for installation of TC trees in the assumed leaker ferrocyanide tanks will be written and submitted to DOE.

DOE approval to pump tank 241-T-101, expected by February 1, 1993, will probably not be received until the end of February because the transmittal date for the revised SA for pumping ferrocyanide tanks does not allow sufficient time for DOE review and authorization.

Work started on a limited SAR for rotary core drill sampling of Watch List and non-Watch List tanks containing saltcake. Submittal of the Westinghouse Hanford approved limited SAR is scheduled for May 7, 1993.

The JCO will be completed and transmitted to DOE for approval.

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

- **Milestone Status.**

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

  - **October 31, 1992**: Issue SA and EA documentation to DOE for rotary-mode core sampling of ferrocyanide tanks. Work started on SA and EA documentation, but was stopped when equipment design changes were required. After a review of current plans, a decision was made to submit a limited SAR, instead of a SA. The scheduled date for submittal of the limited SAR to DOE is May 7, 1993.

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

  - **January 29, 1993**: Submit revised SA for pumping non-stabilized ferrocyanide tanks to DOE for concurrence.

  - **January 29, 1993**: Revise draft JCO for selected ferrocyanide tank operations and submit to DOE for approval.

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

- **March 30, 1993**: Submit SA and EA documentation for installation of TC trees in assumed leaker ferrocyanide tanks to DOE for review and comment. See also Section 2.1.1.

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

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

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

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

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

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

2.5.1 Chemical Reaction Studies at Pacific Northwest Laboratory

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

Laboratory tests at PNL (Hallen et al. 1992) have demonstrated that near-stoichiometric mixtures of concentrated (undiluted) sodium nickel ferrocyanide and nitrate/nitrite chemicals, when dry, can propagate at temperatures as low as 220 - 240 °C (430 - 465 °F) to release heat. Waste studies addressing DNFSB Recommendation 90-7.5 are being conducted to determine (1) the quantities of water and other diluents expected in the ferrocyanide waste; (2) actual species of cyanide expected in the waste; and (3) effects of solid diluents, water, additional fuel sources (e.g., sodium acetate, other organics, and sulfides), and the presence of possible catalysts on waste reactivity.

The bulk (about 70%) of the ferrocyanide waste stored in the Hanford Site waste storage tanks was produced by the U Plant flowsheet process. Simulated wastes produced from this flowsheet have been shown not to propagate even when dried and heated above 400 °C. However, a 70 g propagation test of the more concentrated dried U Plant simulant (U Plant 2, bottom fraction) did exhibit self-heating between 270 and 620 °C (Fauske 1992). The potential for aerosol generation with this material needs further evaluation.

About 20% of the ferrocyanide waste stored in the Hanford Site waste tanks was produced by the In Farm flowsheet. The In Farm waste simulant (preparation included centrifuging at 2500 g for an equivalent 30 gravity-years settling time) did not propagate when the moisture content was 12 wt% or greater. Centrifuged In Farm waste simulant has a water content of about 50 wt%. Dry (0 wt% water) In Farm waste simulant exhibits propagation rates up to 10 cm/min when external heat is applied, and can produce temperatures up to 1200 °C. This shows the importance of measuring the water content of the actual tank waste, to ensure that there is sufficient water present to prevent propagation in the In Farm waste.

The T Plant simulant has not been tested, but is expected to be at a much lower ferrocyanide concentration than the In Farm waste simulant, and comprises about 10% of the stored ferrocyanide waste. The T Plant simulant is scheduled to be tested later in FY 1993. As stated in Section 4.4.3, the T Plant simulant is expected to behave similar to U Plant simulant.

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

- **Progress During Reporting Period.**

  Preparation and Characterization of Ferrocyanide Waste Simulants. During the quarter, PNL completed investigations on the thermal stabilities of the Westinghouse Hanford-prepared simulated ferrocyanide wastes. The investigations used the PNL time-to-explosion (TTX) test, differential scanning calorimetry (DSC), scanning thermogravimetry (STG), and in some cases STG coupled with infrared (IR) analysis of the gases evolved during heating.

  The results of the STG and differential scanning STG (DSTG) analysis of UPLANT2-REV-7 (U Plant 2, top fraction) are presented in Figure 2-5. Figure 2-5 also presents selected IR spectra obtained at various times during the STG analysis. During heating from 50 to 200 °C, the sample lost water; however, evolution of product gases was not observed by IR, as was the case for In Farm 1 simulant (Cash et al. 1992). This may be because of the low ferrocyanide concentration in U Plant simulant wastes and/or the limited detection capability of the IR gas analysis. These low temperature reactions tend to produce small amounts of gases.

  Above 250 °C the sample stops losing water and the product gases CO_2 and N_2O begins to evolve. At 400 °C, the CO_2 peak has increased substantially while the N_2O peak remains essentially constant. Between 440 °C and 470 °C both the N_2O and CO_2 peaks grew. At 490 °C only CO_2 is observed and above 550 °C no product gases were observed.

  The STG and DSTG analysis for the Westinghouse Hanford-prepared U Plant 2, bottom fraction, waste simulant (UPLANT2-REV-8) yielded similar results to those obtained for UPLANT2-REV-7. Only slight differences were observed in the DSTG curves between 100 and 200 °C. The IR analyses of the offgas from UPLANT2-REV-8 gave the same results as presented in Figure 2-5 for UPLANT2-REV-7.

  These analyses were run to determine the thermal behavior of U Plant waste simulants; they indicate that little reaction between the ferrocyanide and the nitrate and/or nitrite in the waste occurs prior to 250 °C. It should be noted that N_2 is not IR active and would not be detected in the gas analysis.

Figure 2-5. The STG and DSTG Analysis of U Plant 2, Top Fraction, Ferrocyanide Waste Simulant (UPLANT2-REV-7) and FTIR Spectra of the Gases Evolved at Various Temperatures During the Analysis.

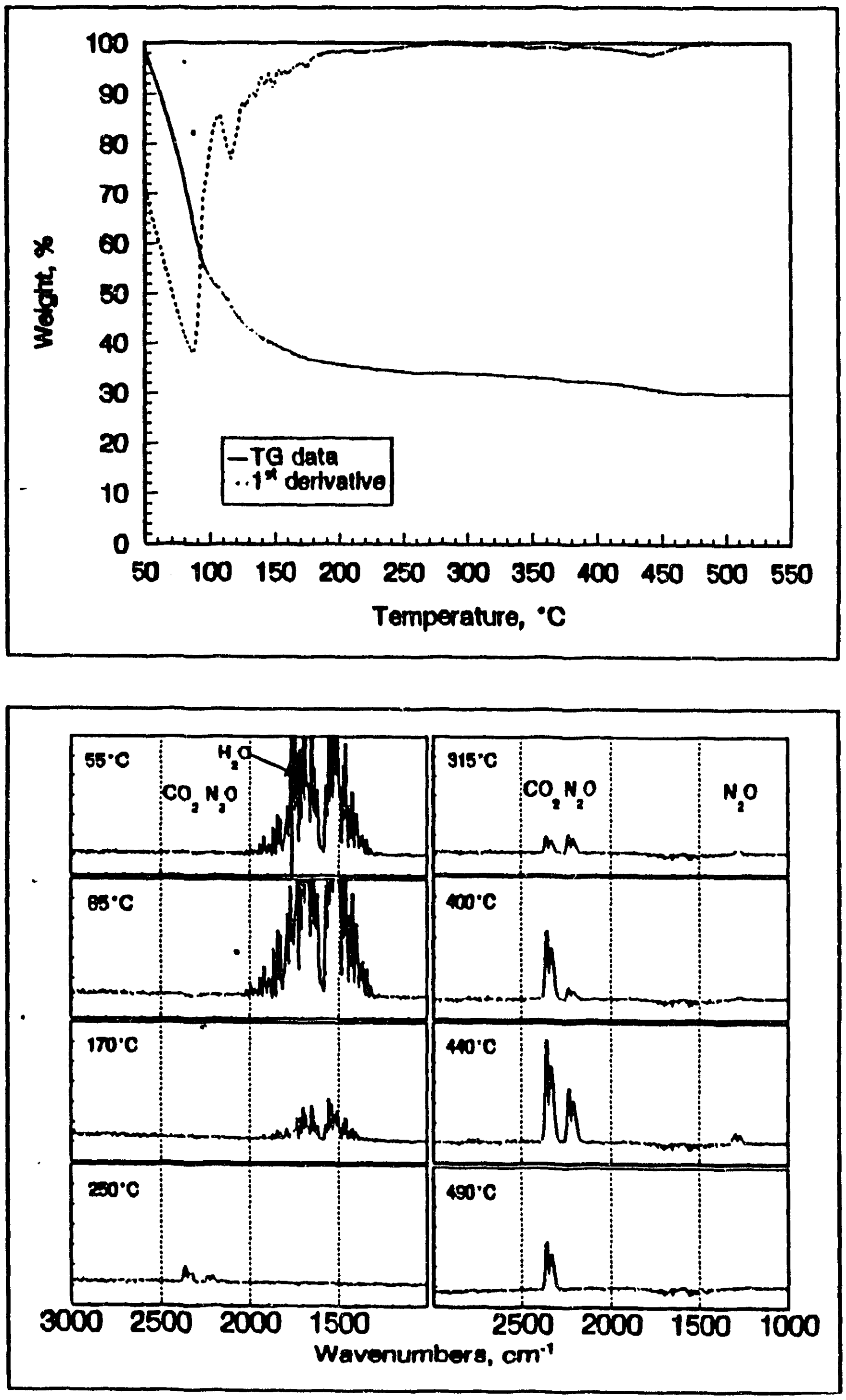


Figure 2-6 shows the STG and DSTG scans and analysis of evolved gases for the Westinghouse Hanford-prepared In Farm 1, bottom fraction, waste simulant (INFARM1-REV-8). Comparison of Figures 2-5 and 2-6 indicates that the thermal behavior of the In Farm 1, bottom fraction, simulant differs from that observed for U Plant simulants. There is a rapid reaction beginning at about 340 °C for In Farm 1, bottom fraction, simulant, while there is only a slight indication of this reaction for the U Plant simulants. The analysis of evolved gases for INFARM1-REV-8 is similar to that observed for the U Plant simulants except that the latter does not evolve NO gas.

These characterization studies of simulated wastes have shown little reaction between ferrocyanide and nitrate and/or nitrite at temperatures below 200 °C. The gaseous products include N_2O, CO_2, and NO for the In Farm simulants. These wastes exhibit different thermal behaviors in terms of reaction rates and the temperatures at which reactions occur.

Ferrocyanide Waste Simulant Aging Studies. A report summarizing all aging studies work completed in FY 1992, and approved for public release, was distributed as PNL-8387 (Lilga et al. 1992).

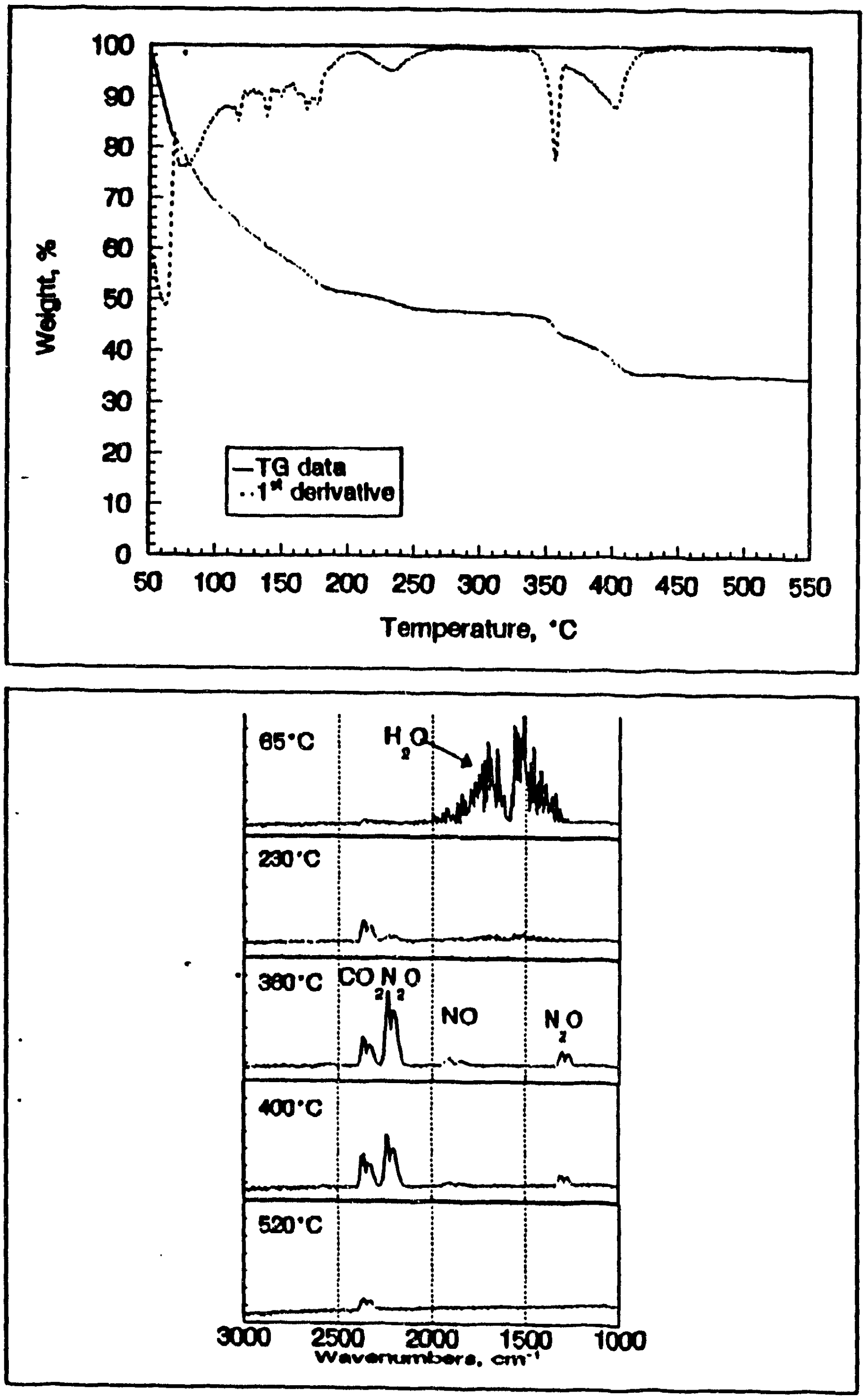
Dissolution of vendor-prepared sodium nickel ferrocyanide was conducted in 6 *M* $NaNO_3$ at pH 13. As shown in Figure 2-7, the rate of dissolution was suppressed compared with two other solutions containing 0.1 and 1.0 *M* Na^+ at pH 13. Ferrocyanide continued to slowly dissolve until the experiment was stopped after 480 h, at which time 40% of the iron from the sodium nickel ferrocyanide was in solution. Additional dissolution experiments are being conducted in 1 *M* $NaNO_3$ and 1 *M* Na_3PO_4.

