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

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

R. J. Cash
G. T. Dukelow

ABSTRACT

This is the fourth 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 planned and underway to address each of the six parts of the recommendation.

Activities listed in the implementation plan are continuing except for penetrometer testing and those tasks that have been completed. Waste properties expected from penetrometer tests will be obtained from auger samples. A number of ferrocyanide program milestones were completed this quarter; others were delayed because implementing preparations for and obtaining the approval to proceed with intrusive tank operations took longer than planned. Restricted access to all tank farms was also imposed on January 28, 1992, when an unrelated incident near the BX and BY Tank Farms occurred that released noxious vapors. At the time, the vapors were suspected

to have come from these tanks, however, the gases were later traced to an overcharged battery. Although the restrictions have been reduced, all work in or around a ferrocyanide tank still requires supplied air respirators, because of the safety concerns from potential emission of cyanide-based gases.

A revised implementation plan was drafted this quarter. It is currently being reviewed internally and will be issued to the U.S. Department of Energy next quarter. The revised plan will provide an updated schedule and will factor in the current status of understanding on the ferrocyanide safety issue.

A decision was made this quarter not to install multifunctional instrument trees in ferrocyanide tanks. The first unit presently being fabricated by Los Alamos National Laboratory will be put into tank 241-SY-101, the hydrogen generating tank, to support planned mitigation efforts. Instead, four thermocouple trees are being fabricated for installation on a priority basis in ferrocyanide tanks. At the end of the quarter hardware fabrication and inspection of the four trees had been completed and only installation of the thermocouple elements remained.

Preparations for completing an infrared scan in a non-watchlist tank are nearly complete. The scan of tank 241-S-110 is scheduled for April. Results from this work will help determine whether infrared scanning is feasible for detection of hot spots in ferrocyanide tanks, and whether additional scans are warranted.

Vapor space sampling and push-mode core sampling of tank 241-C-112 were completed in March. A total of seven cryogenic trap gas samples and three core samples were taken from the tank. Field monitoring at the tank showed less than 1 percent of the lower flammability limit on the combustible gas meter, less than 0.01 percent hydrogen on the sampling van gas chromatograph, and non-detectable amounts of toxic vapors using Draeger tubes. The cryogenic samples are currently undergoing analyses. Two 48 cm (19 in.) segments per core sample were obtained with the push-mode core sampling truck, as expected because this tank contains less than 400,000 L (104,000 gal) of waste. Readiness preparations have begun on the next tank, 241-C-109, to be sampled in the third quarter of FY 1992.

Four of the five batches of ferrocyanide flowsheet simulant have been prepared by the Westinghouse Hanford Chemical Engineering Laboratory for testing at various participating laboratories. Chemical reaction studies at Pacific Northwest Laboratory and Fauske and Associates, Inc. on In-Farm flowsheet ferrocyanide simulants show that the concentration of material is high enough to allow propagation when the material is dry. Other analyses show that this material also retains about 50 wt% water even after 30 equivalent gravity years of centrifugation.

Comments were not received in time this quarter from the Tank Advisory Panel and other offsite reviewers to be able to revise the three predecisional documents (see Section 2.4) issued in November 1991 and to release them for public availability. This action will be completed next quarter.

The action to develop and issue Tank Farm emergency event recognition and classification procedures, protective action recommendations, and an emergency notification plan was recently completed ahead of the May 15, 1992, scheduled date. These procedures have been issued to the U.S. Department of Energy for their required approval.

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
CTMS	Continuous Temperature Monitoring System
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DSC	differential scanning calorimetry
EA	environmental assessment
EDTA	ethylenediaminetetraacetic acid
FAI	Fauske and Associates, Inc.
FY	fiscal year
FTIR	Fourier Transform Infrared
HEDTA	hydroxydiaminetetraacetic acid
HLW	high-level radioactive waste
HWVP	Hanford Waste Vitrification Plant
IC	ion chromatography
ICP	inductively coupled plasma
LANL	Los Alamos National Laboratory
LOW	liquid observation well
MIT	multifunctional instrument tree
PNL	Pacific Northwest Laboratory
RL	U.S. Department of Energy, Richland Field Office
RSST	Reactive Systems Screening Tool
SA	safety assessment
SEM	scanning electron microscopy
STG	scanning thermogravimetry
TAP	Tanks Advisory Panel
TC	thermocouple
TMAC	Tank Monitoring and Control System
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*
VSP	Vent Sizing Package
Westinghouse Hanford	Westinghouse Hanford Company
XRD	X-ray diffraction

QUARTERLY REPORT ON DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7 FOR THE PERIOD ENDING MARCH 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, an DNFSB Implementation Plan (Cash 1991a) was prepared and sent to the DNFSB responding to the six parts of Recommendation 90-7. All of the activities in the DNFSB Implementation Plan are underway and the status of each is described in Section 2.0.

1.2 QUARTERLY HIGHLIGHTS

- A decision was made this quarter to install the first multifunctional instrument tree (MIT) now being fabricated at Los Alamos National Laboratory (LANL) in hydrogen tank 241-SY-101 to support the planned mitigation effort on this tank. The decision was also made that unless requirements dictate otherwise, only thermocouple (TC) trees will be installed in the ferrocyanide tanks.

- The first four TC trees scheduled for installation in ferrocyanide tanks in fiscal year (FY) 1992 were completed in the Westinghouse Hanford Company (Westinghouse Hanford) shops. An order was also placed offsite for fabrication of eight additional TC trees, with the option to order more in multiples of 10 trees each.

- Attempted repair and/or recovery of TCs reported as failed or marginal in WHC-SD-WM-ER-134 (Bussell 1991) is underway in FY 1992. Over 30 TC elements have been restored in five BY Farm ferrocyanide tanks.

- Preparations are on schedule for performing in April an infrared scan of the waste surface in a non-watchlist waste tank [241-S-110]. Any decision to use this system in a ferrocyanide tank will depend upon the results of this test and other studies in progress.

- A workshop on moisture monitoring techniques was held in February 1992 in order to survey state of the art technology that might be applicable to measuring the in situ water content of the waste as a function of elevation. The consensus of attendees was that the neutron probe approach appeared to be the most promising technique. Enhancement analysis of the existing neutron scanning system now used routinely at Hanford shows that moisture determinations from 0 to 70 wt% should be feasible.

- A development contract was placed this quarter with Florida State University (FSU) to enhance Raman scattering capabilities for quantitative measurement of ferro and ferricyanides in a waste matrix. U-Plant and In-Farm ferrocyanide waste simulants were shipped to FSU for test materials.

- A computer analysis of the air space in tank 241-BY-104 was completed to determine if the convective airflow through the tank could cause the waste to dry out with time and to also calculate the heat loss from this airflow. The analysis determined that a conservative estimate of water loss amounted to only 0.13 L/h (0.8 gal/day) with an airflow of 1.9 L/s into the tank. Heat loadings were calculated for three tanks; values are significantly lower than listed in Table A-1 of Appendix A.

- The design to connect three tanks in TY Farm and one tank in TX Farm into the continuous temperature monitoring system was completed. Installation is currently underway. The FY 1992 scope of work was expanded to include four ferrocyanide tanks in C Farm and two in T Farm.

- Gas sampling of the dome space in ferrocyanide tank 241-C-112 was completed in March. Field instrumentation showed no detectable concentrations of flammable or toxic gases for the tank. The cryogenic trap samples were submitted to the laboratory for analysis.

- Full-depth core samples [two segments each] were taken from tank 241-C-112 risers 2, 7, and 8 in March. Activities for obtaining surface samples from tank 241-BY-104 by use of the auger technique were delayed as a result of new administrative requirements for supplied air respiratory protection when working near ferrocyanide tanks.

- Three of the four remaining simulant wastes for testing were produced during the quarter: In-Farm 1, In-Farm 2, and U-Plant 2. In-Farm dried materials exhibit propagating reaction tendencies, as expected. These test materials represent wastes in the four C farm tanks.

- The safety assessment (SA) for installing new TC trees was in progress at the end of this quarter.

- Dissolution experiments using sodium nickel ferrocyanide were run in 1.0 N NaOH, 0.1 N NaOH, and 0.01 N NaOH at room temperature in order to determine how quickly the precipitate would become soluble as nickel hydroxide is formed. This work is important because a high pH within the ferrocyanide tanks could have caused the ferrocyanide to become soluble and be transferred to other tanks during waste transfers.

- A matrix of catalyst/initiator time-to-explosion (TTX) tests was completed to determine if certain elements present in the waste tanks could initiate a ferrocyanide - nitrate/nitrite reaction at

lower temperatures. Ethylenediaminetetraacetic acid (EDTA) and EDTA with some transition metals and/or chromium show a slight lowering of the explosion temperature.

- Although agreement had been reached among Westinghouse Hanford Company (Westinghouse Hanford), Pacific Northwest Laboratory (PNL), and LANL on sensitivity testing of four waste simulants, placement of the contract with LANL has been held up due to several quality assurance clauses. Resolution of the problems was achieved in early April and the contract has now been placed.

- Fauske and Associates, Inc. (FAI) completed adiabatic scanning calorimetry (ASC) tests on upper and lower fractions of In-Farm 1 and In-Farm 2 centrifuged waste simulants. Upper and lower fractions were tested because definite color differences were noted after centrifugation. The measured water content of these simulated wastes after centrifugation is 50 wt%.

- The action to develop and issue tank farm emergency event recognition and classification procedures, protective action recommendations and an emergency notification plan was completed, ahead of the May 15, 1992 scheduled date.

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 DNFSB Implementation Plan (Cash 1991a)*. 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 1940's. During the 1950's, additional tank storage space was required to support the defense mission. To obtain this additional storage volume within a short period of time and without constructing additional storage tanks, Hanford Site scientists developed a process to scavenge radiocesium from tank waste liquids. In implementing this process, approximately 140 metric tons of ferrocyanide were added to 24 single-shell tanks.

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*See Appendix B for metric-to-English and English-to-metric conversions.

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, ferrocyanide can be made to explode in the laboratory by heating it to high temperatures (above 285 °C) or 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 possible that an intimate mixture of ferrocyanides with nitrates and nitrites exists in parts of some of the single-shell tanks.

Efforts have been underway since the mid-1980's to evaluate the potential for a ferrocyanide explosion in the Hanford Site single-shell tanks (Burger 1989; Burger and Scheele 1988). In 1987, the environmental impact statement 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 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 environmental impact statement (DOE 1987). 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 (DOE 1990) 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).

Using process knowledge and transfer records, an evaluation process that is still ongoing, 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 Hanford Site environmental impact statement (DOE 1987). Work in and around any of the

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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."

ferrocyanide tanks requires detailed planning with the preparation of supporting safety and environmental documentation and approval by U.S. Department of Energy (DOE) top management. These restrictions are required for safety and increase the time required to complete work or install equipment in the tanks.

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2.0 DEFENSE NUCLEAR FACILITIES SAFETY BOARD IMPLEMENTATION PLAN TASK ACTIVITIES

The DNFSB Implementation Plan (Cash 1991a) addresses each task activity set up in response to the six parts of DNFSB Recommendation 90-7 (FR 1990). In this progress report, each part of the recommendation is stated, and then the progress of activities relating to that part is described.