An In Farm 1 ferrocyanide waste simulant (In Farm 1-A-Rev-4), consisting of settled and centrifuged solids and containing about 9 wt% ferrocyanide on a wet basis ($\approx$ 50 wt%), will be used for many of the aging studies to be conducted this fiscal year.

Cyanide Species Analytical Development. A report, *Ferrocyanide Safety Project, Task 3.5 Cyanide Species Analytical Methods Development: FY 1992 Annual Report*, PNL-8399 (Bryan et al. 1992), was cleared for public release and distribution.

Earlier work on cyanide species analytical methods development demonstrated the use of solution attenuated total reflectance (ATR) infrared (IR) spectroscopic methods for the quantitative measurement of $Fe(CN)_6^{-4}$ (ferrocyanide ion) in solution using a ZnSe ATR element. Although this technique worked well for the ferrocyanide ion, problems were experienced with the $Fe(CN)_6^{-3}$ (ferricyanide ion) and CN^- (cyanide ion) chemically reacting with the ZnSe crystal material.

Figure 2-6. The STG and DSTG Analysis of In Farm 1, Bottom Fraction Ferrocyanide Waste Simulant (INFARM1-REV-8) and FTIR Spectra of the Gases Evolved at Various Temperatures During the Analysis.



Crystalline cubic zirconia has been demonstrated to have chemical compatibility with the cyanide species in solution and has the proper transmission properties in the infrared region of interest.

To evaluate the chemical compatibility of the cubic zirconia ATR element with various cyanide species of interest, solutions containing known quantities of $Fe(CN)_6^{-3}$, $Fe(CN)_6^{-4}$, and CN^- were prepared for use with this IR cell material. Figure 2-8 shows IR spectra obtained with a solution containing the three cyanide species. The concentration of each species in the solution was between 0.5 and 1 wt%. The infrared absorption bands for the species are well separated and sufficiently intense to allow detection of these cyanide species in solution to at least an order of magnitude lower concentration, even when all three species are present.

Standard absorbance curves were prepared for $Fe(CN)_6^{-4}$ and $Fe(CN)_6^{-3}$ in the concentration range of 0.02 to 0.8 wt% . There were no indications of reactivity or chemical incompatibility between the zirconia ATR element and the cyanide complexes during the measurements.

Diluent Screening and Scoping Studies. Investigations to determine the effect of nickel sulfide on the explosivity of mixtures of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite using the PNL TTX test were completed during the quarter. NiS was added to the In Farm Flowsheet for several runs in the 1950s to enhance precipitation of ^{60}Co. Sulfide compounds can react as fuels and nickel may act as a catalyst. Figure 2-9 shows the effect that nickel sulfide (NiS) has on the explosivity of a near-stoichiometric mixture of sodium nickel ferrocyanide and an equimolar mixture of sodium nitrate and nitrite. The figure shows the effect of adding NiS to a mixture of 26 mg of $Na_2NiFe(CN)_6$ and 38 mg of equimolar $NaNO_3$/NaNO2. As the amount of NiS is increased from 0 to 26 mg, the TTX is lowered. The addition of 26 mg of NiS reduced the temperature for a TTX of one hour from >330 °C to 280 °C.

These studies indicate that NiS can both accelerate and reduce the minimum explosion temperature for a near-stoichiometric mixture of sodium nickel ferrocyanide and an equimolar mixture of sodium nitrate and nitrite.

A catalyst/initiator screening study using the PNL version of the Henkin (Henkin and McGill 1952) time-to-explosion (TTX) test, to determine effects other potential waste constituents may have on the reaction between sodium nickel ferricyanide and equimolar sodium nitrate and nitrite, has been completed. The study was designed to allow use of statistical analysis techniques to discern whether the organic complexant sodium ethylenediaminetetraacetate (EDTA), nickel hydroxide, ferric hydroxide, or chromium (III) hydroxide act as catalysts or initiators for the reaction between sodium nickel ferricyanide and equimolar sodium nitrate and nitrite.

Figure 2-7. Dissolution of Vendor-Prepared Sodium Nickel Ferrocyanide in 6 *M* $NaNO_3$ at pH 13 Compared With Dissolution in Solutions Containing 0.1 and 1.0 *M* Na^+ at pH 13.

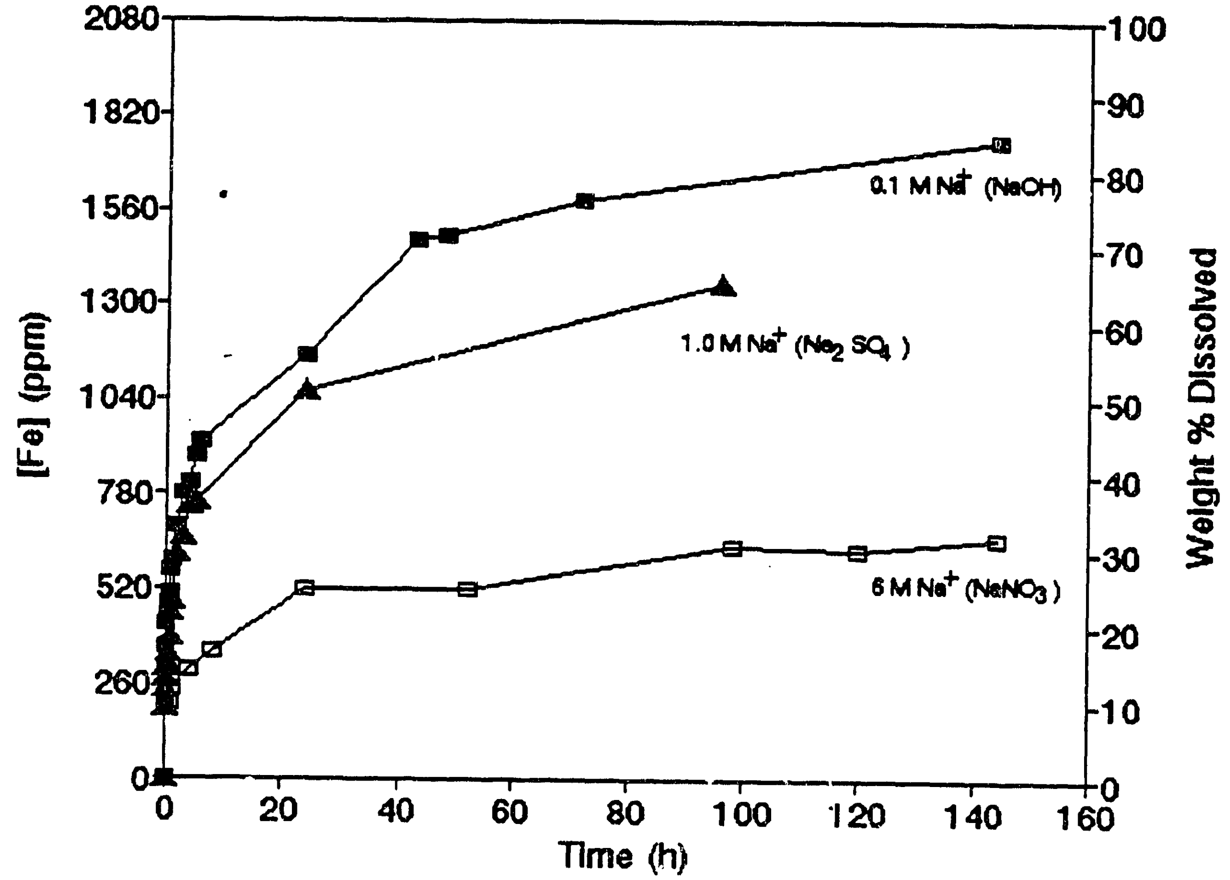


Figure 2-8. Infrared Spectra of Cyanide (2080 cm^{-1}, 0.98 wt%), Ferrocyanide (2038 cm^{-1}, 0.51 wt%), and Ferricyanide (2118 cm^{-1}, 0.78 wt%) Ions in Aqueous Solution.

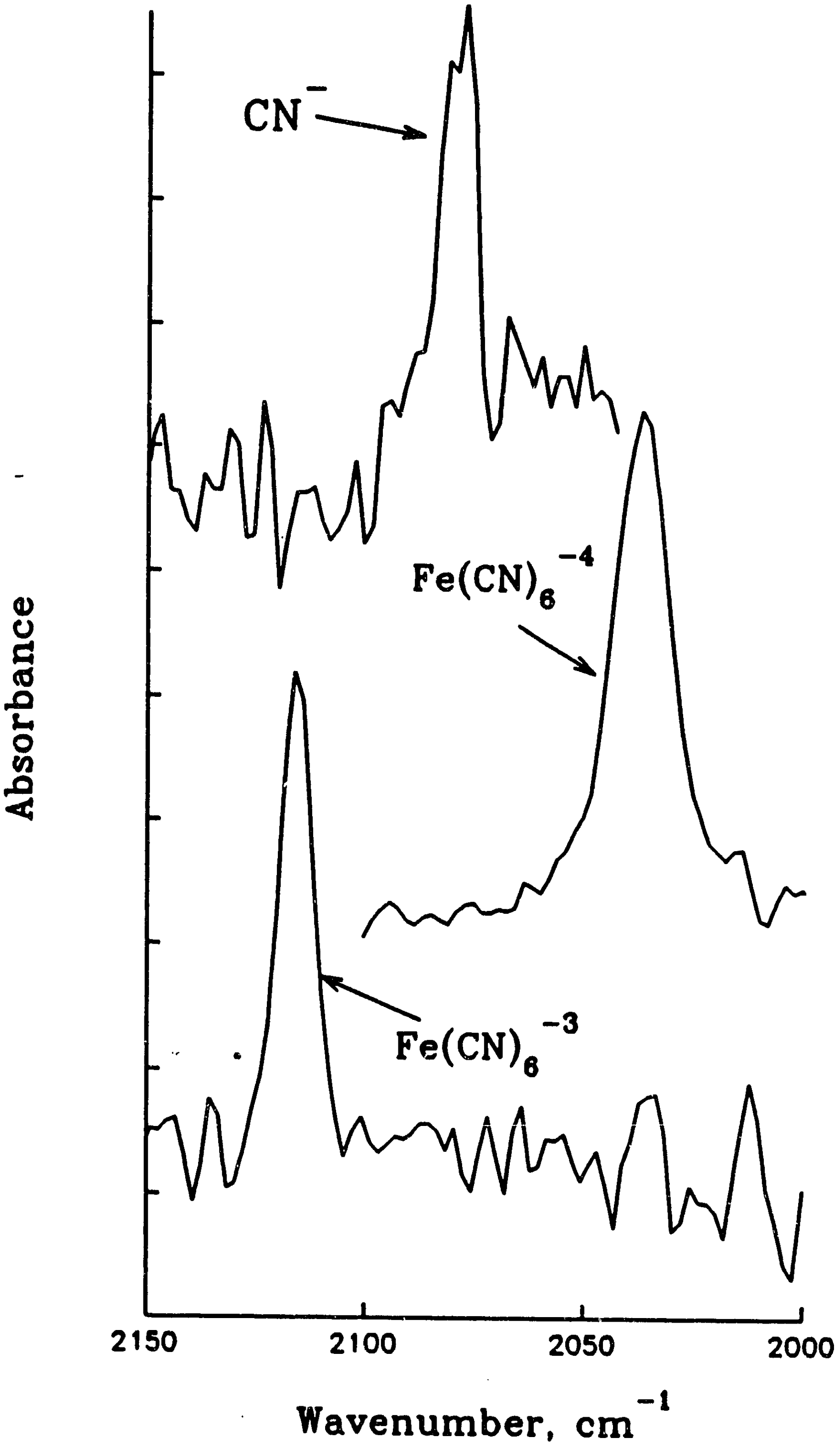
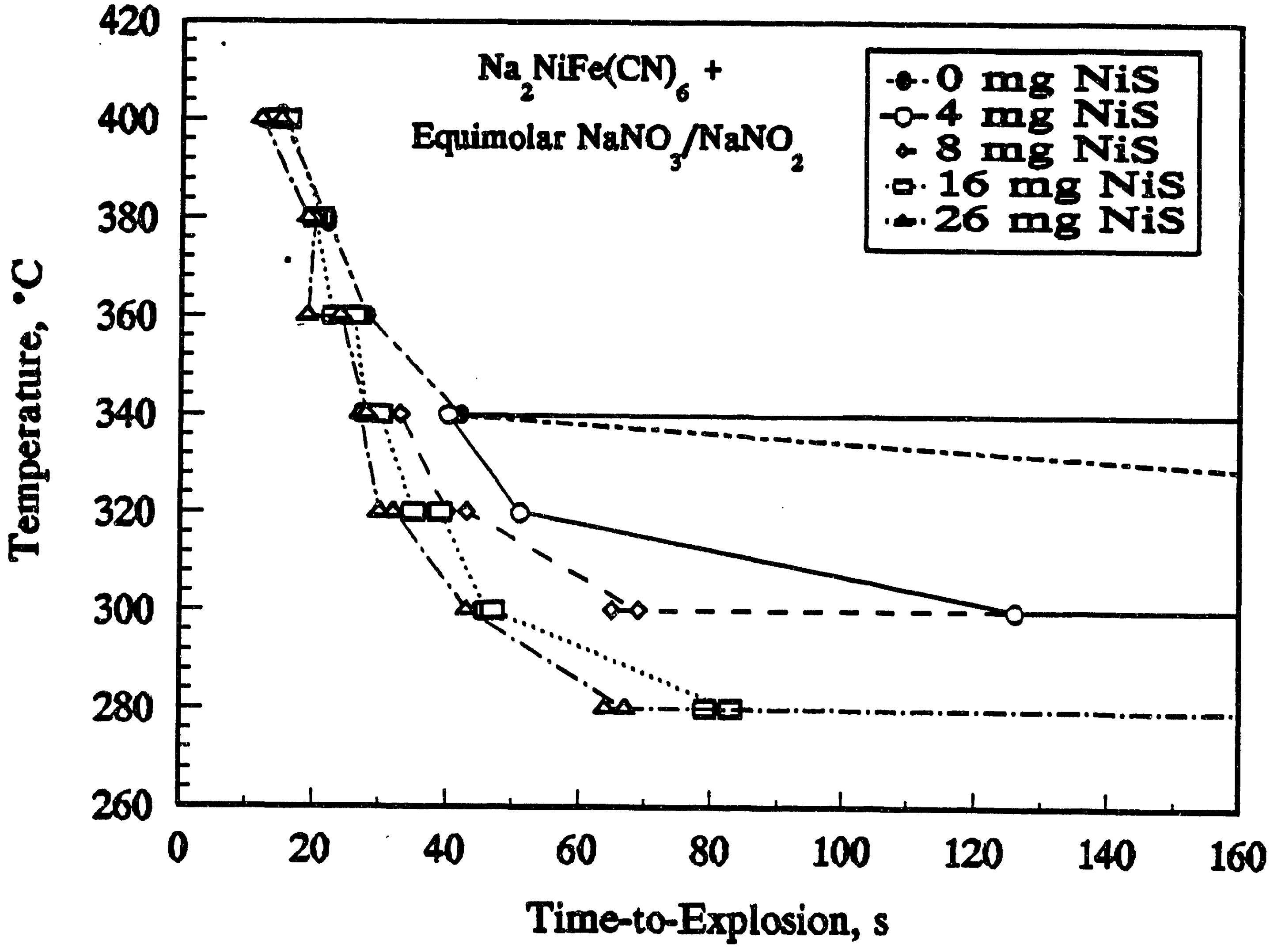


Figure 2-9. Effect of NiS on the Explosivity of Admixtures of Thrice-Washed Sodium Nickel Ferrocyanide and an Equimolar Mixture of Sodium Nitrate and Nitrite as Determined Using the PNL TTX test.



In Figure 2-10, the TTX is presented as a function of the additive at the four temperatures used. To illustrate the effect of an additive on the TTX, a horizontal line is shown which marks the control mixture's mean TTX at each temperature. The control mixture is the pure mixture of ferricyanide and oxidant without any additives.

The additives are identified by code in Figure 2-10. The additive identified as "E" is EDTA added at 0.03 mole EDTA/mole ferricyanide.

Likewise the tests with chromium (III) hydroxide, ferric hydroxide, and nickel hydroxide, added at the same mole ratio, are identified as "C", "F", and "N". EC indicates the case with EDTA and chromium hydroxide added, each at the 0.03 mole/mole ferricyanide level. All combinations were tested and the additives are identified as a combination of the coding described earlier.

Inspection of Figure 2-10 shows that many of the additives reduce the TTX relative to the control. However, using the Dunnett (Dunnett 1955) statistical analysis test which allows comparison of a treatment to a reference or control, it was found that only EDTA alone caused a statistically significant (95% confidence level) effect at 380 °C. This indicates that EDTA can accelerate the reaction between ferricyanide and nitrate and nitrite. Since EDTA is being tested as a representative organic complexant, this suggests that other organic complexants used at Hanford may have similar effects.

The results of a brief study to determine the effect of different amounts of sodium aluminate on the explosivity of a near stoichiometric mixture of sodium nickel ferrocyanide and equimolar sodium nitrate and nitrite at different temperatures is presented in Figure 2-11.

Figure 2-11 shows the effect of temperature on the ln(TTX) for the mixture without aluminate, and for two levels of added sodium aluminate, with weight ratios of 2:1 and 4:1 sodium aluminate to ferrocyanide. The figure shows that addition of sodium aluminate delays the explosive reaction but increasing the amount of added aluminate by a factor of two has little additional effect.

<u>Sensitivity Tests with Simulated Ferrocyanide Wastes</u>. Los Alamos National Laboratory (LANL) completed a report on small-scale sensitivity tests using ferrocyanide flowsheet waste simulants. The report, "Evaluation of Ferrocyanide/Nitrate Explosive Hazard," was submitted to DOE for review on September 30 as a predecisional document. The sensitivity tests included impact, friction, spark, differential thermal analysis (DTA), vacuum thermal stability, Henkin, and accelerating rate calorimetry (ARC) measurements on selected ferrocyanide flowsheet waste simulants. Initial results from the ARC test were questionable, with either low temperature exotherms or instrument drift being indicated. The ARC was recalibrated and the test repeated with no low

Figure 2-10. Effect of EDTA (E), Chromium (III) Hydroxide (C), Ferric Hydroxide (F), and Nickel Hydroxide (N) on the Explosivity of a Near-Stoichiometric Mixture of Sodium Nickel Ferrocyanide and Equimolar Sodium Nitrate and Nitrite.

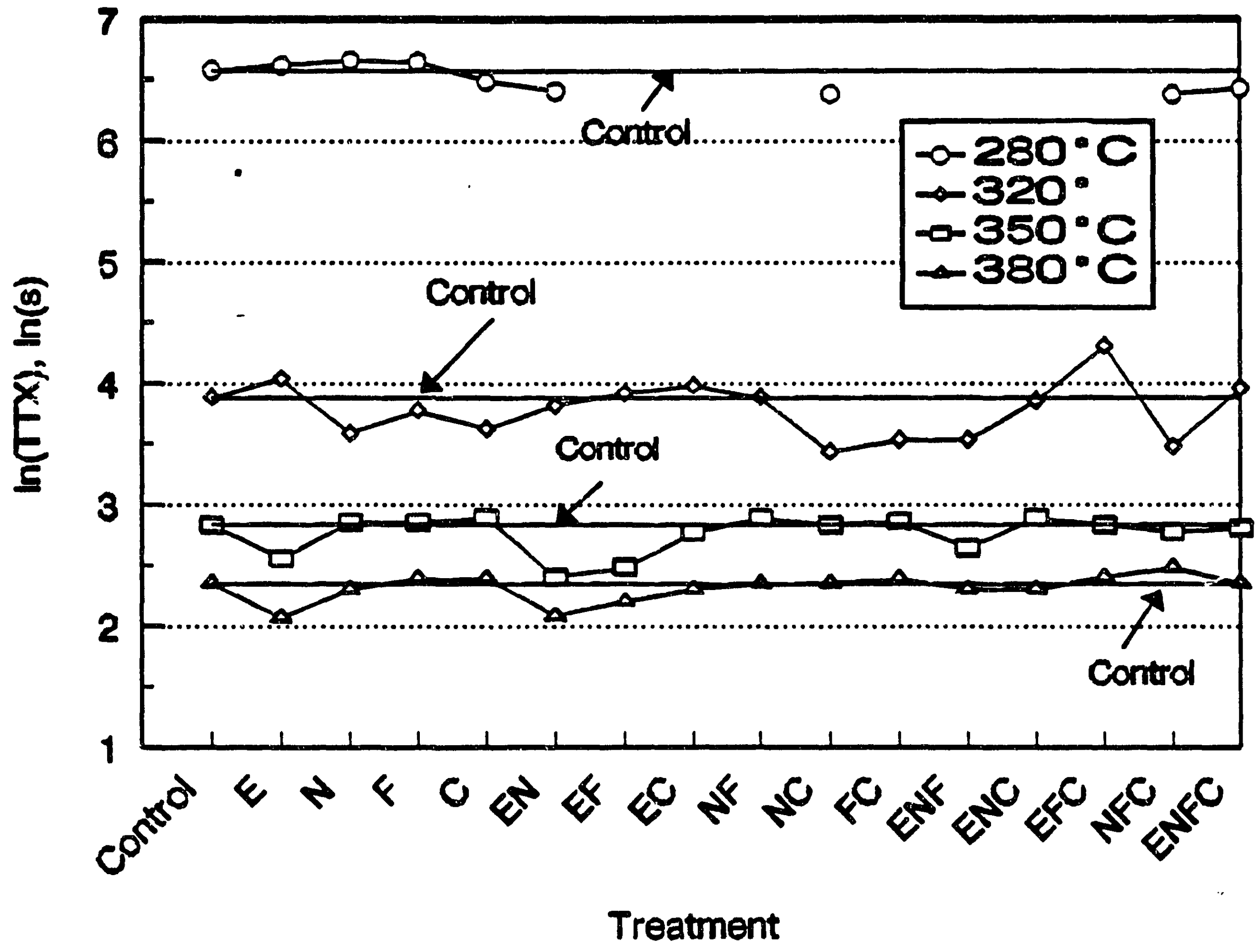
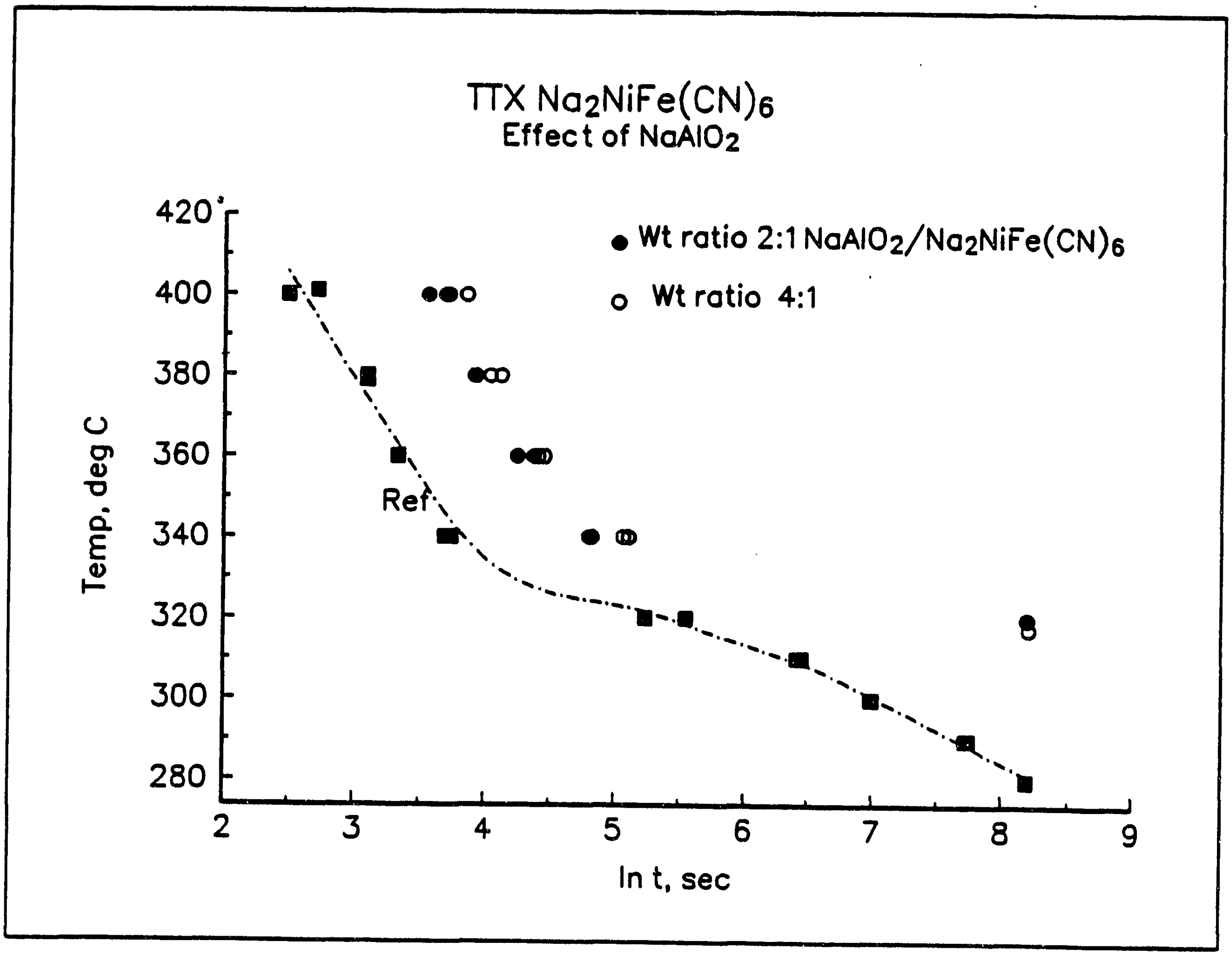


Figure 2-11. Effect of Added Sodium Aluminate on the Time-to-Explosion of a Mixture of Sodium Nickel Ferrocyanide and Equimolar Sodium Nitrate and Nitrite.



temperature exothermic reactions being observed. A joint meeting of representatives from Westinghouse Hanford, PNL and LANL was held during September to discuss the results of the sensitivity tests. Dr. Hans Fauske of Fauske and Associates, Inc. also participated in the meeting via a conference telephone call.