2.1 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.1

"Immediate steps should be taken to add instrumentation as necessary to the single-shell tanks containing ferrocyanide that will establish whether hot spots exist or may develop in the future in the stored waste. The instrumentation should include, as a minimum, additional thermocouple trees. Trees should be introduced at several radial locations in all tanks containing substantial amounts of ferrocyanide, to measure the temperature as a function of elevation at these radii. The use of infra-red 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

The DNFSB Recommendation 90-7.1 requested action be taken to add instrumentation to the ferrocyanide waste tanks 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 waste tanks of high concern 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 MITs in those tanks that have a limited number of risers available. The TC trees would provide temperature monitoring but would not provide any other needed data such as gas sampling, although a review will be made to determine if it might be possible to install tubing on the TC trees for gas monitoring.

- **Progress During This Reporting Period.** The TC tree fabrication has been completed for ferrocyanide tanks 241-C-109, 241-C-112, 241-BY-104, and 241-BY-110. The TC trees were fabricated from designs that were updated during the last reporting period. Once these trees are installed, there will be two functioning TC trees in each of the four tanks, spaced as far apart inside the tanks as available riser space allows. The first of the four new trees is currently scheduled to be installed in May 1992.

  Safety and environmental assessments were drafted and are in the final review/approval cycle at Westinghouse Hanford at the end of the quarter. Supporting studies were also completed, including an

engineering evaluation of alternatives, a seismic analysis, and laboratory work to determine the effects of using water to sluice the TC tree into the waste.

A higher quality TC element specification was prepared that will provide Westinghouse Hanford with retrievable vendor calibration data for each TC element ordered. Since the last reporting period, TC elements have been ordered for the first 12 TC trees. The TC elements are scheduled for receipt at Hanford by mid April 1992.

A decision was made this quarter to install the first MIT in tank 241-SY-101 to support the hydrogen program mitigation efforts. Consideration is being given to eliminating MITs in ferrocyanide tanks and installing TC trees instead. Thermocouple trees can be procured at a faster rate and are considerably less expensive. Most of the advantages offered by the MIT are not needed for the FeCN tanks. The one exception is the installed capability to monitor dome gases. Other options will be reviewed as necessary for that capability.

- **Planned Work for Subsequent Months.** Installation procedures for the TC trees have been started and will be completed. An operational readiness review will be started and completed in time to support installation of the first TC tree.

  An order for eight more TC trees for the next eight highest priority tanks has been placed with an option for ordering more trees in multiples of ten. Planning, scheduling, and cost estimates are being prepared for the additional TC trees.

- **Problem Areas and Action Taken.** To install equipment such as TC trees into waste tanks, water is normally used to sluice the equipment into the desired depth in the water. Water additions to ferrocyanide tanks, classified as assumed leakers, raises an environmental issue of whether waste could leak from the tank. The first four tanks to receive the new TC trees are listed as sound; however, 13 of the 24 ferrocyanide tanks are on the assumed leaker list. Water sluicing is the only technology currently available for installing equipment into tank wastes. The safety and environmental assessments are being reviewed to determine how this issue is to be addressed.

  The SA is now one month behind schedule because of safety concerns and the water addition issue. The safety concerns have been resolved, however the water addition issue continues to delay issuance of this document.

  The *National Environmental Policy Act of 1969* documentation process (i.e., environmental assessment and finding of no significant impact) for the identified work scope has been underway since the last reporting period.

- **Milestone Status.** The first TC is scheduled to be installed in a ferrocyanide tank by May 29, 1992, and the additional three by

September 30, 1992. As a result of the issues discussed above, the first installation may be delayed because the safety and environmental documentation generally takes a minimum of two months to obtain Washington State review and DOE final approvals. Westinghouse Hanford and the U.S. Department of Energy, Richland Field Office (RL) will be requesting an expedited review. Installation of the remaining TC trees will be scheduled for FY 1993, and possibly through 1994.

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 new 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.** Work packages have been assembled for repairing non-functional TCs identified by previous evaluation efforts. Priority is given to those TCs that are located within the waste. By the end of the quarter over 30 marginal or failed TCs had been recovered in 5 BY Tank Farm ferrocyanide tanks. These TCs have been added to the computerized continuous monitoring system. The schedule for repairing these TCs has slipped because of the recently added requirement that air supplied respirators must be used for entry into all farms containing ferrocyanide tanks.

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

- **Planned Work for Subsequent Months.** Work is continuing on correcting problems with TCs and making repairs to thermocouples that are classified as marginal or failed. These repairs will improve the quality of the temperature measurements and will reduce the number of personnel required to make these measurements in the field.

- **Milestone Status.** The original planned date of March 31, 1992, for completing repair of TCs has been delayed due to other high priority safety work and tank farm entry restrictions. This work is being scheduled for completion during the next two quarters.

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 ±0.5 °C (1 °F) or less under ideal conditions, they may prove 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; however, it is currently believed it would be very marginally detected. This assumes surface irregularities and other factors affecting sensitivity are negligible or can be accounted for during analysis of infrared tank data. However, the hot spot temperature may increase too rapidly to be detected in time at the surface of the waste. In addition, apparent warm temperature irregularities on the surface could be from lower temperatures than from a hot spot at a variety of elevations above the bottom. 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. 1992).

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 single-shell tanks of 150 R/h, the useful life of an infrared camera may be limited to approximately 100 h. Therefore, deployment for surface monitoring would have to be done periodically, perhaps monthly, unless tank anomalies dictate otherwise. Another concern 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.** Questions regarding the usefulness of data that would be obtained from this system resulted in the decision to install the infrared Scanning System in a non-watchlist tank for testing during early April 1992. The results of this test will be analyzed and reported in May 1992. Any decision to use the system in a ferrocyanide tank will depend upon the results of this test and an analysis of its results. Based upon this decision, activities on the SA and environmental assessment (EA) were put on hold. They will be resumed in the future if the results of the non-watchlist tank test indicate that installation in a ferrocyanide tank is advisable.

  All fabrication, assembly, and tests of the system were completed during this report period. The acceptance test was successfully completed along with the in-tank test plan, and preparation of the field work package. The formal design review was completed and no significant issues were raised as a result of this review. All activities are now complete in preparation for the in-tank tests scheduled for completion in April 1992.

- **Planned Work For Subsequent Months.** The test in a non-watchlist tank will be completed and the results reported. These test results will be analyzed and incorporated into a final report that will include a recommendation as to the value of the system for use in ferrocyanide tanks.

- **Problem Areas and Action Taken.** No new problems or outstanding unresolved problems were encountered during this reporting period.

- **Milestone Status.** The infrared scan of tank 241-S-110 was completed on April 21, 1992, after several delays caused by mechanical and weather-related problems. Results will be reported next quarter.

2.1.3.2 In Situ Tank Moisture Monitoring. Ferrocyanide waste tank neutron and gamma scan interpretation work using data analysis and available surveillance techniques is being done to identify a method for determining in situ moisture content of the waste. Well-logging techniques coupled with computer analysis are being developed to determine their potential for obtaining new and useful information about moisture levels, material density, and other waste characteristics from the existing tank scans. This approach would then be used primarily to determine the axial moisture profile within the waste of ferrocyanide tanks.

The neutron probe used routinely to determine liquid levels utilizes closed-bottom, liquid observation wells (LOW) for access to the tank contents. This probe is sensitive primarily to thermalized neutrons, while relatively insensitive to the fast neutrons produced by the americium-beryllium source and 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 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 upon the distance between the detector and the neutron source. For short separation distances, the observed countrate increases with increasing moisture content. For larger separation distances, the observed countrate decreases for the same conditions. Using the existing scan techniques, modeling was performed to investigate the change in detector countrate as a function of the moisture content of the waste. The existing scans were acquired with an intermediate source-to-detector separation. The LOW neutron probe was designed to permit adjustment of source-to-detector separation distance by changing the detector mounting hardware. However, all of the acquired scans for liquid-level measurement have always been performed with an intermediate distance, limiting the high-resolution moisture concentration calculated measurements to below 30 wt% water.

- **Progress During Reporting Period.** On February 19, 1992, a workshop on moisture detection methods was held in Richland, Washington. Technical experts from the University of Washington Center for Process Analytical Chemistry (CPAC), Massachusetts Institute of Technology, Lawrence Livermore National Laboratory, PNL, and Westinghouse Hanford considered a wide variety of methods that could be utilized to measure moisture levels in materials in ferrocyanide tanks. An evaluation survey completed by the attendees indicated that the neutron probe approach appeared to be the most promising technique for early deployment in tanks with LOWs. Recommendations were made to explore alterations to the existing probe and to improve data processing to enhance sensitivity over a wider moisture range.

A Monte Carlo Neutron Photon code model of the probe and the tank were used to perform scoping studies. Graphic representations of these studies investigating detector response as a function of moisture content and the source-to-detector separation distances are shown in Figure 2-1. A significant improvement over past methods was achieved. Well chosen source-to-detector distances reveal discernable moisture levels over the entire range in question of 0 to 70 wt% water. Figure 2-2 shows the near-field (7.93 cm) and far-field (21.68 cm) detector response as a function of moisture content. The near-field to far-field ratio is then compared to the existing scan probe configuration (near field). It can be seen that the near-field to far-field ratio increases monotonically throughout the water concentration range.

To further enhance near field effects, a shorter axial detector region closer to the source can be partially achieved by shielding the upper region of the detector with a thin layer of cadmium. Figure 2-3 shows the near-field response with and without the cadmium shielding. This ratio with cadmium is then compared to the ratio without cadmium. A better response in the low water concentrations is obtained without the cadmium shielding whereas a better response in the high water concentrations is achieved with the cadmium shielding.

The possibility of validating the neutron probe in known hydrogen-containing materials was explored. The container used to store the neutron probe was modeled; countrate data exist and the material composition is known.

- **Planned Work for Subsequent Months.** Westinghouse Hanford plans to determine the depth of material the probe is interrogating for various source-to-detector separation distances and different material compositions. This will be an important factor in characterizing the region around the LOW.

  The neutron probe's ability to discern small inhomogeneous perturbations in the tank media, including voids, will be studied over a range of various source-to-detector distances. Because calibration is strongly sensitive to the borehole and media under investigation, a calibration facility will be needed that simulates an LOW and the tank environment.

  Guidance will be provided to the data acquisition organization. This will modify source-to-detector distances, to suggest data acquisition methodology and to provide data processing and interpretation.

  Further proposals for moisture measurement technology are being solicited, primarily in the area of chemical sensor technology. When all proposals have been received, an evaluation will be made to select the most promising. A development program will be initiated and a schedule will be developed.

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

Figure 2-1. Simplified Geometry for Monte Carlo Neutron Photon Code Calculations.