The LANL report is currently being reviewed by a technical editor and cleared for public release. The results of the small-scale sensitivity tests were presented this quarter to the Waste Management External Advisory Committee.

Reaction Pathways. Washington State University (WSU) is under contract to PNL to conduct reaction studies of ferrocyanide materials using dynamic (programmed temperature) x-ray diffraction (DXRD). In initial WSU experiments, ferrocyanide concentrations were followed by scanning a sodium nickel ferrocyanide x-ray diffraction peak found at about 21 degrees 2θ while heating the sample at 2 or 5 °C/min in an atmosphere of either air or helium.

Tests were performed with FECN36 (PNL prepared sodium nickel ferrocyanide which had been triple washed in water) alone and mixed with sodium nitrite, sodium nitrate and equimolar mixtures of nitrate and nitrite. It was found that the ferrocyanide peak began to decrease at about 180 °C in helium with no crystalline products being detected until temperatures exceeded 300 °C. During discussion of these preliminary results at PNL, there was speculation that the $Na_2NiFe(CN)_6$ peak at 21 degrees 2θ could represent a hydrated form of $Na_2NiFe(CN)_6$ and that the loss of crystallinity in the temperature range 180 - 210 °C could be caused by loss of waters of hydration.

Subsequently, WSU conducted an experiment in which a FECN36 sample, without any nitrite or nitrate added, was heated at 2 °C/min in helium to 225 °C. The peak being followed at 21 degrees 2θ and a second peak at 42 degrees 2θ began to shift to higher 2θ angles at 190 °C and had shifted completely at 225 °C. At this point, the purge gas flowing through the DXRD reaction chamber was changed to 5% steam in helium and the sample cooled at 2 °C/min to room temperature. The results of this experiment are shown in Figure 2-12. The shift that occurred previously was reversed and the original peaks at 21 and 42 degrees 2θ began to reappear at a temperature of about 160 °C. It is apparent that the $Na_2NiFe(CN)_6$ was readily rehydrated by the helium-steam purge gas. In a control experiment, which was identical except that steam was not added to the purge gas during the cooling period, the shift to higher 2θ angles that occurred at 190 °C remained permanent even after the cool-down period. This provides conclusive evidence that the low temperature $Na_2NiFe(CN)_6$ decomposition reaction originally observed was a dehydration process. Further confirmation was provided by tests in which WSU quenched samples of FECN36 which had been heated in the DXRD to 225 °C. The quenched samples were then analyzed by Fourier transform infrared spectroscopy (FTIR) at PNL. When compared to unheated FECN36, the only difference in spectra observed for the heated samples was a lack of absorbance in the infrared region where water absorbs.

As a result of the work by WSU showing loss of crystallinity of the sodium nickel ferrocyanide without nitrate or nitrite present, PNL performed an isothermal thermogravimetric (ITG) analysis of the thrice-washed sodium nickel ferrocyanide simulant (FECN36) at 160 °C. The results of the ITG analysis are shown in Figure 2-13. The mass loss is most likely water and would correspond to between 3 and 4 waters per ferrocyanide.

At least four different exothermic reaction steps have been observed in the oxidation of sodium nickel ferrocyanide by sodium nitrate using isothermal calorimetry. Figure 2-14 presents an Arrhenius plot, ln t versus 1000/T, for each of the reaction steps; t is time to peak minimum and T is temperature in °K. The slope should be equal to the activation energy (E_a) for each of the different reaction steps.

Using the results presented in Figure 2-14, the E_a's, for each of the reactions observed in order of appearance from the start of the isothermal analysis, were 104 kJ, 191 kJ, 139 kJ, and 123 KJ, respectively. The most energy is associated with the third reaction and this should be the reaction which controls the explosivity of the mixture. Either or both of the first two reactions may provide the necessary heat required at lower temperatures to cause an explosion and will thus be the rate determining step of the explosive reaction. At higher temperatures the first two reactions either merge into one or cannot be resolved.

- **Planned Work For Subsequent Months.**
  - Continue aging dissolution experiments using sodium nickel ferrocyanide and Westinghouse Hanford prepared ferrocyanide flowsheet simulant (In Farm 1-A-Rev-4) in SST simulant salts at tank temperatures and in the presence of an ionizing radiation field.
  - Continue work on IC methods, and solution IR methods to determine probable interferences that will be encountered in developing analytical methods for actual waste samples. Work will also continue on solids methods development using IR and Raman techniques. These methods will be explored further using flowsheet materials.
  - A report, approved for public release, will be completed on catalyst, initiator, and diluent screening tests conducted to date.

Figure 2-12. Programmed Temperature X-ray Diffraction Scans Showing Dehydration of $Na_2NiFe(CN)_6$ (FECN36) at 225 °C in Helium Followed by Rehydration at Temperatures Below 160 °C in Helium Containing 5% Steam.

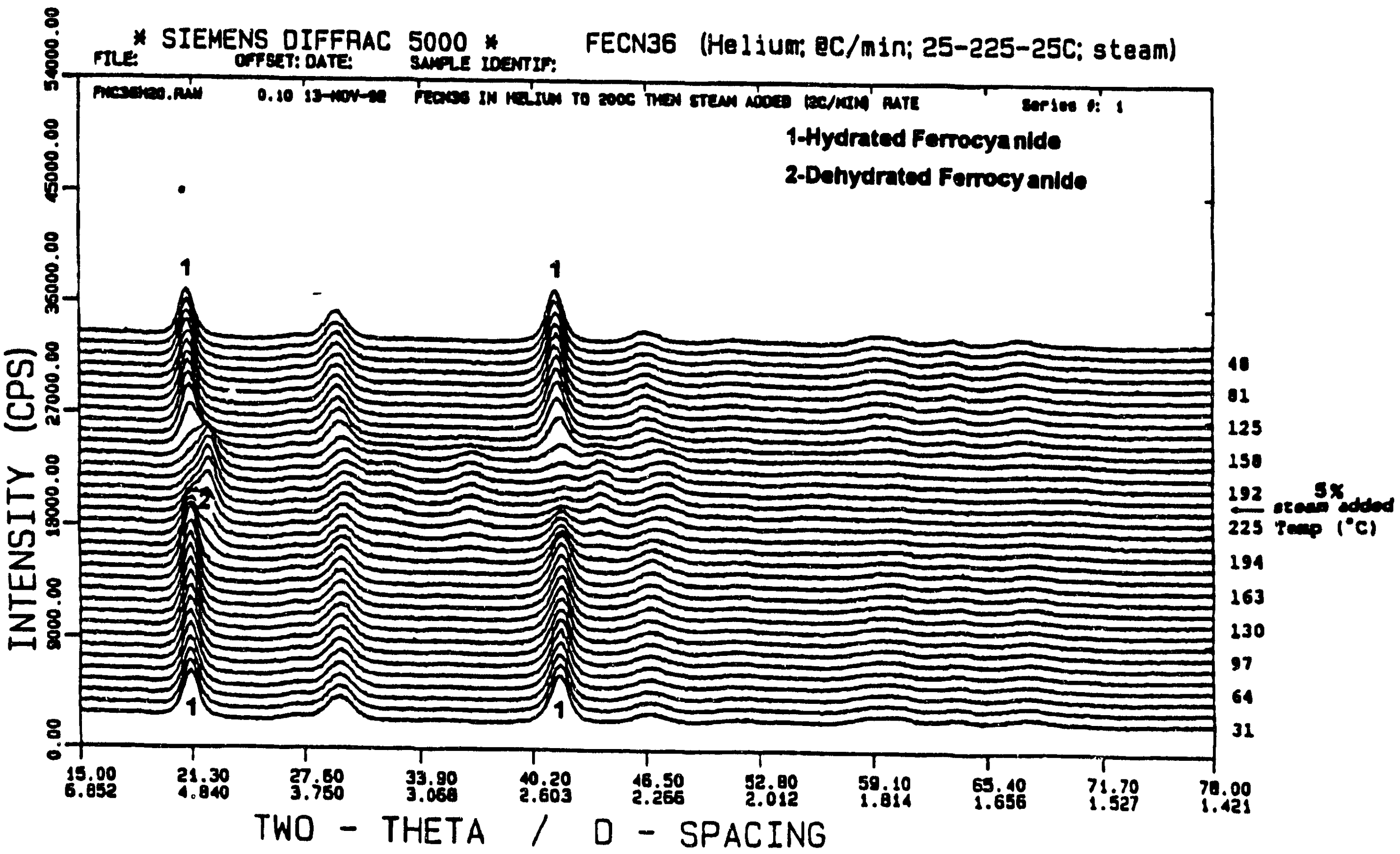


Figure 2-13. Isothermal Thermogravimetric (ITG) Analysis of Thrice-Washed Sodium Nickel Ferrocyanide (FECN36) at 160 °C From -10 to 100 Minutes.

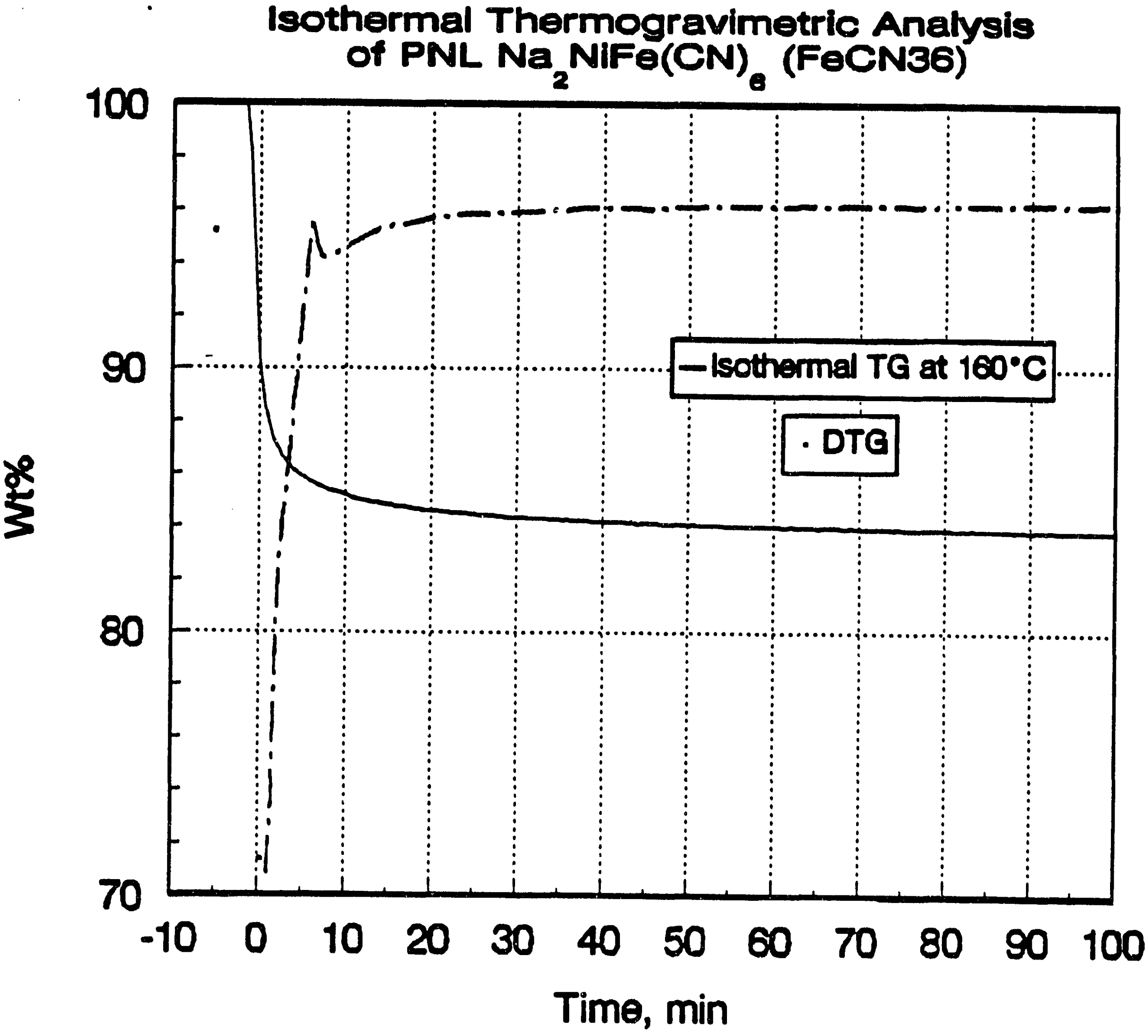
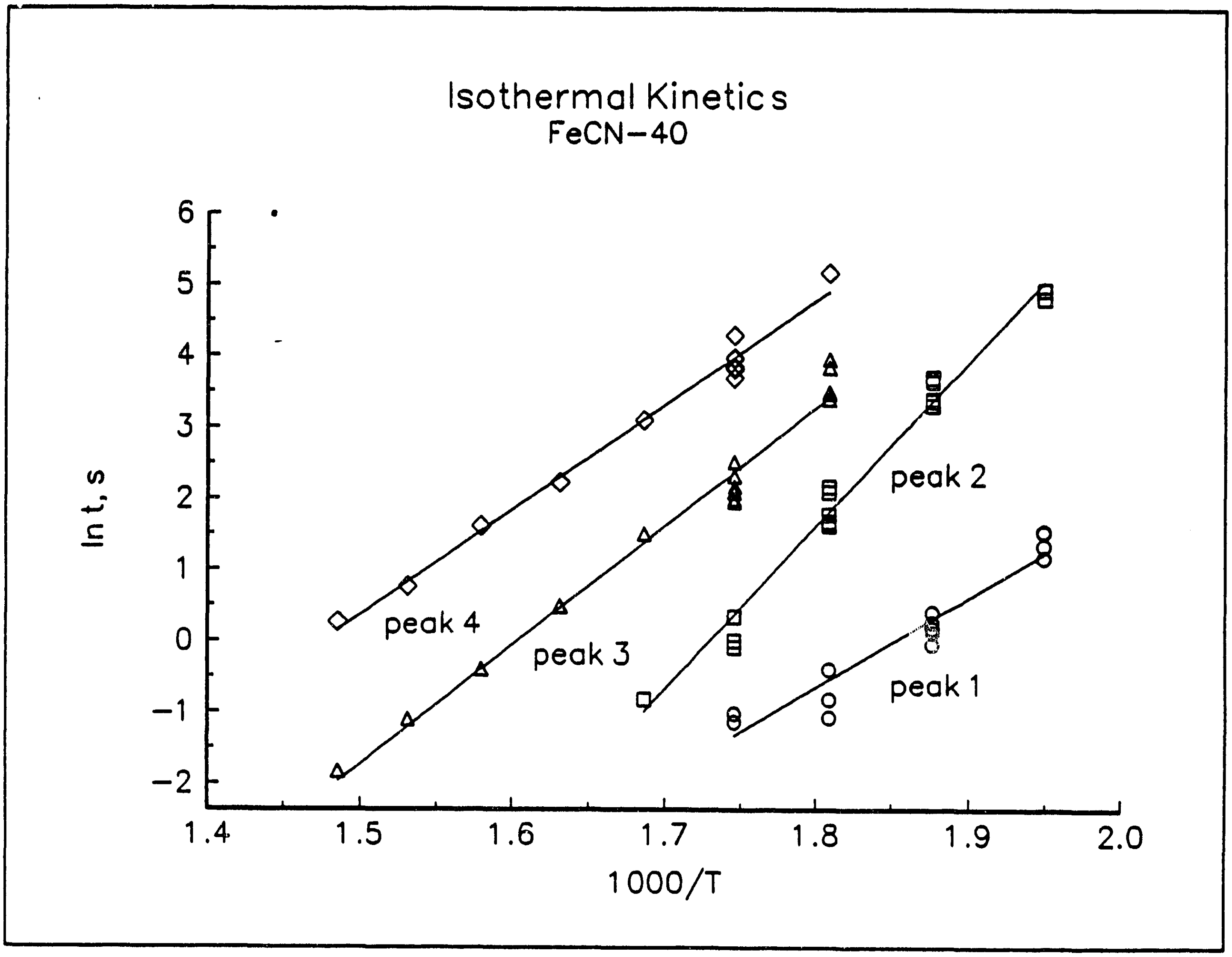


Figure 2-14. Arrhenius Plots for Thermal Reaction Steps Observed for Sodium Nickel Ferrocyanide and Sodium Nitrate Dried Together.



  - Data will be assembled that contain key physical and chemical properties of the waste in ferrocyanide tanks for use in microconvection modeling studies.

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

- **Milestone Status.**

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

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

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

  - **June 30, 1993**: Issue the final, cleared report on small-scale sensitivity tests of ferrocyanide flowsheet simulants conducted by LANL.

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

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

  - **September 30, 1993**: Issue final PNL report on the effects of aging on ferrocyanide waste as a cleared document.

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

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

Investigations of the thermal stabilities of the Westinghouse Hanford prepared simulated ferrocyanide flowsheet wastes were completed during the quarter. It was found that simulated In Farm 1 flowsheet wastes exhibited a rapid reaction beginning at about 340 °C while U Plant flowsheet materials exhibited only a slight indication of reaction at this temperature.

Dissolution trials with vendor-prepared sodium nickel ferrocyanide were conducted in 6 *M* $NaNO_3$ at pH 13. The rate of dissolution in the in 6 *M* Na^+ solution was suppressed compared with dissolution in solutions containing 0.1 and 1.0 *M* Na^+ at pH 13.

Earlier work on cyanide species analytical methods development indicated that ferricyanide ion and cyanide ion chemically reacted with ZnSe crystal cell material. Crystalline cubic zirconia has been found to be chemically compatible with the cyanide species in solution and has the proper transmission properties in the infrared region of interest.

Nickel sulfide was found to both accelerate and reduce the minimum explosion temperature for a near stoichiometric mixture of sodium nickel ferrocyanide and an equimolar mixture of sodium nitrate and nitrite. Similarly, Dunnett (Dunnett 1955) statistical analysis of PNL time to explosion test data for mixtures of various additives added to near stoichiometric mixtures of sodium nickel ferrocyanide and an equimolar mixture of sodium nitrate and nitrite indicate that EDTA can accelerate the reaction between ferricyanide and nitrate and nitrite.

2.5.2 Ferrocyanide Propagation Studies

Propagation studies are continuing at FAI under contract to Westinghouse Hanford. These propagation tests are being performed to determine if simulated Hanford ferrocyanide waste will ignite and burn to spread and involve additional waste from a potential ignition point. The propagation velocity is a key parameter in determining the safety consequences of postulated burns, including a potential radioactivity release from confinement. Since the composition of the waste in the storage tanks varies, and is unknown at all locations, ranges of material compositions have been tested.

Present work is focused on the more concentrated ferrocyanide sludge as produced by the In Farm 1 flowsheet. Sludge produced by the In Farm flowsheet was stored in four C Farm tanks and represents about 20 wt% of the total ferrocyanide added to the Hanford tanks. The present concentration of ferrocyanide in the sludge is in question since ferrocyanide can degrade by radiolysis and also undergo alkaline hydrolysis in the presence of high pH waste. Also, possible mechanisms that might have concentrated the ferrocyanide during the last 40 years have not been completely ruled out.

- **Progress During Reporting Period.** The gases released during four propagation tests at FAI have been identified and quantitatively measured. Gas analysis shows that nitrogen, carbon dioxide, oxygen, nitric oxide, and some hydrogen are released from the dry In Farm 1 sludge reaction. Two aerosol/propagation tests and one intermediate pressure propagation test were specified for performance at a meeting with Dr. H. K. Fauske of FAI at Hanford on December 9 and 10, 1992. Preparations are underway to conduct these tests at FAI.

Quantities of various gases generated during the previously completed propagation tests were determined and are listed in Table 2-5 below for four propagation tests. The results, shown in moles of gas per mole of ferrocyanide in the simulant, indicate that the theoretical amount of nitrogen is released but that only about one third of the theoretical carbon dioxide is released. This supports previous results and indicates that some metal carbonates are formed, thus minimizing the amount of carbon dioxide released. Some nitric oxide was observed to be formed and may come from the decomposition of nitrate or nitrite or as a reaction product from the ferrocyanide reaction with the nitrate/nitrite oxidant. A small amount of hydrogen was also observed and may result from the decomposition of sodium hydroxide. The ferrocyanide in the fourth test was not consumed because the reaction as started by the strong ignition source did not go to completion. Chemical analysis of the solid reaction products will be made to provide the final information necessary to determine the reaction mechanisms.

Two scoping aerosol/propagation tests were defined to assess release of cesium and other metals from dry In Farm 1, bottom fraction simulant. These scoping tests are to be conducted by FAI in a similar configuration as the previously conducted propagation tests except they will be conducted in a larger (49 L) containment chamber. The test material will be vacuum-dried simulant to which 1 wt% water will be added and well mixed. This may permit possible conversion of all cesium to cesium hydroxide during the reaction. Cesium hydroxide has a relatively low boiling point near 1050 °C and is considered to be the radioactive species which could have the greatest dose consequence in the event of a postulated reaction.

The propagation rates will be measured by thermocouples imbedded into the test material. The containment atmosphere, temperature, and pressure will be measured during the test. An aerosol sample will be obtained from a measured quantity of containment gas and the aerosol metallic species release will be calculated using the analysis of the aerosol sample. This test will be performed at an initial absolute pressure of 3 atmospheres of argon with delayed exhaust gas venting through a filter to collect the aerosol as shown in Figure 2-15. Other parameters are: a 25 mm diameter test material cylinder about 100 mm long, a 60 °C initial temperature, dried material screened through 140 mesh screen, and a specific gravity of about 1.2. The second aerosol/propagation test will be conducted at an initial temperature of 120 °C with other conditions being kept the same as the first test, and the same data measurements being made. At 120 °C the 1 wt % water added is expected to remain in the test material.

A parametric pressure propagation test was also identified to determine a propagation rate measurement for an intermediate pressure (10 atmospheres absolute) test. This test will be conducted at FAI using dry (0 wt% water) In Farm 1, bottom fraction, simulant with a 25 mm diameter test bed, an initial temperature of 60 °C, a specific gravity of about 1.2, and particle size as

Table 2-5. Gases Released from Ferrocyanide Simulant Reaction Tests.

	Moles of gas released per mole of ferrocyanide				
Propagation test	N_2	CO_2	NO	O_2	H_2
25 mm diameter, ≈53 Atm absolute, VWW-IF-1* mixture dry, 1.23 sp gr	7.5	2.5	0.046	0.6	0.0
25 mm diameter, ≈2.7 Atm absolute, VWW-IF-1 mixture dry, 1.23 sp gr	8.2	2.7	2.7	0.007	0.005
50 mm diameter, ≈53 Atm absolute, VWW-27.6/70/2.4** 18 wt% water 1.87 sp gr	5.8	2.0	0.52	0.46	0.52
25 mm diameter, ≈53 Atm absolute, VWW-27.6/70/2.4 25 wt% water 1.72 sp gr	4.2	1.4	0.02	0.07	0.05

*VWW-IF-1 is vendor-prepared, Westinghouse Hanford-washed disodium nickel ferrocyanide mixed with other constituents at estimated In Farm 1 simulant concentrations.

**VWW-27.6/70/2.4 is vendor-prepared, Westinghouse Hanford-washed disodium nickel ferrocyanide at 27.6 wt%, nitrate/nitrite at 70 wt%, and inert solid diluent at 2.4 wt%.

screened through 140 mesh screen. This test will be conducted in the 49 liter chamber. A propagation rate will be measured for this test with thermocouples imbedded in the test material. Gas and solid reaction product samples will be analyzed to determine the reactions that occur.