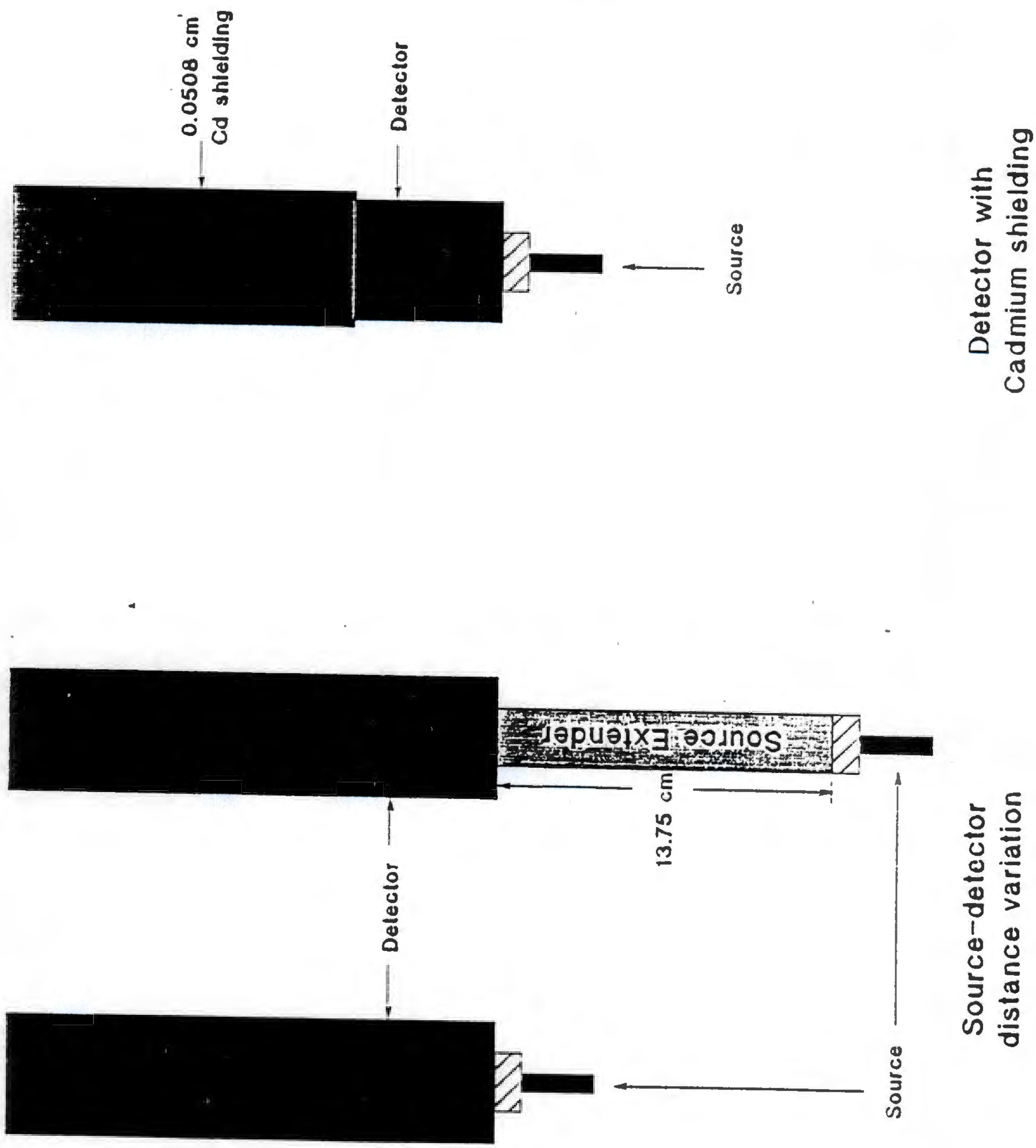


Figure 2-2. Calculated Neutron Detector Response as a Function of Moisture Content at Varied Source-to-Detector Distances.

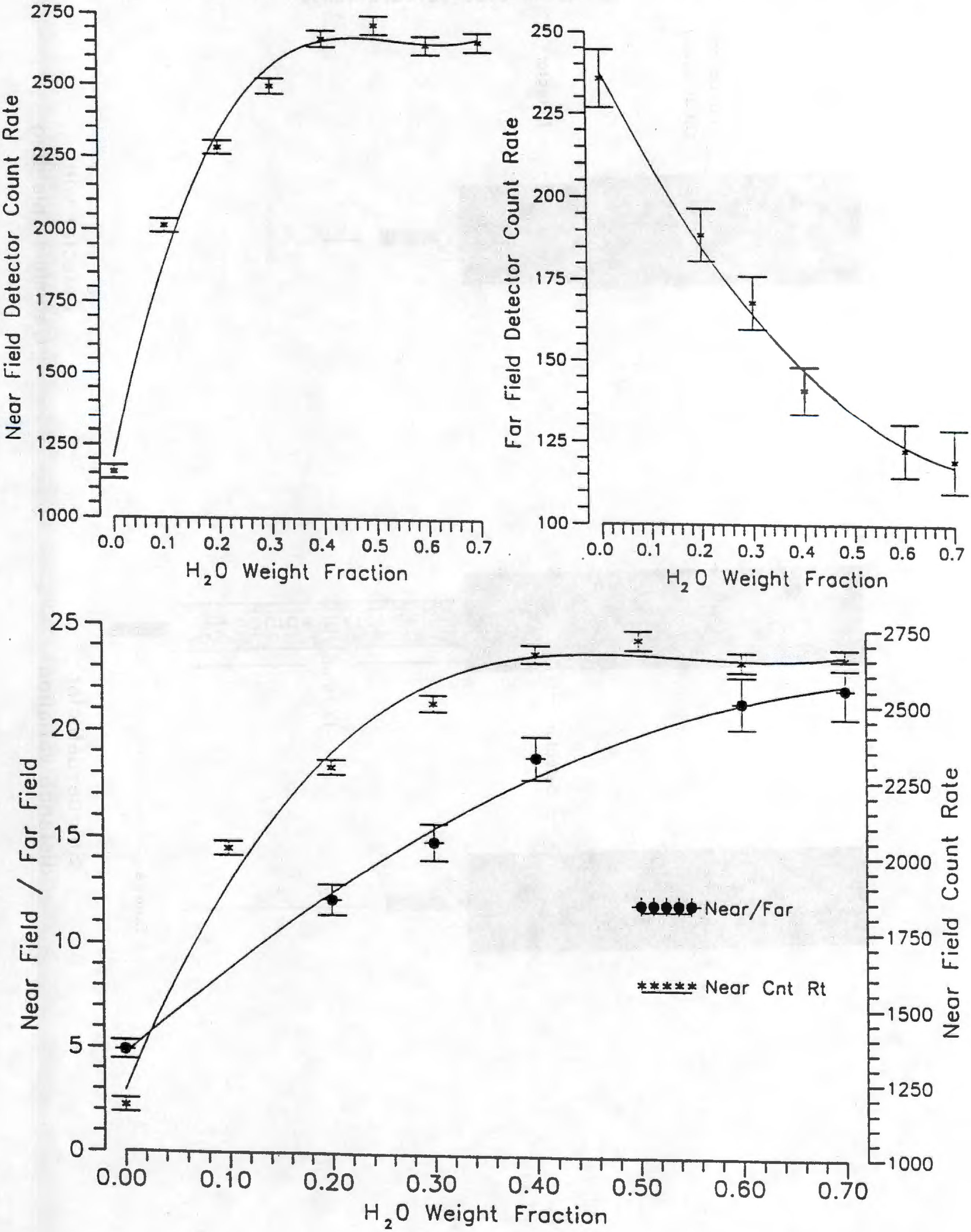
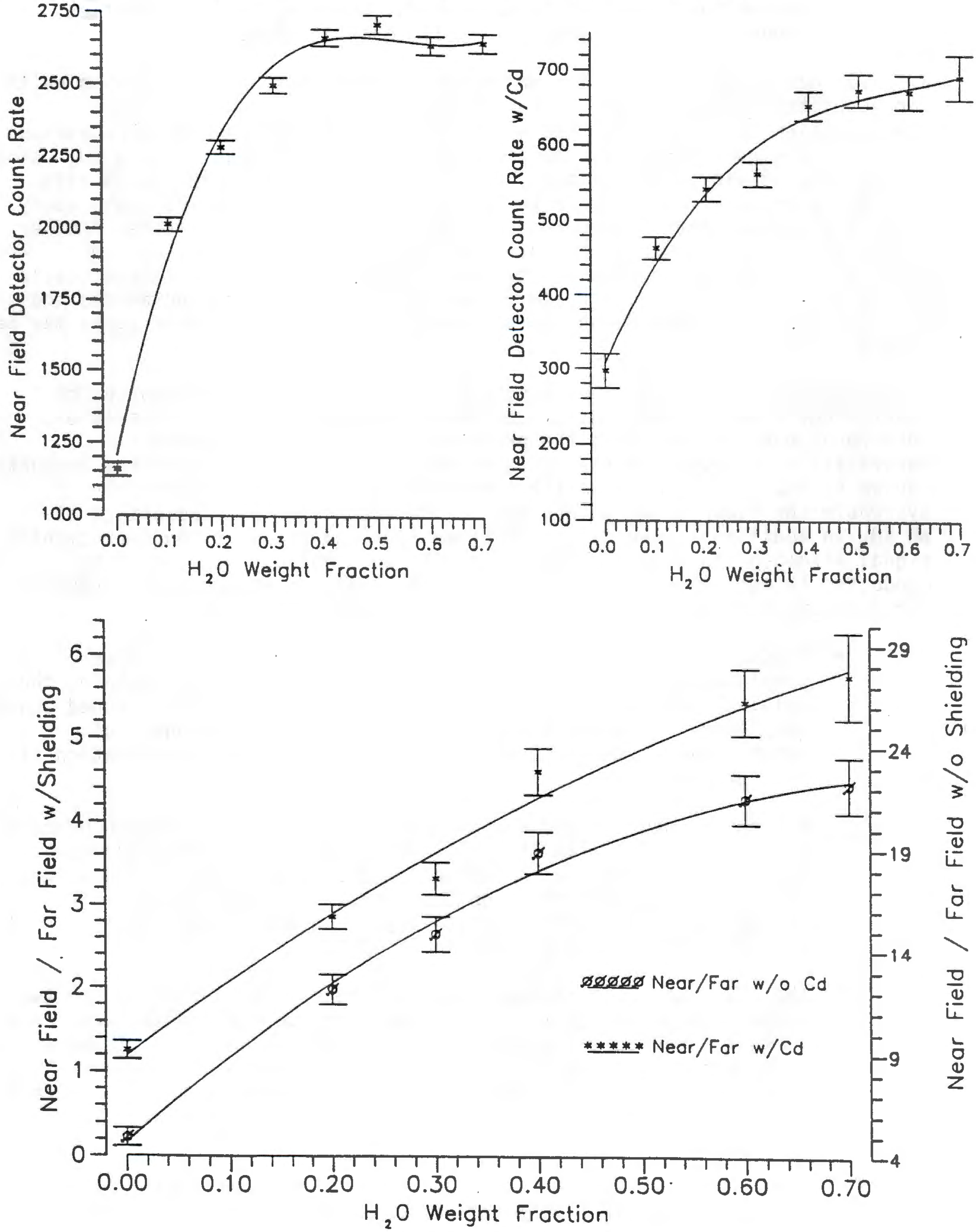


Figure 2-3. Calculated Neutron Detector Response as a Function of Moisture Content With and Without Cadmium Shielding.



- **Milestone Status.** A letter report documenting the Monte Carlo methodology, the basis for the methodology, and the modeling results obtained was completed. The report also included a description of recommended tasks to be performed, including field activities. This report will be cleared for public distribution.

2.1.3.3 Raman Scattering. The objective of this work is to develop a method for quantitative measurement of ferrocyanide and ferricyanide in the concentration levels and morphology existing in each of the 24 ferrocyanide tanks. Techniques for measuring ferrocyanide and ferricyanide in situ, using remote sensing via optical fibers, will be pursued in addition to ex situ methods, where core samples are to be 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 hydroxydiaminetetraacetic acid (HEDTA). Both ferrocyanides and nitrates exhibit strong Raman scattering, but in a mixture these peaks may be masked.

Screening studies will be conducted to identify possible sources of interferences and limitations of the Raman scattering 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 will be studied. Tests will be conducted to establish detection limits and levels of accuracy and precision for ferrocyanide in the presence of other components.

- **Progress During Reporting Period.** Contract negotiations were completed this quarter with FSU. The university is examining their original work tasks to determine if the original work planned can be completed within the remainder of FY 1992. The lateness of establishing a contract with FSU is forcing this re-evaluation of deliverables.