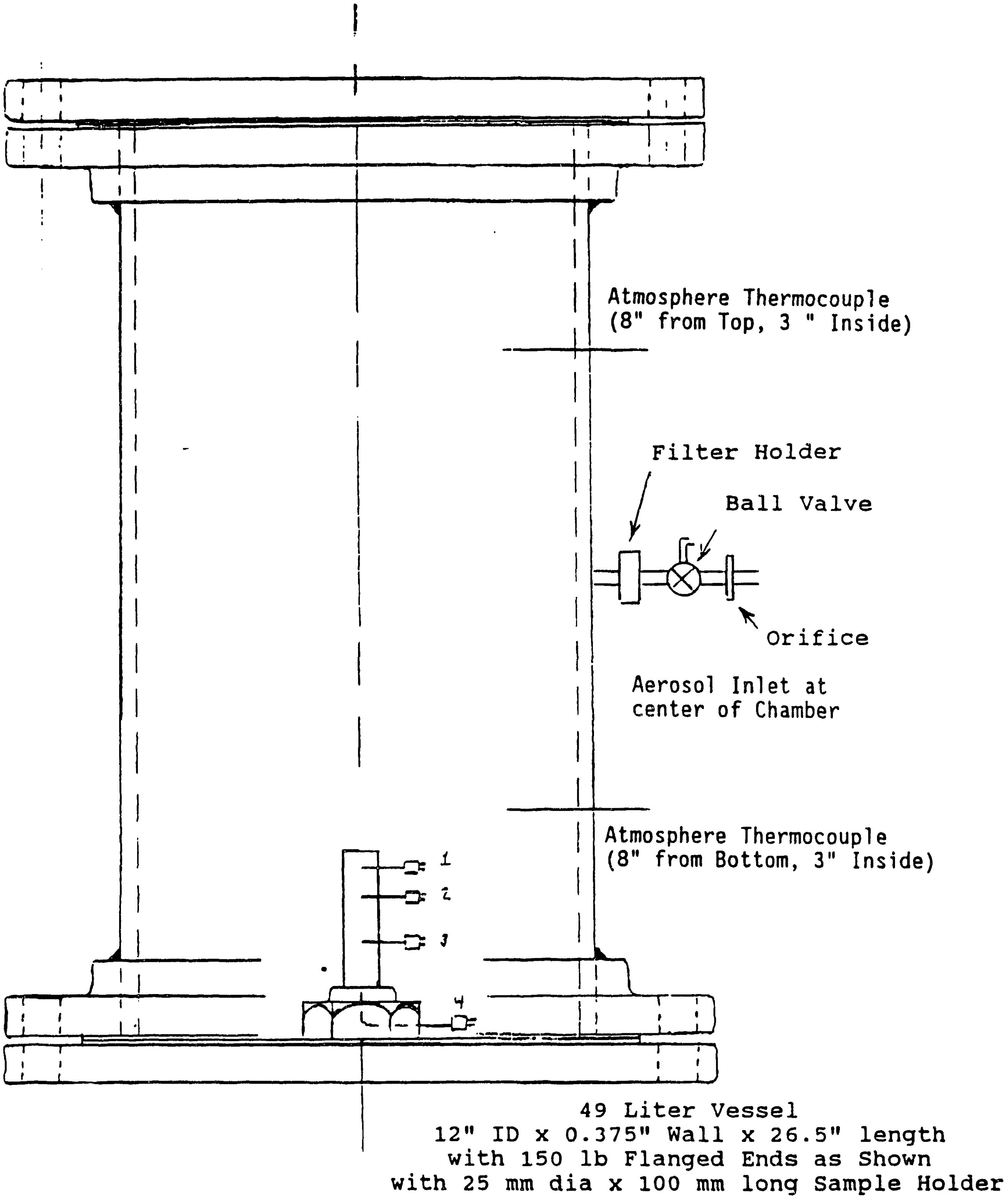
Planned Work for Subsequent Months. Propagation screening tests will be completed with stoichiometric mixes to identify most important parameters. Additional parametric and confined geometry tests will also be conducted. Sample analyses of residue samples will be completed to identify reaction products and determine the fraction of cesium which is released as aerosol from the In Farm 1 simulant reaction. Measurements will be made of the aerosols released from the In Farm 1 simulant reaction.

- **Problem Areas and Action Taken.** None.
- **Milestone Status.**
  - **December 31, 1992**: Define parametric and aerosol sampling tests to be conducted at FAI using In Farm and U Plant flowsheet ferrocyanide waste simulants. Parametric tests and the scope of aerosol tests to be conducted at FAI were defined with Dr. H. K. Fauske of FAI on December 10, 1992. The letter to FAI authorizing these tests was issued January 12, 1993.
  - **July 31, 1993**: Complete parametric and selected aerosol tests on the most reactive (In Farm) flowsheet simulant at FAI and issue a test report that is approved for public release.

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

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

Figure 2-15. Aerosol Test Containment Vessel at Fauske and Associates, Inc.



2.6.1 Action Plan for Response to Abnormal Conditions

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

Also addressed in this section are actions in response to other abnormal conditions that might be encountered with the ferrocyanide tanks, such as a leak to the environment. Of the 24 ferrocyanide tanks, 14 are classified as assumed leakers, including 241-T-101 which was added to the assumed leaker list of tanks on October 4, 1992. Six of the assumed leaker tanks have not been interim stabilized; i.e., the remaining pumpable liquid has not been removed from these tanks. Eight tanks still require some pumping to be classified as interim stabilized. Authorization to pump these tanks must be granted by DOE because the activity involves the ferrocyanide USQ. This authorization requires that SA and EA documentation be prepared for this activity.

- **Progress During the Reporting Period.** The safety assessment for removing pumpable liquids from ferrocyanide tanks addresses two different safety aspects: (1) the safety of waste storage in the tanks after pumpable liquids are removed; and (2) the safety of the pumping/transfer operations (e.g., saltwell installation, pump operation, and transfer of the liquid to a doubly contained receiver tank). Part 1 focuses on the issues that need resolution to support the recommendation on the safety of emergency pumping for the eight tanks. An evaluation of the adequacy of existing safety analyses of interim stabilization activities had previously been conducted. The results of that evaluation completed the baseline needed to perform Part 2 of the safety assessment. Both parts were completed in time to support the predecisional safety assessment transmitted to DOE on September 30, 1992. Comments were received from DOE on both the SA and EA. Comments were incorporated into the EA and it was resubmitted to DOE.

  Incorporation of comments on the SA were still in progress at the end of the quarter. The transfer line from 241-T-101 was successfully pressure tested to the receiver tank, 244-TX. The waste will be subsequently transferred to 241-SY-102. No further decreases in liquid level as measured by the Food Instrument Corporation (FIC) have occurred in 241-T-101 since plans for pumping were initiated. Several activities are requiring USQ screening evaluations to insure the activity can be completed with an acceptable risk. Some of these activities include the need to install manual liquid and solids level measurement devices, photography of the interior of the tank, and installation of the saltwell screen and pump.

- **Planned Work for Subsequent Months.** Requirements governing the frequency of ferrocyanide tank vapor monitoring may be added to the action plan if planned vapor space sampling identifies significant gas concentrations that would justify routine or constant surveillance. Once sufficient data are available from the vapor sampling program to form a sound technical basis, these requirements will be established and implemented if appropriate.

  Comments received on the SA are being reviewed and will be incorporated by January 29, 1993. It is expected that DOE will authorize pumping of 241-T-101 during the second quarter of FY 1993. Preparations for pumping are being made with procurement and fabrication of a saltwell screen, a pump, and associated equipment.

- **Problem Areas and Action Taken.** A Justification for Continued Operations (JCO) was previously submitted to DOE to address the USQ involving criticality safety in the waste tanks. The JCO was revised this quarter to allow stabilization of the ferrocyanide tanks. Tank stabilization is on administrative hold until the consequences of stabilization, as related to tank criticality safety issues, are reviewed. The criticality USQ impacts pumping of both Watch List and non-Watch List tanks.

- **Milestone Status.**

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

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

  - **December 31, 1992**: Incorporate comments into the SA and EA documents as appropriate and submit revised documents to DOE for review. The EA was revised and resubmitted to DOE but the SA will not be submitted until January 29, 1993.

  - **February 1, 1993**: Receive authorization from DOE, based upon revised SA and EA documentation, to proceed with pumping of leaking ferrocyanide tank 241-T-101. The schedule date for initiation of pumping has been changed to the first part of March 1993.

  - **March 31, 1993**: Complete an evaluation report to determine which gases, if any, need to be continuously monitored on selected ferrocyanide tanks.

2.6.2 Response to an Airborne Release from a Ferrocyanide Tank

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

- **Progress During Reporting Period.** As noted in the previous report, all of the planned milestones had been completed.

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

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

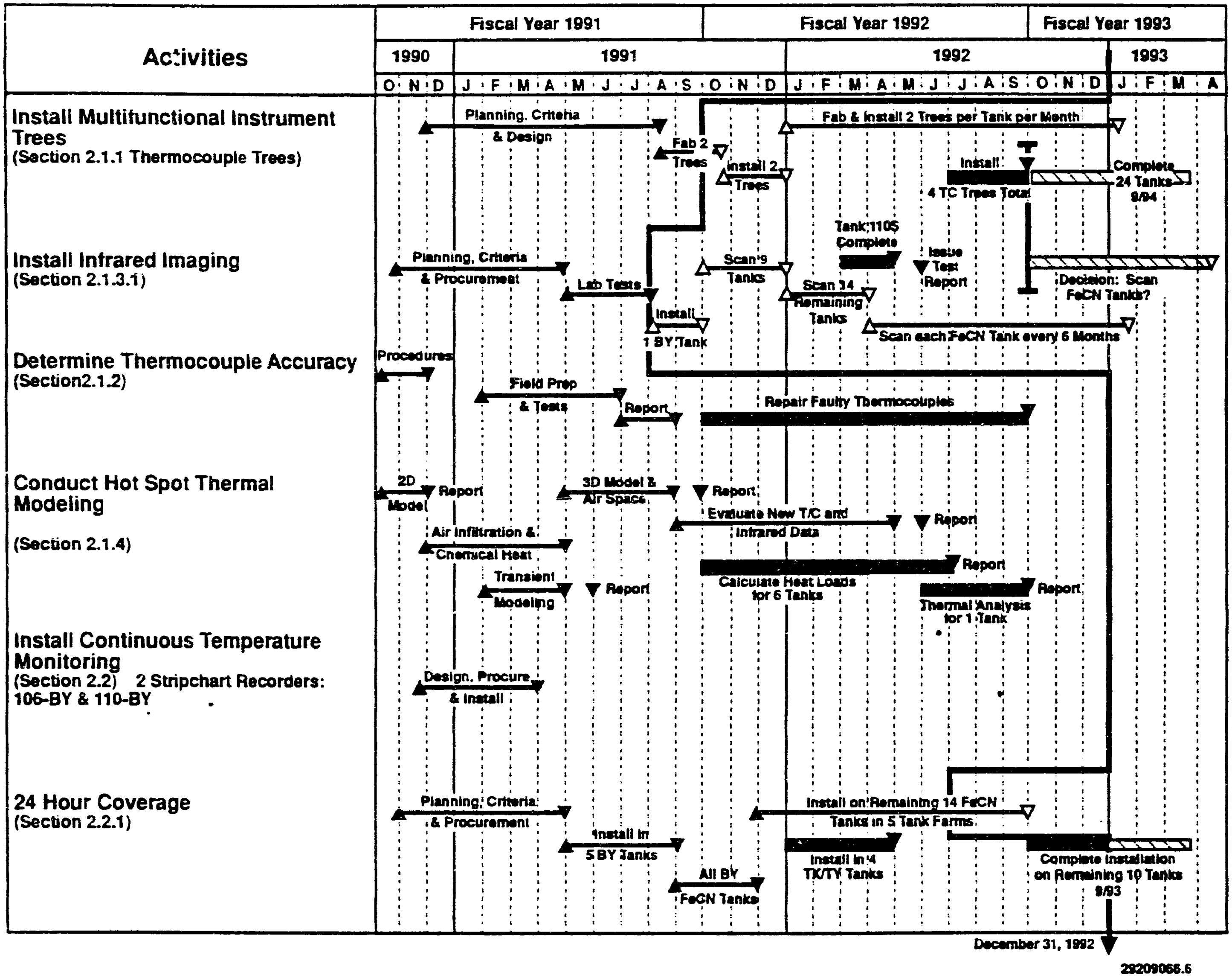
- **Milestone Status.** None applicable.

3.0 SCHEDULES

Two sets of schedules are provided in this section, as shown in Schedules 3-1 and 3-2. Each set of schedules has been statused for the first quarter of FY 1993, ending December 31, 1992. The old schedule was originally established when the implementation plan (Cash 1991) was issued in March 1991; it is provided to show work completed through the first quarter in FY 1993. The new schedule (3-2) was prepared for the revised implementation plan (Borsheim et al. 1992) and shows work on the Ferrocyanide Safety Program for FY 1991 through FY 1994. Because the scope of some of the program activities has changed over the past two years, it is appropriate that progress in the future be tracked against the new schedule.

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

Schedule 3-1. (Sheet 1 of 3)



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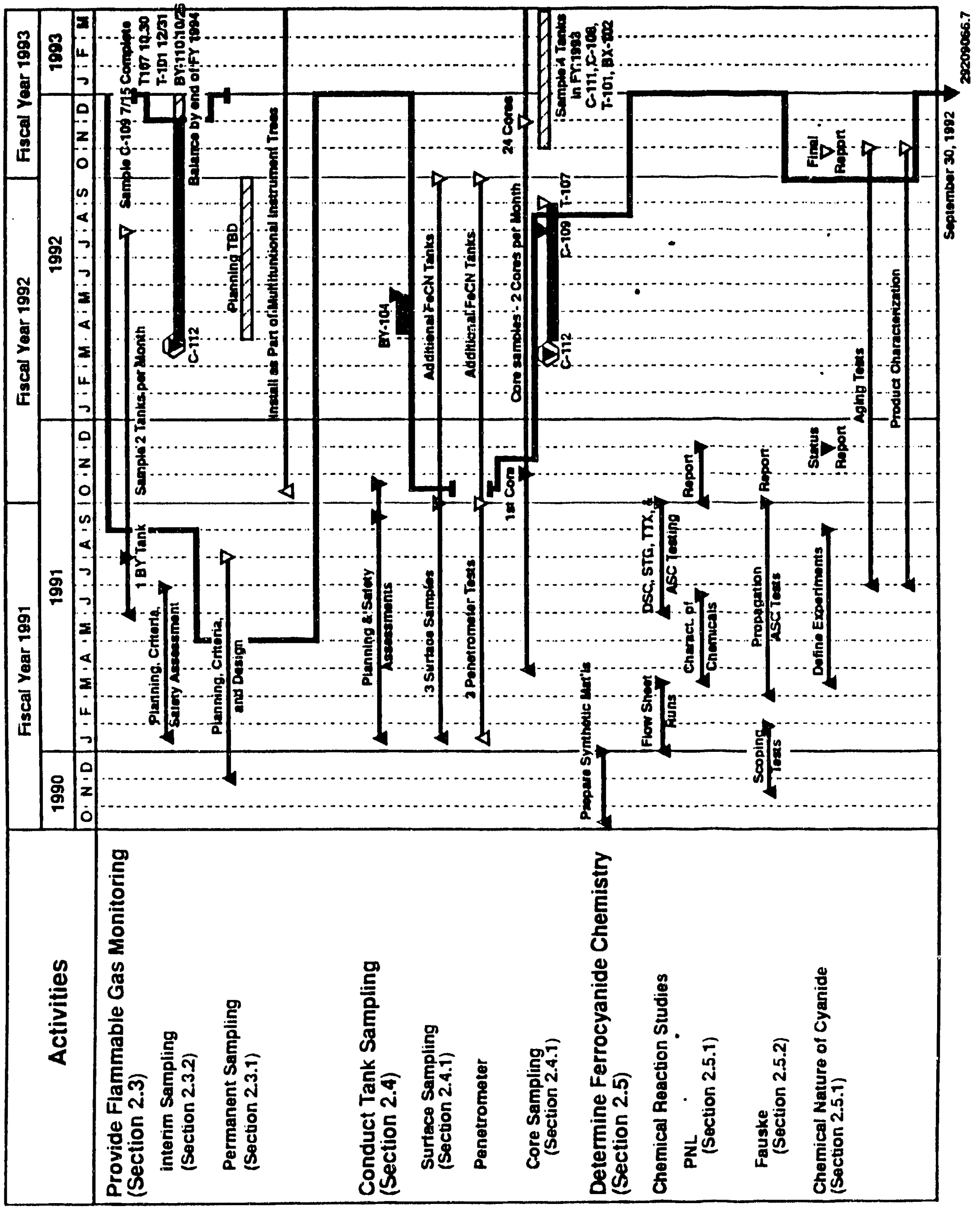