  A team of chemical and engineering experts at Westinghouse Hanford developed a test plan that will be used to guide the experimental work at FSU. The FSU is currently assessing this proposed work and will make recommendations on the completion of the tests in the recommended test matrix. Initially, it appears that FSU can still meet their deliverable dates in FY 1992.

  The FSU Raman spectroscopy work will be carried out using the two waste tank surrogate materials (Westinghouse Hanford In-Farm 2 and U-Plant 2 samples) that have already been sent to FSU. These waste tank surrogates contain both low (U-Plant) and high (In-Farm) ferrocyanide levels (Cash et al. 1992) and will be used to establish impacts from morphology, interferences, pH, and concentrations on the Raman responses.

  The FSU Raman spectra from an initial, preliminary waste tank surrogate sample clearly indicate appropriate levels of sulfate and

nitrates (1.7 wt% sulfate and 19.6 wt% nitrate). A 0.103 wt% level of ferrocyanide was detectable but this concentration is in the range of their current Raman system's sensitivity--at least a 0.1 percent threshold. These results were easily obtained without the benefits of any signal enhancement or the new Raman spectroscopy system FSU is procuring that should have an order of magnitude better response sensitivity. These Raman signals show appropriate response levels and indications for nitrates, sulfates, and ferrocyanides.

The preliminary FSU tests also show that Raman responses from solids will be slightly different from those of slurries and liquids. Although this remains to be confirmed with the In-Farm and U-Plant samples, the Raman peaks of solids appear to be shifted to slightly shorter wavelengths than those from the same species that are in liquids or slurries.

- **Planned Work For Subsequent Months.** Westinghouse Hanford will work with FSU to establish a test matrix that FSU can complete within the FY 1992 timeframe. This work will lay the basis for applying Raman spectroscopy instrumentation in hot cells as a waste tank sample screening tool, in situ waste tank materials characterization, and possible process control functions for grout and Hanford Waste Vitrification Plant (HWVP) flow streams. Westinghouse Hanford's Electrical and Instrumentation Engineering function is coordinating these Raman spectroscopy development efforts.

  The FSU contract is expected to last approximately 1 yr and result in data that will support the determination of various analyte concentrations in samples from the tanks. Future work will focus on the deployment of a fiber optic sensor in hot cells or in the tanks at Westinghouse Hanford as part of the Tank Characterization Task sponsored by the Underground Storage Tank-integrated Demonstration program. Complementary work on Raman scattering is also being funded at Lawrence Livermore National Laboratory 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.** Previous milestones were based on the assumption that the contract with FSU would be placed by January 31, 1992. Because the contract was not placed until February 20, 1992, some of the anticipated milestones are still undergoing negotiated alterations.

  - March 16, 1992: Complete the definition of the test matrix and testing sequence. The test matrix was defined and transmitted to FSU as scheduled. Westinghouse Hanford developed a testing sequence and transmitted it to FSU for their concurrence. Because of the delay in placing the contract, the testing sequence is presently being negotiated.

- May 1, 1992: Initial experimental data available from tests of surrogate tank materials. Some preliminary data was received in March. Data from initial tests on the In-Farm and U-Plant simulates is still expected by this date.

- September 30, 1992: Initial data collection and validation methods documentation available. Due to the delayed placement of the purchase order, this activity is being negotiated. The anticipated milestones are as follows:

  -- September 30, 1992: Complete final report on initial data collection and validation methods for ferrocyanide.

  -- December 31, 1992: Complete final report on initial collection and validation methods for remainder of the specifications.

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 given the presence of a sufficient ferrocyanide concentration and a high enough temperature in the tank to cause an exothermic excursion and local propagation. Because there is only one TC tree in each ferrocyanide tank* 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 to determine the heat load and temperatures as a function of axial and radial distance within the tank. 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 propaging reaction to occur.

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

- **Progress During the Reporting Period**. An analysis of the air space above the waste in tank 241-BY-104 was completed to determine the airflow through the tank resulting from air in-leakage, and to calculate the heat loss resulting from this airflow. The analysis determined that with gaps in the penetrating piping of as little as .08 cm (1/32 in.) the resulting airflow was 1.9 L/s (4.1 ft^3/min). The heat removed from the tank was dependent upon the moisture evaporated. A conservative estimate of water loss of 0.13 L/h (0.8 gal/day) with the airflow of 1.9 L/s removed 124 W (426 Btu/h). The report of this analysis has been approved and has been transmitted for internal distribution; this report is currently being cleared for public availability.

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*Exceptions are tank 241-BY-105 that has two TC trees and tanks 241-BY-111 and -112 that have no TC trees.

An analysis of transient hot spot characteristics for tank 241-BY-104 was completed. A model was created for the HEATING7 code, containing a small volume whose parameters could be different from the surrounding medium. This volume was used to describe the hot spot. The hot spot was assumed to be a .91 m (3 ft) cube at the bottom of the tank, 2/3 of the radius from the center. The source strength for this hot spot, described in watts/cubic meter, was allowed to vary with time in order to create the various conditions to be analyzed. It was assumed that the hot spot would take one yr to reach its full intensity.

A very conservative chemical heat versus temperature curve was entered into the model, such that a condition where an elevated temperature could cause the chemical reaction to release more heat could be modeled. Should this extra heat be too great for the system to transmit it away to the heat sinks, the temperature would start to rise uncontrollably, resulting in a thermal runaway condition. It should be noted that thermal runaway cannot be described by reaching a set temperature. The temperature at which thermal runaway begins is dependent upon the conditions of the hot spot, such as size, placement, etc. It is possible to describe a temperature limit such that thermal runaway will not occur should the temperatures be maintained below it.

Two cases with different hot spot source strengths were analyzed. The first was a hot spot source that represented a concentration of 120 times the average of the heat source in the rest of the waste, which was just under that required to reach a thermal runaway condition. The second was a hot spot source with a concentration of 150 times the average of the heat source in the rest of the waste, which was a level high enough to reach thermal runaway. In the runaway case, the time for the surface temperature to reflect a temperature change of (1/2 °F) was 5.6 months. The temperature of the hot spot was 91.9 °C (197.5 °F), at that time. Runaway was reached in 13 months. In the non-runaway case, a surface temperature change of (1/2 °F) was reached in 6.1 months, the maximum surface temperature increase was reached in 4 yr, and the maximum temperature in the hot spot was reached in 2.5 yr. The maximum temperature reached was less than that predicted by a steady-state analysis using the same conditions. Graphical presentation of these two cases were published in WHC-EP-0474-3 (Cash et al. 1992). The report of this analysis was approved and has been transmitted for distribution.

Analyses of tanks 241-BY-105, -106, -108, -110, -111, and 241-C-109 are being conducted to determine the heat loads within these tanks, and to determine the thermal conductivity of their contents.
A generic model of the single-shell tanks containing ferrocyanide was developed. Analyses of tanks 241-C-109, -BY-105, and -BY-106 were completed this quarter. The results of these analyses indicate that the actual heat loads of these tanks are much lower than previously considered. The analysis of tank 241-C-109 shows that it has a heat load of 1.113 kW (3,800 Btu/h). Tank 241-BY-105 has a heat load of .996 kW (3,400 Btu/h). Tank 241-BY-106 has a heat load

of 0.967 kW (3,300 Btu/h). These values can be compared to previously published values in Table A-1, in Appendix A. The indications from the TC readings are that the heat generation in these tanks is not uniform but appears to have a concentration in a bottom layer. This is indicated by the temperature versus depth data and the gamma scans taken of the tanks. See WHC-EP-0474-3 for quarter ending December 31, 1991.

- **Planned Work for Subsequent Months.** The following items will be completed during the third quarter of FY 1992.

  - Complete analyses to verify the power level and thermal characteristics of the waste in tanks 241-BY-105, -106, -108, -110, -111, and 241-C-109, and issue a report of the analysis.

  The following work is planned for the subsequent months.

  - Conduct a detailed analysis of one of the above tanks to determine the effect of hot spots and the necessary concentrations of the heat source for hazardous conditions to occur, and issue a report of the analysis.

- **Problem Areas and Actions Taken.**

- **Milestone Status.**

  - January 31, 1992: A two-dimensional analysis of gas space was performed to evaluate air temperature sensitivity to heat load and hot spots as well as to determine airflow patterns. The analysis was started in August and completed last quarter on schedule. An approved report was issued in March 1992.

  - January 31, 1992: Complete a transient analysis of hot spot formation in tank 241-BY-104 to evaluate the times required for detection of hot spots and the temperature reached by the hot spot. The analysis has been completed on schedule and the approved report was issued in March 1992. The scheduled issue date was April 1992.

  - June 30, 1992: Verify power and characterize contents of six tanks. Determine the heat load and conductivity of the contents of tanks 241-BY-105, -106, -108, -110, -111, and 241-C-109. Determine the upper and lower bounds of these parameters. An approved report is scheduled for issuance in June 1992.

  - September 30, 1992: Perform a detailed thermal analysis of one tank. One of the tanks above will be analyzed to determine the response of the tank contents to a hotspot of various intensities. This analysis will include both steady-state and transient analyses. The scheduled issuance of an approved report is September 1992.

2.1.5 Cover Gas Modeling

The radiolysis of water and the interaction of various chemicals generates hydrogen and other gases. Some of these gases have the potential to be explosive or otherwise hazardous should their concentrations become large enough and be mixed properly with air. This is of concern as sampling efforts are prepared and the risk of causing a fire or explosion is determined. This task models the air space in the tanks above the waste to determine the flammability potential in the tank in conjunction with the gas space sampling program that is being conducted for the ferrocyanide tanks. This work will include development of a methodology for gas space analysis for all ferrocyanide tanks.

State-of-the-art validated computer codes are used in the modeling. They are benchmarked with existing data and use two- and three-dimensional capabilities.

- **Progress During the Reporting Period.** A model of tank 241-C-109 has been created for the GOTHIC code and tested. A surface temperature map has been obtained and input into the model. Preliminary results indicate very low airflows within the tank but adequate mixing in all areas. Gas generation and release rates are being obtained to perform final calculations.

- **Planned Work for Subsequent Months.** The following item will be completed during the third quarter of FY 1992.

  - The model created for the gas space in ferrocyanide tanks will be used to predict the spacial concentrations of hydrogen and other potentially flammable gases as a function of time.

  The analysis of this task will be completed during the third quarter of FY 1992. The report will be reviewed and issued during the fourth quarter of FY 1992. The model will also determine heat dissipation by infiltration and moisture loss due to evaporation. The results will be obtained for nominal conditions for comparison against sampling data and for worst case conditions to support safety evaluations.

  The following item will be completed during subsequent months.

  - A second tank will be analyzed for the same results using the previously prepared model.

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

- **Milestone Status.**

  - April 30, 1992: Complete detailed airspace analysis of one ferrocyanide tank and issue approved report by July 1992.

  - August 31, 1992: Complete detailed airspace analysis on a second ferrocyanide tank and issue approved report by November 1992.

2.2 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.2

"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 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 CTUS. Temperature readings from the working TCs in these tanks are being recorded continuously.

- **Progress During Reporting Period.** The design to connect three tanks in TY Farm and one tank in TX Farm was completed this quarter. Installation in these farms is now in progress.

- **Planned Work For Subsequent Months.** The continuous temperature monitoring system will be expanded to include four ferrocyanide tanks in C Farm and two in T Farm. The schedule for this phase is still being established because of the requirement for fresh air respirators and limited resources. The work must be integrated with other priority tank farm work.

- **Problem Areas and Action Taken.** The requirement that supplied-air respirators be used has been imposed for all work in the vicinity of

ferrocyanide tanks. This will slow construction progress on connecting the remaining tanks and may delay the April 30 completion date for TX and TY Farms.

- **Milestone Status.**

  - September 26, 1991: Completed installation of the continuous temperature monitoring system (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 30, 1992: Complete installation of continuous monitoring of three tanks in TY Farm and one tank in TX Farm. (This is a change from the previous milestone for C Farm.)

  The following tasks remain to be rescheduled because of the issues outlined above.

  - Complete installation of continuous monitoring of four tanks in C Farm and two tanks in T Farm.

  - Complete installation of continuous monitoring for four tanks in BX Farm.

  - Complete installation of continuous monitoring for new TC trees installed during the next year.

2.3 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.3

"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

A decision was made this quarter not to install MITs in the ferrocyanide tanks. Therefore, plans for permanently monitoring the dome space gases will need to be changed. Options to install gas monitoring on the TC trees will be reviewed and the use of a separate riser possibly in conjunction with other equipment to achieve an installed capability, where necessary, may be necessary. However, a definite decision to continuously monitor 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.

2.3.2 Interim Flammable Gas Monitoring

An intensive effort is now underway to conduct flammable gas monitoring and analyses in the 24 ferrocyanide tanks. This effort started with

tank 241-BY-104. Because the safety issue associated with ferrocyanide tanks is listed as an 'Unreviewed Safety Question' this activity requires Secretary of Energy approval to perform sampling activities within the tanks. Although past sampling conducted by Industrial Hygiene and Safety has indicated no flammable gas content above 6 percent of the lower flammability limit, no qualitative measurements were obtained. The flammability gas meter is calibrated using methane gas; readings are assumed to be for hydrogen gas, known to be present from radiolysis of water.

All 24 ferrocyanide tanks are passively ventilated through individual high-efficiency particulate air filters. The "breathing" is dependent upon changes in barometric pressure and differences in temperature between the 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.

Initially tank dome space gas samples will be taken through at least two different risers and at three elevations for the first few ferrocyanide tanks. The lowest elevation sample will be 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 have been defined and include identification of the chemicals to be monitored, detection limits, accuracy and precision of the analytical methods, and sample positions inside the tank.

- **Progress During Reporting Period**. Sampling of the gases in ferrocyanide tank 241-C-112 was completed during the past reporting period. Field readings for the tank showed no detectable concentrations of flammable or toxic gases using Draeger tube field instrumentation, a hydrogen monitor, and a combustible gas meter. The cryogenic trap samples were submitted to the laboratory for analysis. Two gas samples taken to the laboratory and analyzed using a GC/MS technique, showed no flammable or toxic gases of concern.

  Laboratory results were received for the cryogenic samples taken from the tank 241-BY-104 in October 1991. There were low part-per-million (ppm) concentrations of gases detected such as acetone, normal paraffin hydrocarbons, and 1-butanol. Ammonia, however, was detected at levels as high as 275 ppm, compared to a threshold limit value of 25 ppm.

- **Planned Work for Subsequent Months**. Readiness preparations for the next series of tanks to be sampled, starting with tank 241-C-109, is expected to begin in early April 1992. It is expected the reviews will be completed in time to support other activities.

- **Problem Areas and Action Taken**. On January 28, 1992, noxious fumes were reported at one of the tank farms. Westinghouse Hanford responded to this potential health hazard by restricting access into certain tank farms to individuals with clean, fresh air supplies. This additional requirement has further slowed normal operations, while operations requiring crane support at a farm were completely halted. Work around or in the ferrocyanide tanks requires fresh air availability because of concerns about the potential generation of

cyanide gas. The tanks will require vapor sampling and management approval before this restriction is removed, with the exception of C Farm, which must have an exhauster installed on a nonferrocyanide tank (241-C-103) before the need for fresh air respirators can be removed. Until then all affected personnel are using fresh air, and crane cabs are being modified to provide fresh air as noted above.

- **Milestone Status.**
  - March 20, 1992: Completed vapor space sampling of tank 241-C-112

Overall priorities and resources are currently being reviewed to establish the frequency at which the remaining vapor samples can be taken.

2.4 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.4

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

2.4.1 Ferrocyanide Tank Waste Sampling and Characterization

Characterization of the ferrocyanide tanks contents is necessary to guide chemical reaction studies, to apply the study results to mitigation and/or remediation of these tanks, to provide a basis for estimating the consequences of a runaway ferrocyanide reaction, and to determine how the ferrocyanide waste can be stored safely in situ until mitigation or remediation actions are completed. Knowledge of the relative position of various waste constituents is also important to determine the proximity of ferrocyanide compounds to potential reactants.

The important reaction 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, and hydroxides). The location of fission products, such as ^{137}Cs and ^{90}Sr, is important because they 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 energetic 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 and 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. Three ferrocyanide tanks suitable for push-mode core sampling have been placed on the list of 10 single-shell tanks to be core sampled in FY 1992.

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 is underway. Surface (auger) samples of the harder overlying saltcakes may be required to support the rotary drilling development and the safety analyses for the rotary-drill core sampling.

- **Progress During the Reporting Period**. The safety and environmental documentation for push-mode core sampling and auger sampling of ferrocyanide tanks was approved. The tank operational readiness review for push-mode core sampling tank 241-C-112 was completed and RL authorized the core sampling activity on March 19, 1992. Full-depth core samples [two 48.3 cm (19-in.) segments each] were taken from tank 241-C-112 risers 2, 7, and 8 on March 22 through 24, 1992.

  Activities for obtaining surface samples from tank 241-BY-104 by use of the auger technique were delayed. The cab of the crane that will suspend the auger sampler in the tank risers must be modified to supply fresh air to the crane operator. This is a result of the new administrative requirements for supplied air respiratory protection within 85 m (28 ft) of ferrocyanide tank potential vapor release points.

  The universal sampler and drill bit design is approximately 90 percent complete. Modifications to the instrumentation of the second core sampling truck has started and will continue during the third quarter of FY 1992. Proof of principal testing to develop a sampling envelope that will enable the safe sampling of watchlist tanks was completed. Additional testing beginning in the third quarter will incorporate appropriate quality assurance reviews and statistical analyses to verify the envelope.

- **Planned Work For Subsequent Months**. Surface sampling of tank 241-BY-104 using the auger technique is scheduled for the third quarter of FY 1992. The work performed for the completed operational readiness review is being examined to ensure all items are still applicable and current. Future surface sampling will depend upon analytical results of the first samples. It is not necessary to obtain surface samples of the waste in all ferrocyanide tanks because the same information can be obtained from core samples.

  Operational readiness reviews are being initiated for the vapor space sampling and push-mode core sampling of additional ferrocyanide tanks in FY 1992. The second ferrocyanide tank to be sampled will be tank 241-C-109.

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

- **Problem Areas and Actions Taken.** It is expected that the majority of the ferrocyanide tanks, particularly those with a saltcake surface, will require rotary drilling to obtain core samples. The work required to demonstrate that rotary drilling of a "harder" solids surface will not produce unacceptable high temperatures was described above. Sampling of the C Farm tanks is taking longer than other tanks because all work in the tank farm presently requires the use of fresh air for respiratory protection.

- **Milestone Status.**

  - September 30, 1991: Complete surface sampling of tank 241-BY-104. This milestone has been delayed because of the added time required to resolve the potential safety issues associated with storing pH 7 waste in the single-shell tanks and the increased time for approval of the SAs and EAs. There was also a requirement to provide supplied air to the crane operator during sampling, as a result of the vapor incident in January.

  - October 31, 1991: Obtain first push-mode core sample from ferrocyanide tank 241-C-112. This sampling is now complete. The first core sample was obtained on March 22, 1992 and cores 2 and 3 were secured on March 24, 1992.

  - July 30, 1992: Obtain push-mode core sample from 241-C-109.

  - August 30, 1992: Obtain push-mode core sample from 241-T-107.

2.4.2 Ferrocyanide Flowsheet Simulant Preparation and Characterization

Ferrocyanide waste simulants have been and are being prepared and analyzed to determine the composition, physical properties, and chemical reaction properties of waste stored in single-shell tanks. The analytical results obtained from these waste simulants, analyses of actual tank waste samples, waste tank monitoring, and waste modeling will provide information to accurately characterize safety concerns in each of the ferrocyanide tanks. They will also provide a technical basis for safety measures to be taken and decisions that lead to safe storage and eventually to final remediation of the waste.

Five synthetic waste simulants (without radioactive species) are being used to represent the various wastes produced in the mid-1950s that are currently stored in single-shell tanks. The wastes produced at the Hanford U-Plant are represented by U-Plant 1 and U-Plant 2 test mixtures. The U-Plant 1 waste simulant represents 41 of 59 batches and the U-Plant 2 represents 9 of 59 batches of U-Plant waste. Each U-Plant batch was approximately 2,300,000 L (600,000 gal). The other nine batches of U-Plant

wastes 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 wastes are represented by In-Farm 1 and In-Farm 2 test mixtures. The In-Farm 1 is representative of one batch (expected to have the greatest ferrocyanide concentration) of 29 In-Farm batches and In-Farm 2 is representative of 11 intermediate ferrocyanide concentration batches of the 29 In-Farm batches. Each of these batches was approximately 1,500,000 L (400,000 gal) Three main adjustments from the actual processes used in the 1950s were made in the laboratory scavenging preparation method. These were done to provide waste simulants thought to closely represent present tank conditions as follows: (1) the solution concentrations were adjusted to include nitrite at a 1:3 mole ratio of nitrite/nitrate to account for nitrite buildup over time in the wastes by radiolysis of nitrate, (2) the prepared waste simulants will not contain radioactive isotopes present in actual waste because of the increased difficulty in working with radioactive materials, and (3) the settled waste simulants from the laboratory scavenging process were centrifuged to an equivalent 30 gravity-year settling period using a 2500 g centrifuge.

- **Progress During the Reporting Period.** Three of the five waste simulants for testing were produced during the quarter: In-Farm 1, In-Farm 2, and U-Plant 2. Some physical property measurements and adiabatic calorimeter testing of the In-Farm 1 and In-Farm 2 waste simulants were completed this quarter. Characterization of the U-Plant 1 synthetic waste simulant, produced prior to this quarter, was also completed. The density of the ferrocyanide crystals was measured. In-Farm 1, In-Farm 2, and U-Plant 2 simulants were prepared and shipped to Westinghouse Hanford laboratories, PNL, FAI, and FSU for analysis and testing. The T-Plant flowsheet simulant will be produced for characterization and testing next quarter.

  Adiabatic calorimetry tests FAI using about 15 g of dried and pulverized (to less than 100 μm diameter particles) In-Farm 1 and In-Farm 2 materials were completed. When dried these materials exhibit propagating reaction tendencies. These test materials represent wastes in the C farm tanks 241-C-108, -C-109, -C-111, and -C-112. The volume of ferrocyanide waste simulant was only 1.0 percent of the feed solution used to prepare the waste. This results in a relatively small volume of solids in each of the four C farm tanks, equivalent to a 10.4-cm (4.1-in.) thick layer in tank C-108, a 21.1-cm (8.3-in.) thick layer in tank C-109, a 15.5-cm (6.1-in.) thick layer in tank C-111, and a 37.6-cm (14.8 in.) layer in tank C-112. The water content of these wastes was shown to be about 50 wt% even after centrifuging for the equivalent 30 gravity years.