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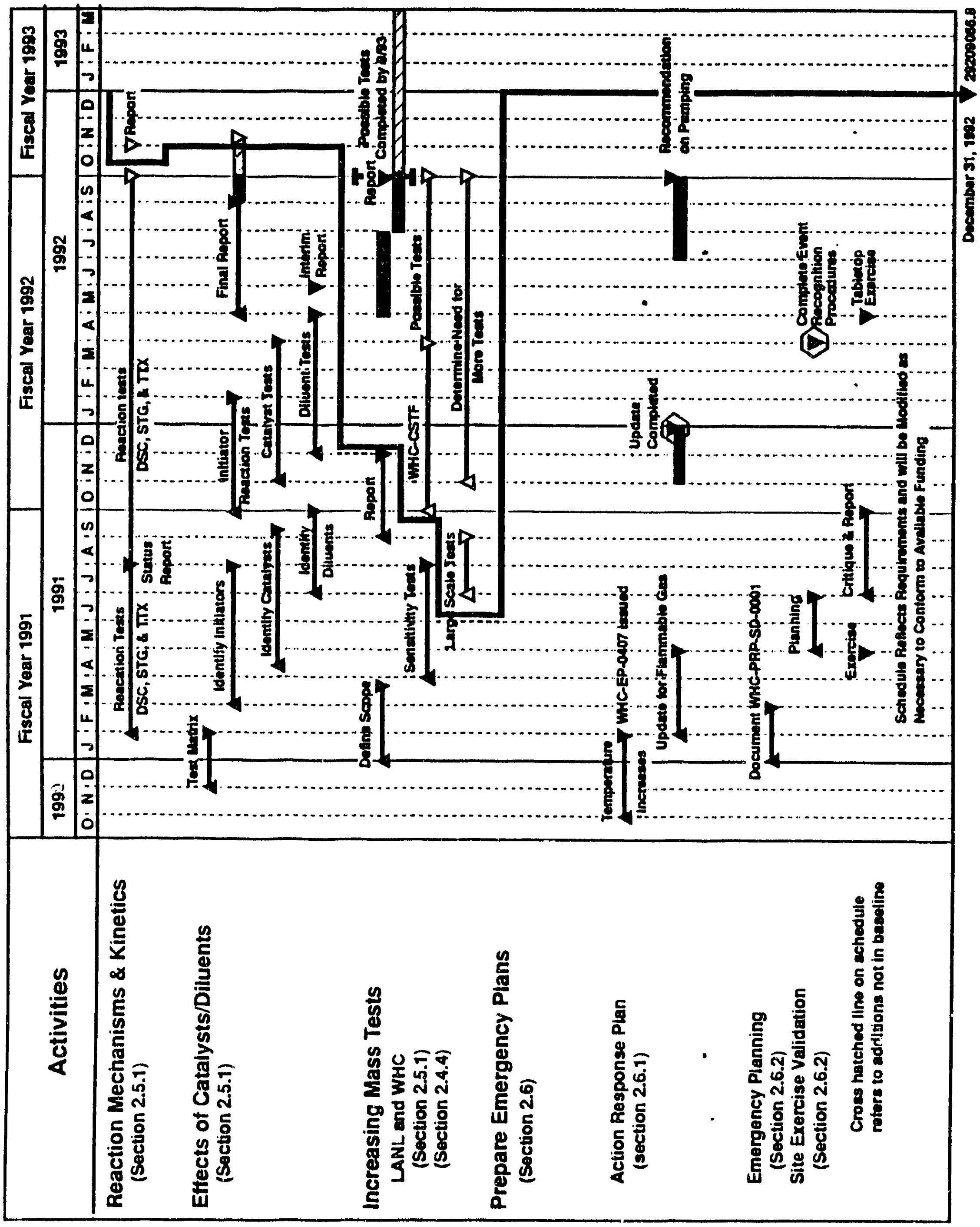

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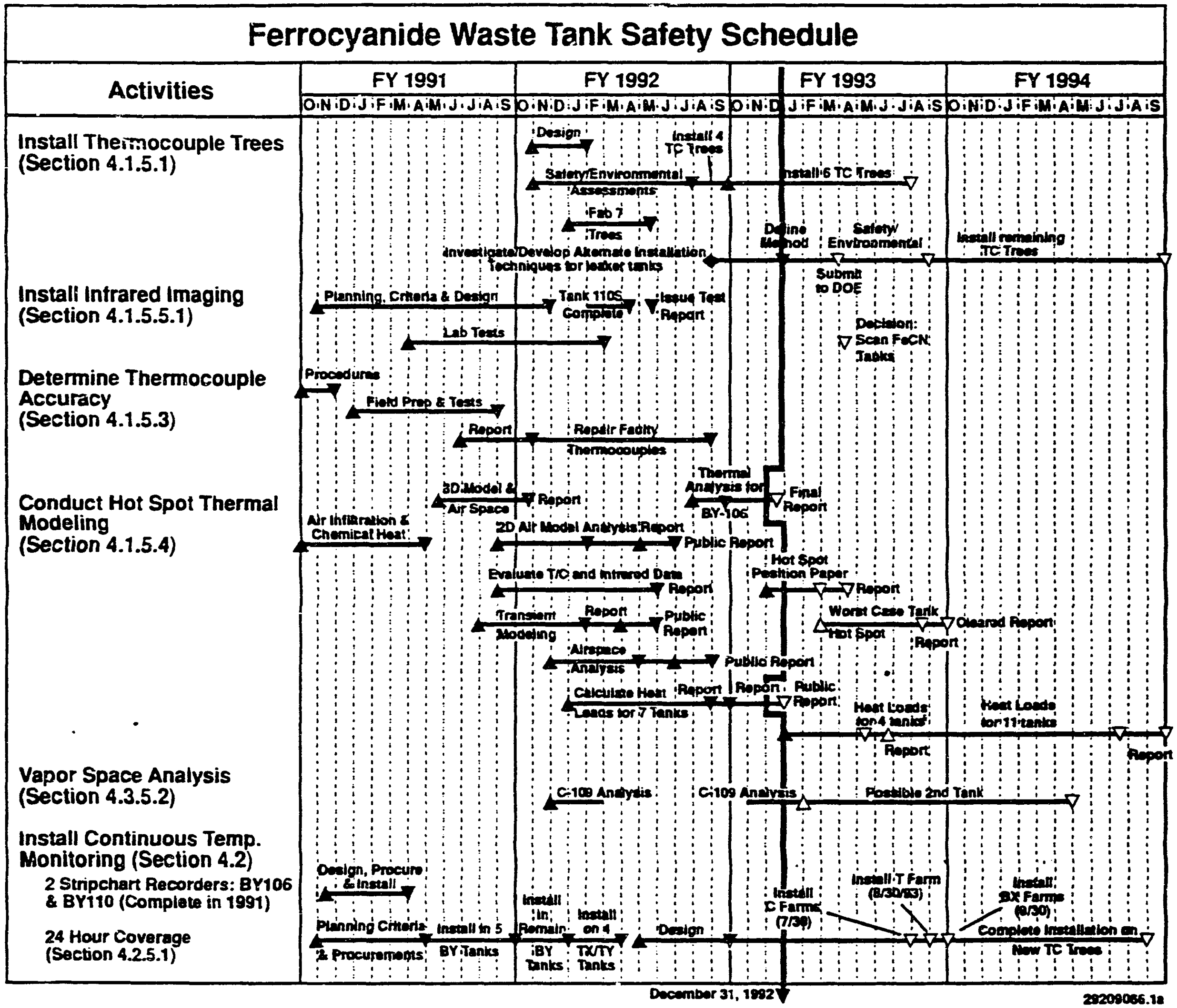

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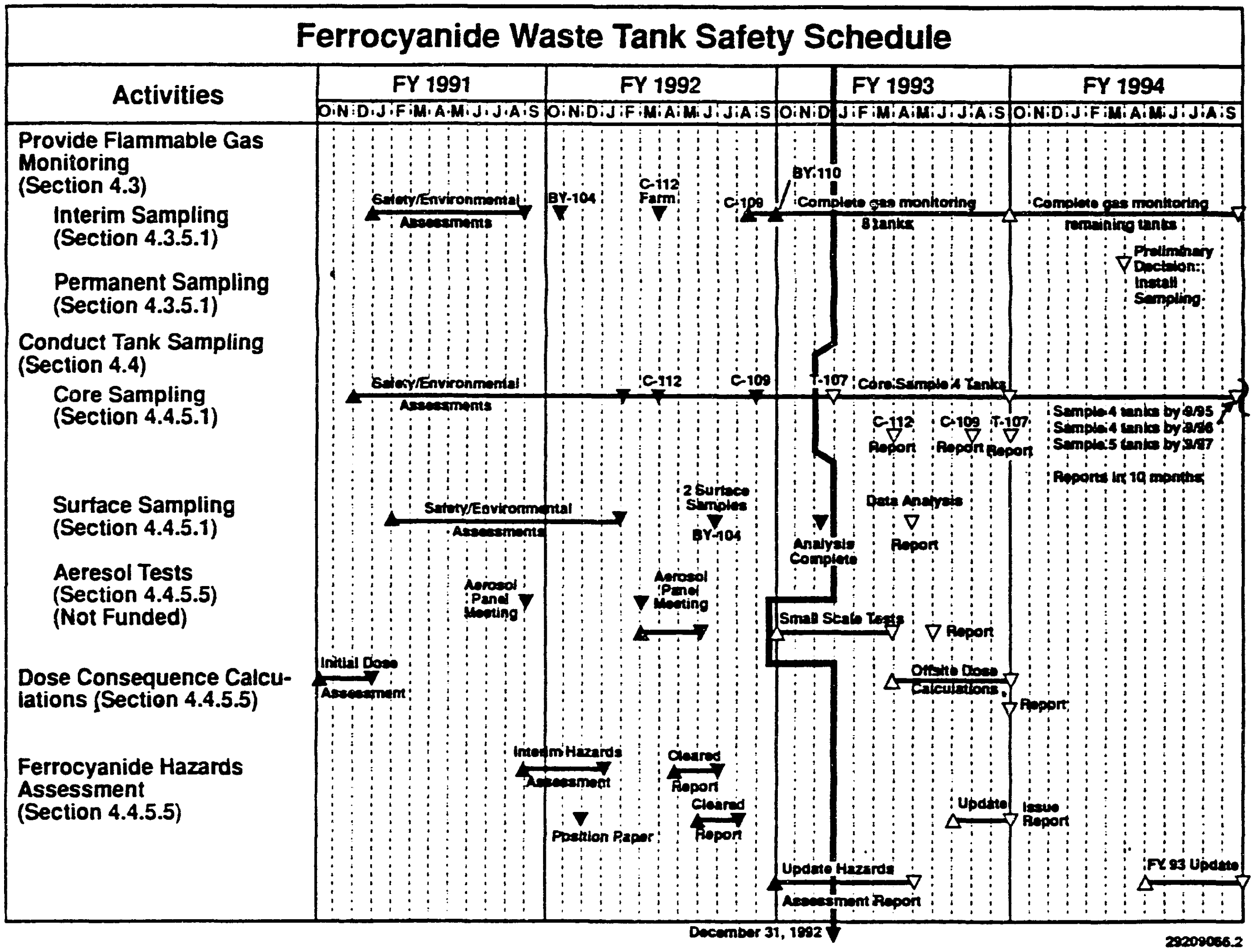