  Differential scanning calorimetry and simultaneous thermal analysis-quadrapole mass spectroscopy measurements were made on In-Farm 1 and In-Farm 2 waste simulants. The results of these measurements show quantitative mass loss, energy changes, and gas species generation simultaneously as a function of temperature. The mass losses and energy changes are shown in Figures 2-4, 2-5, 2-6,

and 2-7 for the top and bottom fractions of In-Farm 1 and the top and bottom fractions of In-Farm 2 waste simulants, respectively. Top and bottom portions were used since two distinct layers were evident. NO and CO_2 gases were released at lower temperatures during endothermies and at the higher temperatures when the exotherms occurred. The background gases and released gases as measured by mass spectroscopy are shown in Figures 2-8 and 2-9 for the In-Farm 1 top fraction and the In-Farm 1 bottom fraction, respectively. The measurements were made in an argon atmosphere. Mass 28 (nitrogen) and mass 32 (oxygen) appear to be background levels. The major gases produced during the heatup are mass 18 (water), mass 44 (carbon dioxide), and mass 30 (nitrogen oxide). Mass 12 confirms the presence of carbon and mass 15 represents doubly charged nitrogen oxide. The quantitative mass and respective gas releases are listed in Table 2-1.

Table 2-1. Mass Release from In-Farm Waste Simulants During Heatup.

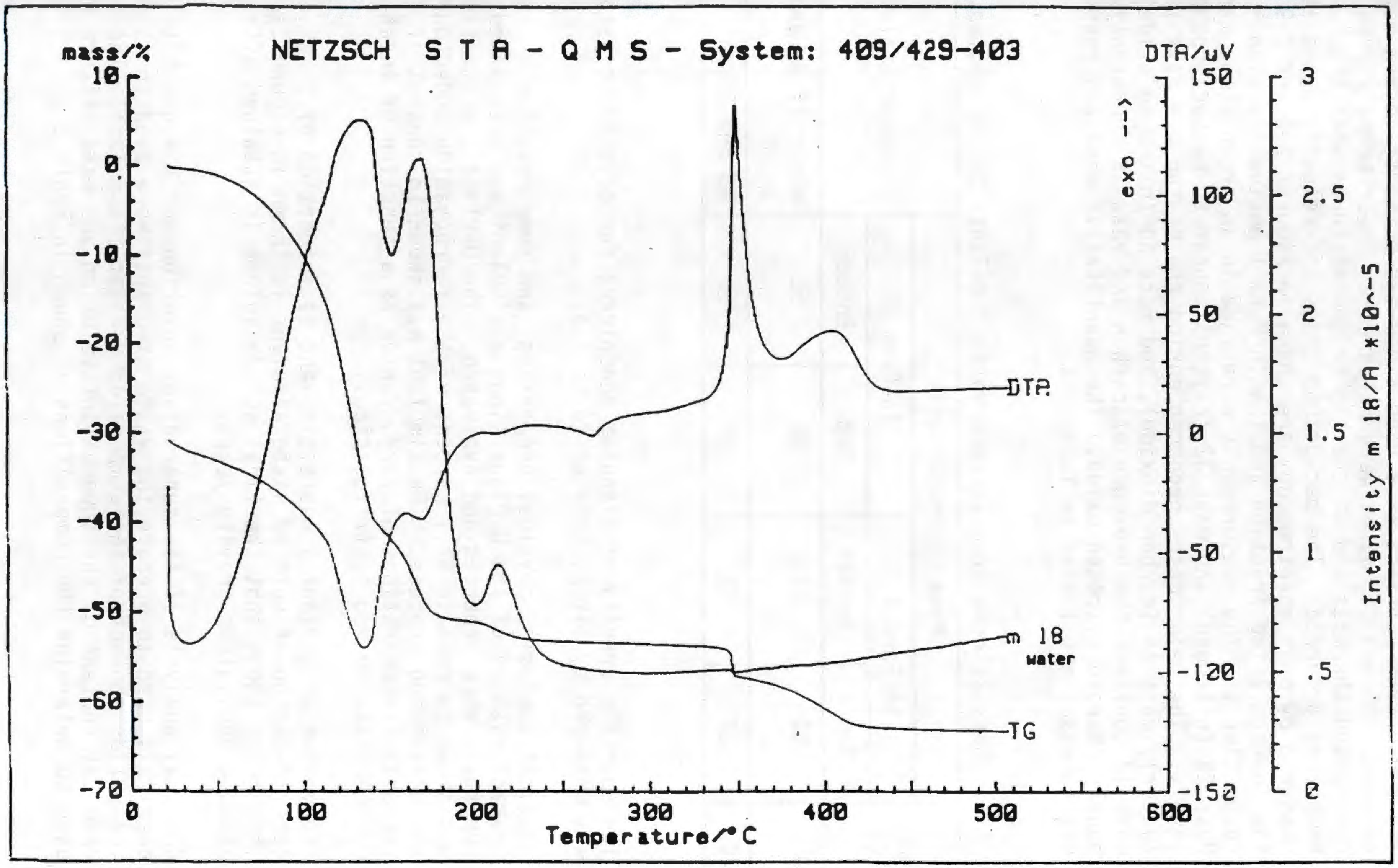
Temperature Range (°C)	Mass Decrease (wt%)				Gases Evolved
	In-Farm 1		In-Farm 2		
	Top	Bottom	Top	Bottom	
20 to 250	50	53	50	50	Water (free and bound)
340 to 420	10	12	10	10	NO and CO_2

The specific gravity of disodium mononickel ferrocyanide crystals was measured by air picnometer to be 2.6.

Chemical analysis, physical properties, and some reaction characteristics of the U-Plant 1 waste simulant and associated supernate were reported and evaluated. The U-Plant 1 waste simulant was shown to contain 97.7 percent of the ferrocyanide added during the scavenging process. The simulant was shown to consist of variable concentrations of ferrocyanide as a function of location during settling and centrifugation.

The volume of U-Plant 1 waste simulant as a function of centrifugation of settled waste simulant is shown in Figure 2-10. This graph shows that the final solids volume is attained after about 4 equivalent gravity years.

Chemical analysis of the supernatant solution and the quantity of chemicals used to prepare the waste simulants were used to calculate the solids content of the composited U-Plant 1 simulant. The chemical content of the supernatant solution and mass balance were used to determine the compositions as shown in Table 2-2.

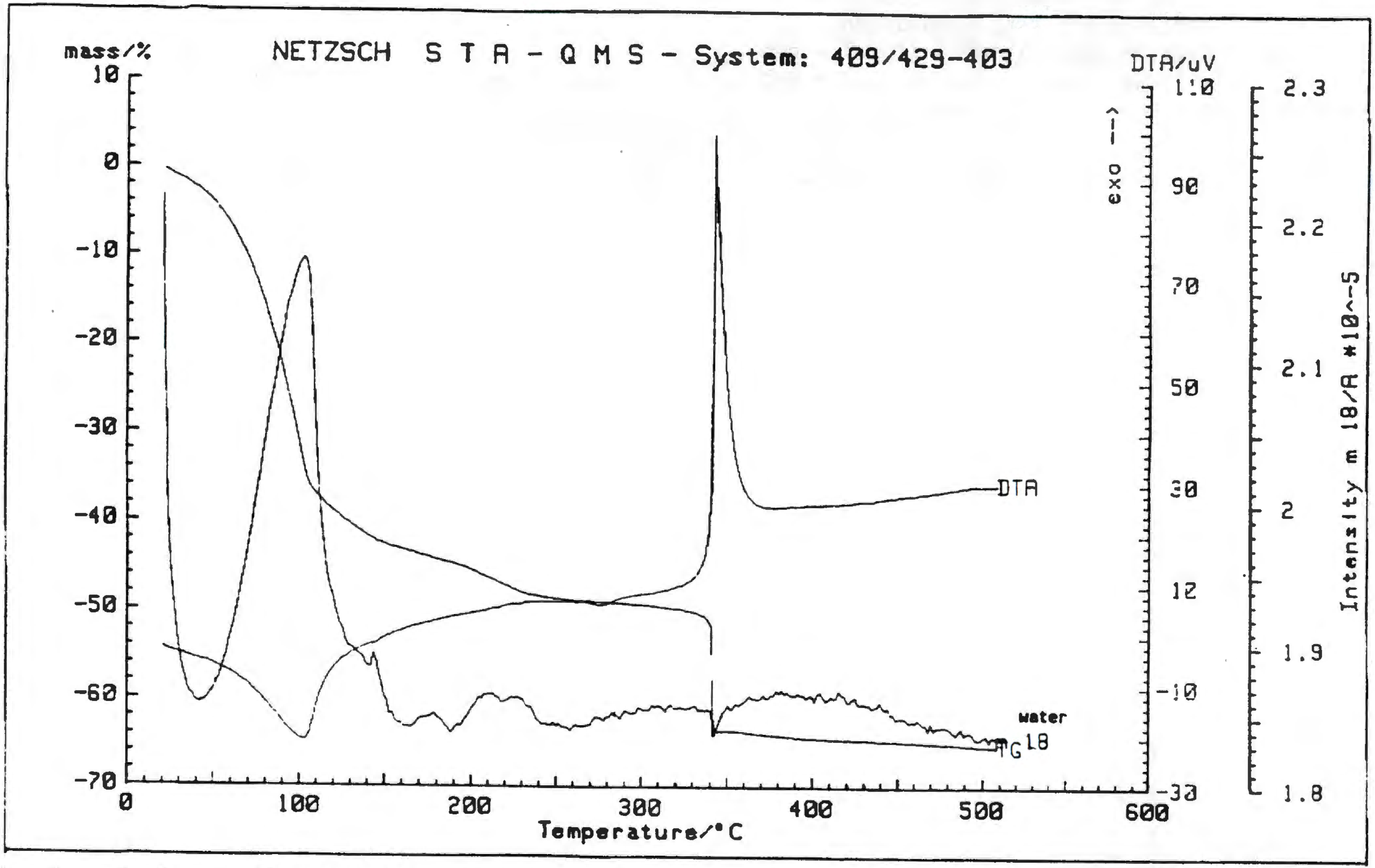


Sample: In-Farm-1 REV-12, Top Fraction - Fuged
Atmosphere: ARGON
Mass: 143.80 mg

DTA = Differential Thermal Analysis
STA-QMS = Simultaneous Thermogravimetric Analysis-Quadrapole Mass Spectroscopy
TG = Thermal Gravimetric Analysis

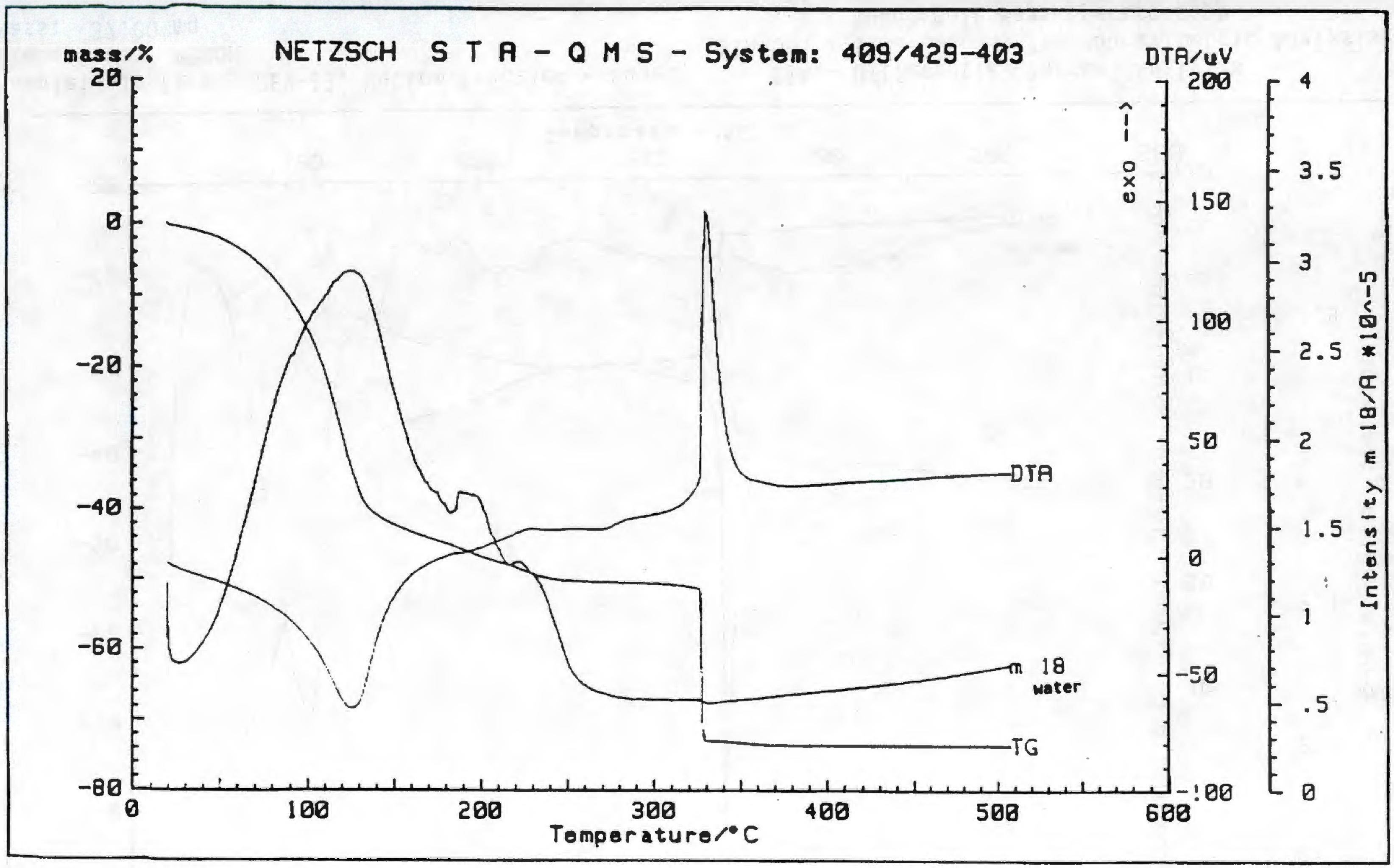
Figure 2-4. Differential Thermal Analysis, Thermogravimetric Analysis and Mass 18 Gas Intensity for In-Farm-1 Top Fraction of Sludge.

Figure 2-5. Differential Thermal Analysis, Thermogravimetric Analysis and Mass 18 Gas Intensity for In-Farm-1 Bottom Fraction of Sludge.



Sample: In-Farm-1 REV-13, Bottom Fraction - Fuged
Atmosphere: ARGON
Mass: 37.00 mg

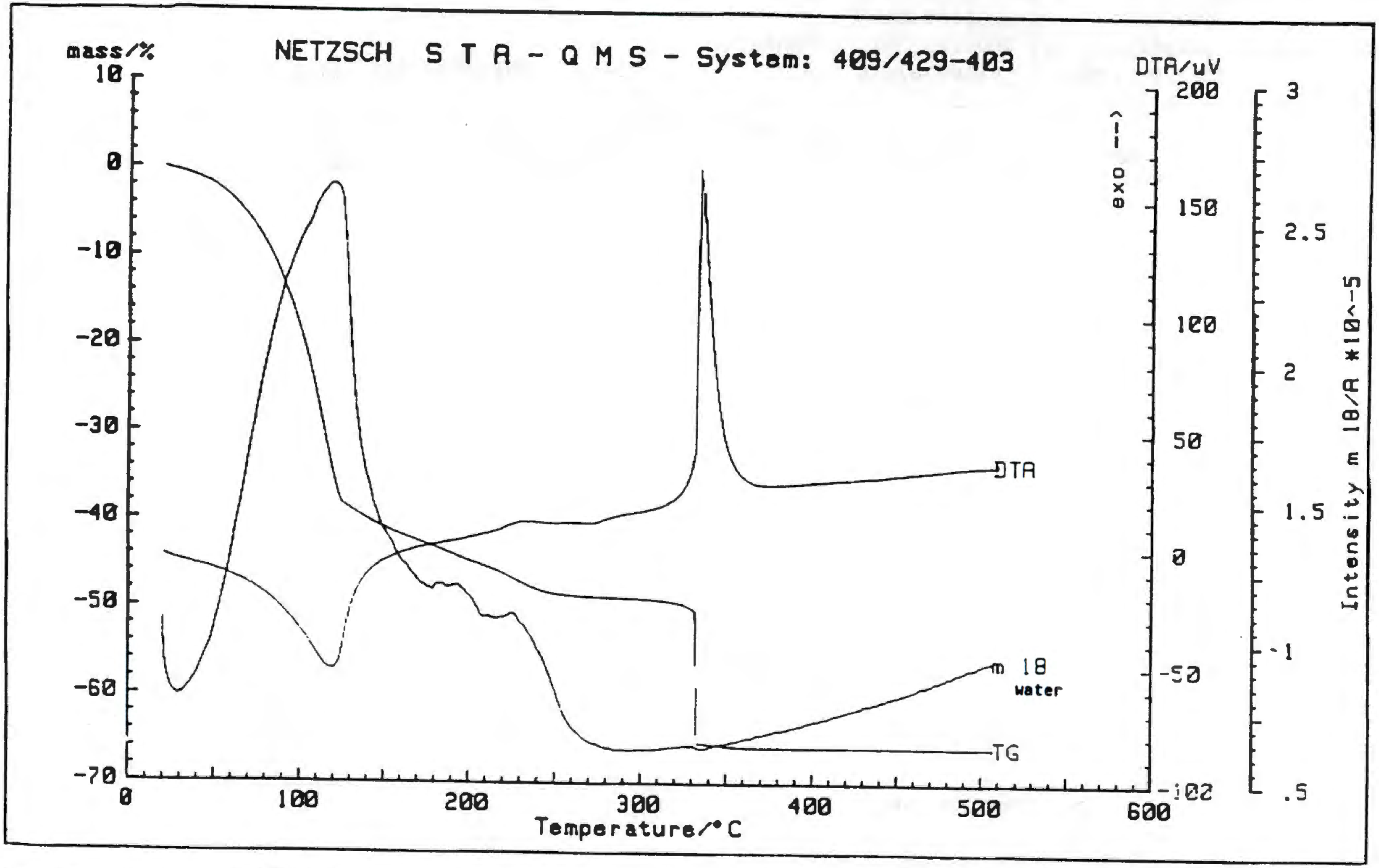
DTA = Differential Thermal Analysis
STA-QMS = Simultaneous Thermogravimetric Analysis-Quadrapole Mass Spectroscopy
TG = Thermal Gravimetric Analysis



Sample: In-Farm-1 REV-13, Top Fraction - Fuged
Atmosphere: ARGON
Mass: 126.40 mg

DTA = Differential Thermal Analysis
STA-QMS = Simultaneous Thermogravimetric Analysis-Quadrapole Mass Spectroscopy
TG = Thermal Gravimetric Analysis

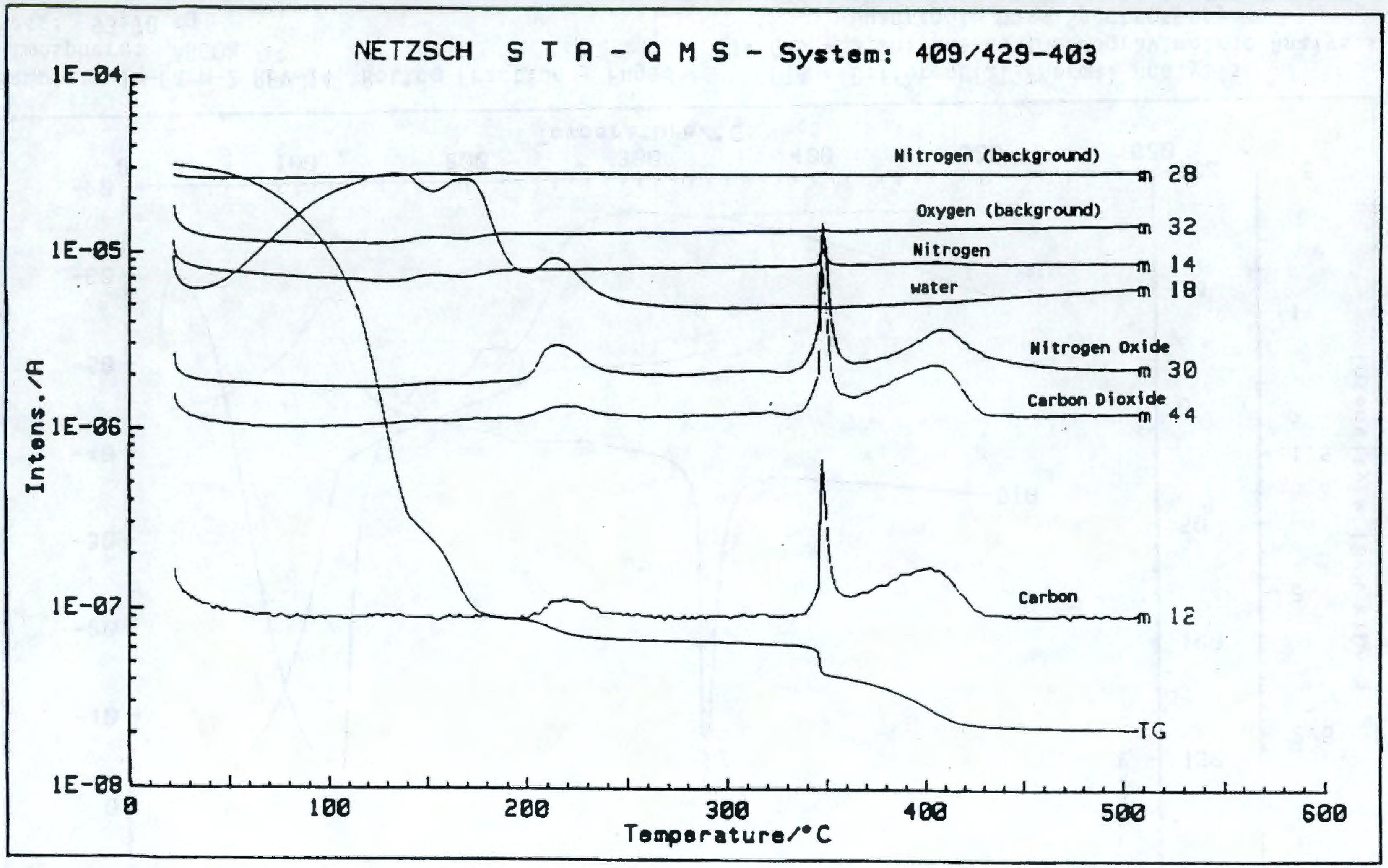
Figure 2-6. Differential Thermal Analysis, Thermogravimetric Analysis and Mass 18 Gas Intensity for In-Farm-2 Top Fraction of Sludge.