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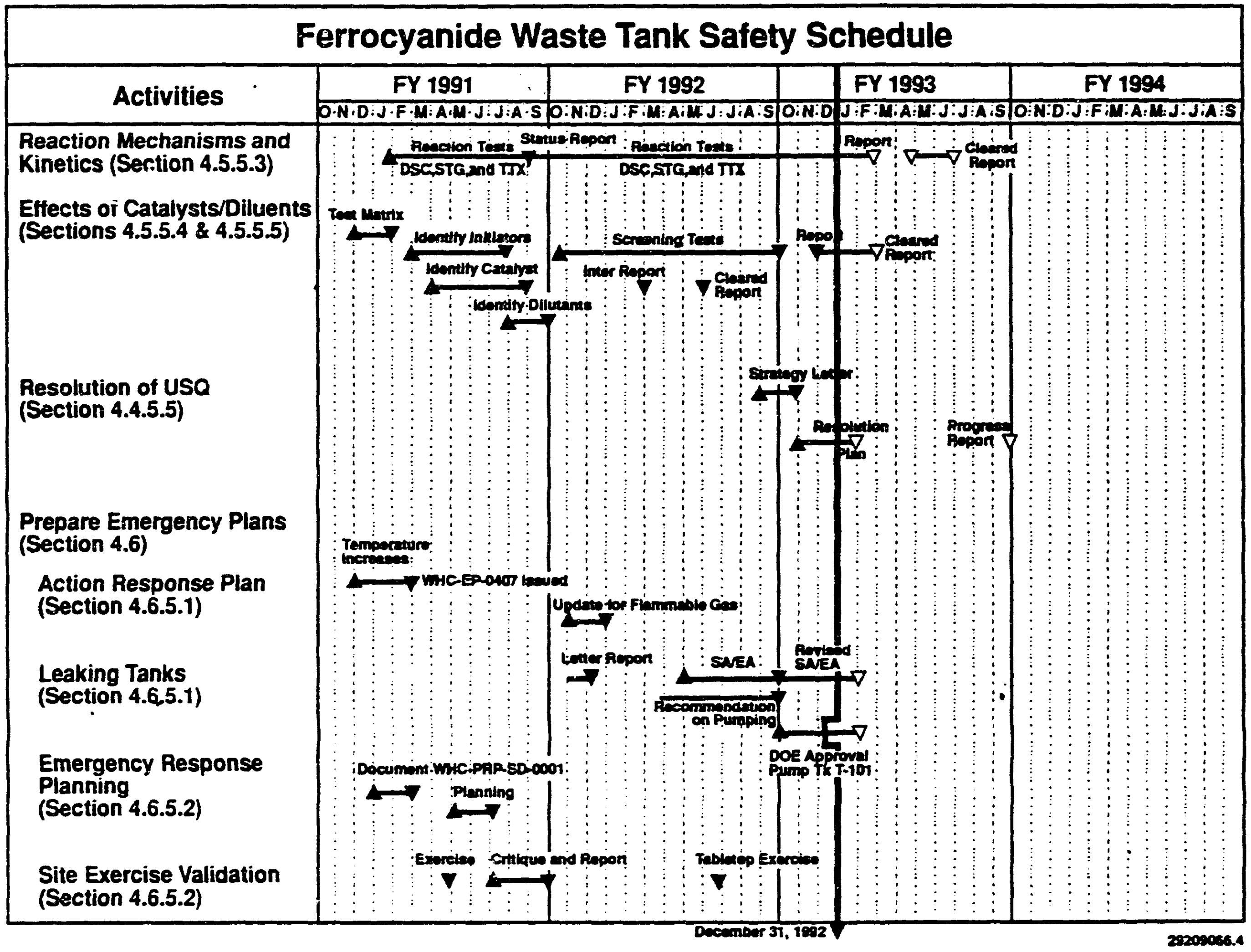

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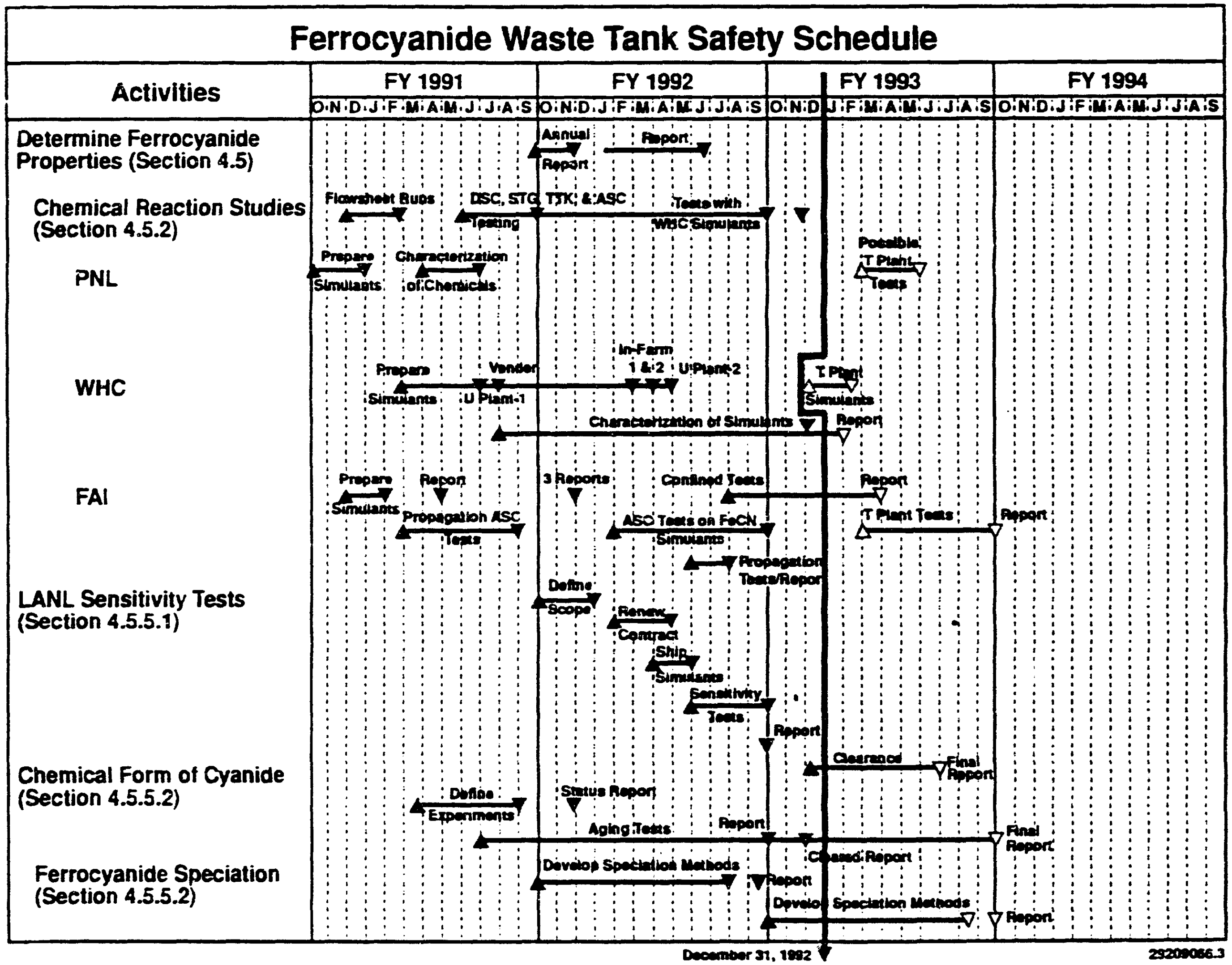

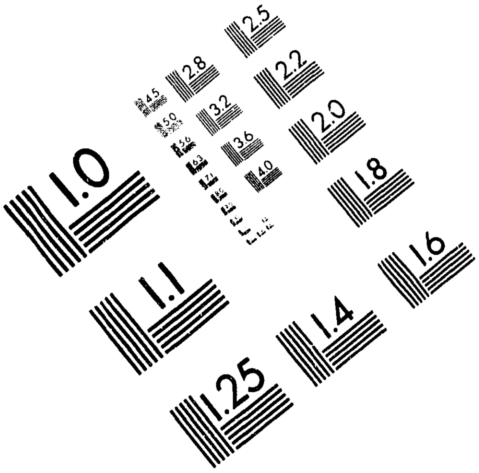

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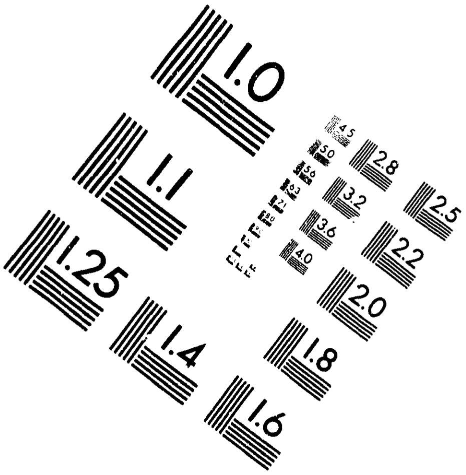

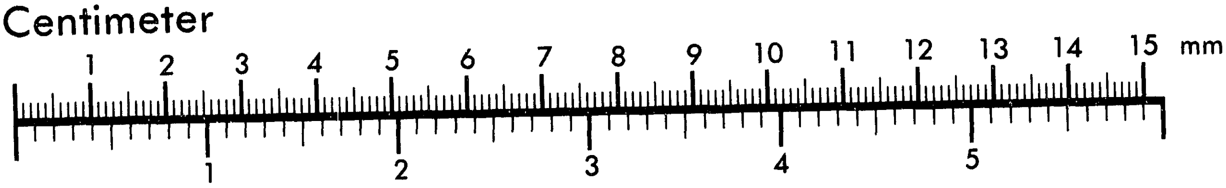

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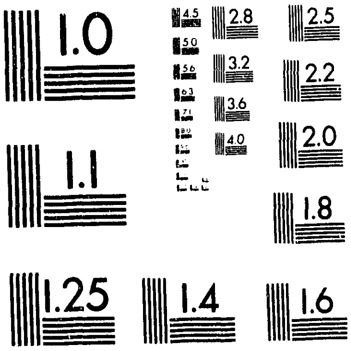

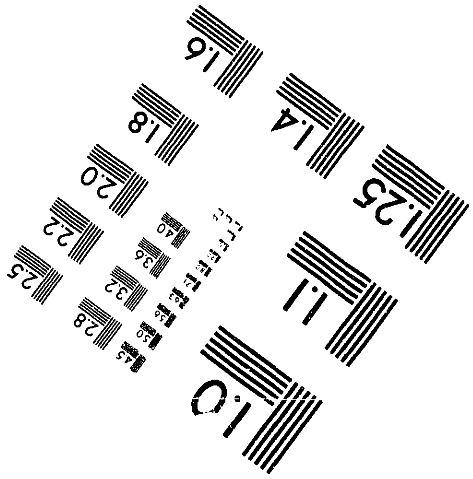

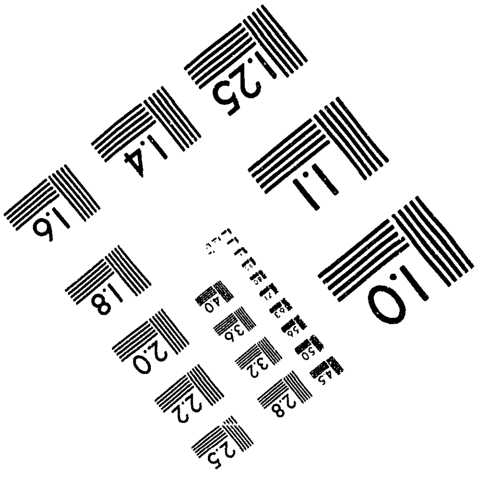

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APPENDIX A

LIST OF FERROCYANIDE TANKS

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

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g mol)	Heat load (1,000 Btu/h)[c]	Maximum temp.		Status of tanks[e]
				(°C)	(°F)	
BX-102	96	< 1	< 10	20	68	S; AL
BX-106	45	< 1	< 10	20	68	NS; Sound
BX-110	199	< 1	< 10	20	68	S; AL
BX-111	230	< 1	< 10	22	71	NS; AL
BY-101	387	< 1	8.2	24	76	S; Sound
BY-103	400	66	8.6	28	83	NS; AL
BY-104	406	83	5.5 - 11.0[d]	54 47[f]	130 116	S; Sound
BY-105	503	36	4.0 - 8.0[d]	46 49	114 121	NS; AL
BY-106	642	70	5.5 - 11.0[d]	55	131	NS; AL
BY-107	266	42	14.5	35	95	S; AL
BY-108	228	58	4.4 - 8.8[d]	44	111	S; AL
BY-110	398	71	4.0 - 8.0[d]	49 42[f]	120 108	S; Sound
BY-111	459	6	2.4 - 4.8[d]	30	86	S; Sound
BY-112	291	2	< 10	28	83	S; Sound
C-108	66	25	< 10	26	78	S; Sound
C-109	66	30	3.5 - 7.0[d]	27 27[f]	80 80	S; Sound
C-111	57	33	< 10	25	77	S; AL
C-112	109	31	< 10	28 28[f]	38 83	S; Sound
T-101	133	< 1	< 10	23	73	NS; AL
T-107	180	5	< 10	22	71	NS; AL
TX-118	347	< 3	4.9	26	78	S; Sound
TY-101	118	23	< 10	20	68	S; AL

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

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g mol)	Heat load (1,000 Btu/h)[c]	Maximum temp. (°C)	(°F)	Status of tanks[e]
TY-103	162	28	< 10	22	71	S; AL
TY-104	46	12	< 10	20	68	S; AL
Totals	5,834,000 gal	624K g-mol.				

[a] Based on information contained in monthly reports (WHC-EP-0182-XX) (Hanlon 1992); temperature data as of December 1992.

[b] Inventories from Borsheim and Simpson, 1991.

[c] Heat load values are conservatively high; new values are being calculated.

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

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

[f] Temperatures recorded for new thermocouple trees installed in September 1992.

APPENDIX B

METRIC CONVERSION CHART

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Table B-1. Metric Conversion Chart.

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

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