Sample: In-Farm-2 REV-14, Bottom Fraction - Fuged
Atmosphere: ARGON
Mass: 93.70 mg

DTA = Differential Thermal Analysis
STA-QMS = Simultaneous Thermogravimetric Analysis-Quadrapole Mass Spectroscopy
TG = Thermal Gravimetric Analysis

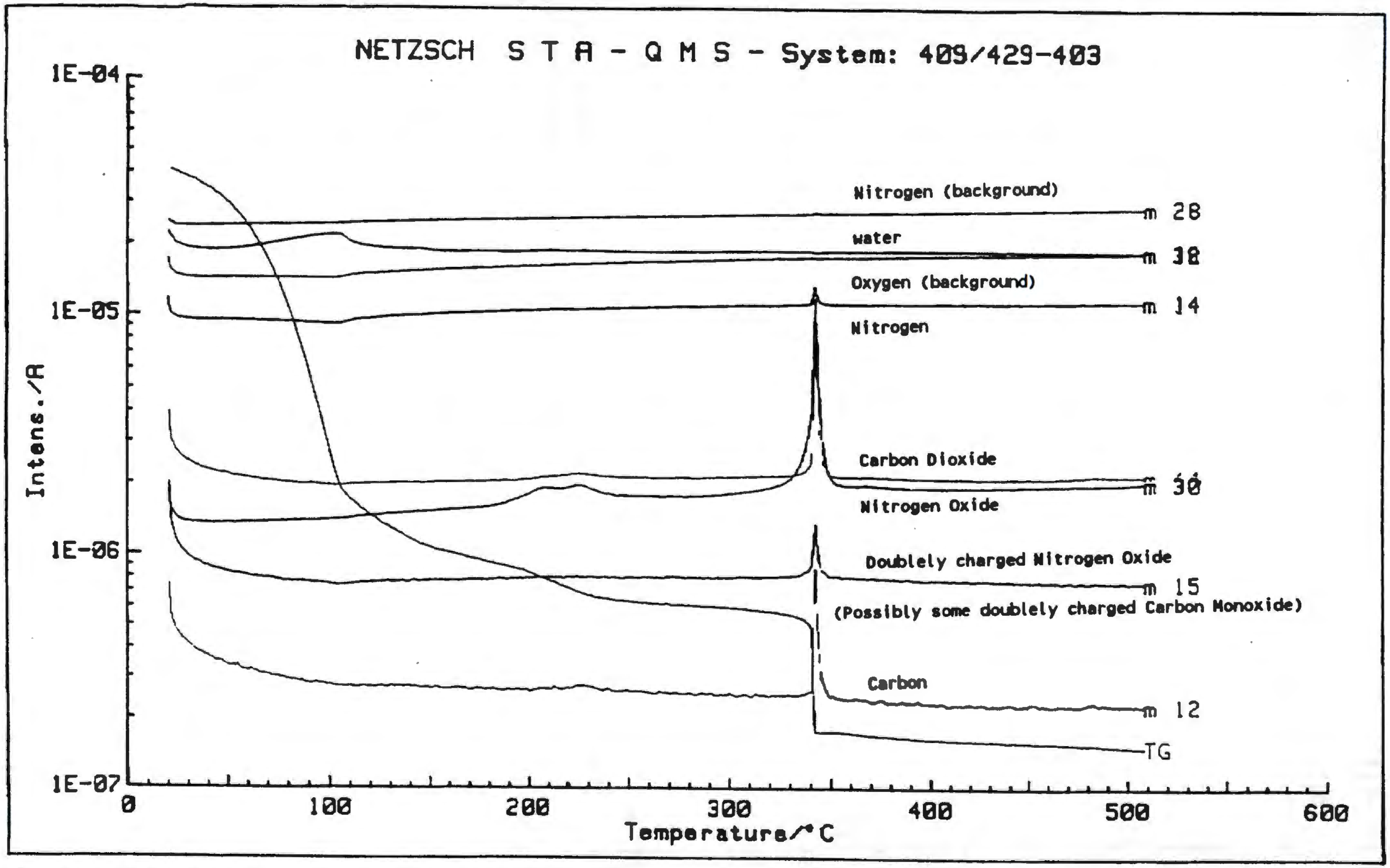
Figure 2-7. Differential Thermal Analysis, Thermogravimetric Analysis and Mass 18 Gas Intensity for In-Farm-2 Bottom Fraction of Sludge.



Sample: In-Farm-1 REV-12, Top Fraction - Fuged
Atmosphere: ARGON
Mass: 143.80 mg

DTA = Differential Thermal Analysis
STA-QMS = Simultaneous Thermogravimetric Analysis-Quadrapole Mass Spectroscopy
TG = Thermal Gravimetric Analysis

Figure 2-8. Mass Spectroscopy Analysis of Gases Above In-Farm-1 Top Layer During Heatup to 500 °C.



Sample: In-Farm-1 REV-13, Top Fraction - Fuged
Atmosphere: ARGON
Mass: 37.00 mg

DTA = Differential Thermal Analysis
STA-QMS = Simultaneous Thermogravimetric Analysis-Quadrapole Mass Spectroscopy
TG = Thermal Gravimetric Analysis

Figure 2-9. Mass Spectroscopy Analysis of Gases Above In-Farm-1 Bottom Layer During Heatup to 500 °C.

Figure 2-10. Volume Percent of Settled In-Farm 1 Flowsheet Waste simulant During Centrifugation.

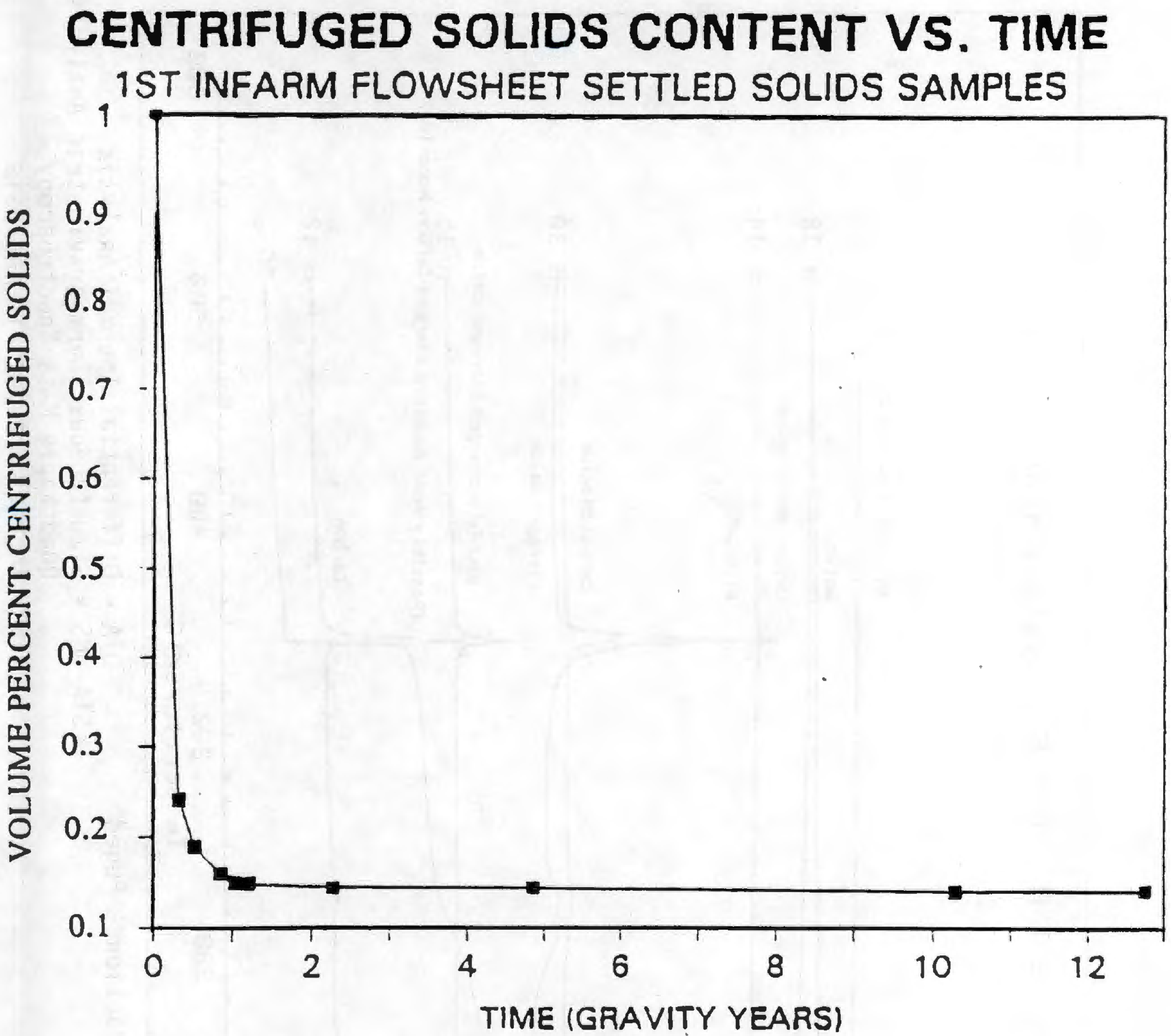


Table 2-2. Measured Chemical and Physical Properties of Ferrocyanide Waste Simulants.

Properties	U-Plant 1	In-Farm 1	In-Farm 2
Volume of solids per volume of feed solution	0.0425	0.013	0.010
Specific Gravity	1.40	1.48	1.39
Viscosity (cp)	>10,000		
Water (wt%)	66	(top) 52 (bottom) 50	(top) 51 (bottom) 48
Disodium Mononickel Ferrocyanide (wt%)	1.32	TBD	TBD
Ferric hydroxide (wt%)	2.53	TBD	TBD
Strontium Phosphate (wt%)	1.02	TBD	TBD
Sodium Nitrate (wt%)	22.3	TBD	TBD
Sodium Phosphate (wt%)	1.3	TBD	TBD
Sodium Sulfate (wt%)	1.9	TBD	TBD
Ammonium Sulfate (wt%)	0.16	TBD	TBD

These results are supported by the chemical analysis of the composited centrifuged solids. Infrared analysis of the centrifuged simulant supports these determinations. Ferrocyanide speciation by infrared techniques is being pursued by the 222-S Analytical Laboratory. An infrared scan of the centrifuged and dried U-Plant 1 simulant is shown in Figure 2-11 in comparison with a scan of pure sodium nitrate. An infrared scan of the centrifuged and dried U-Plant 1 waste is shown in Figure 2-12 in comparison to a scan of pure disodium mononickel ferrocyanide. A speciation subtraction method is being developed to make quantitative anion (including ferrocyanide species) determinations. The Fourier Transform Infrared (FTIR) photoacoustic spectra of In-Farm 1 and In-Farm 2 are shown in Figure 2-13. The photoacoustic peaks are distinctive and are expected to be better than the internal reflectance or diffuse reflectance methods for quantitative measurements of anions present in the waste simulant especially when water is present.

Florida State University has received the In-Farm 2 simulant and began Raman spectroscopy examination to quantitatively measure anions present (Section 2.1.3.4). They have requested Westinghouse Hanford to supply base materials for characterization.

- **Planned Work for Subsequent Months.** The following activities are planned for this task:

  - Prepare the T-plant waste simulant for characterization and testing.

Figure 2-11. Attenuated Total Reflectance Infrared Scan of Centrifuged and Dried U-Plant 1 Simulant in Comparison With a Scan of Pure Sodium Nitrate.

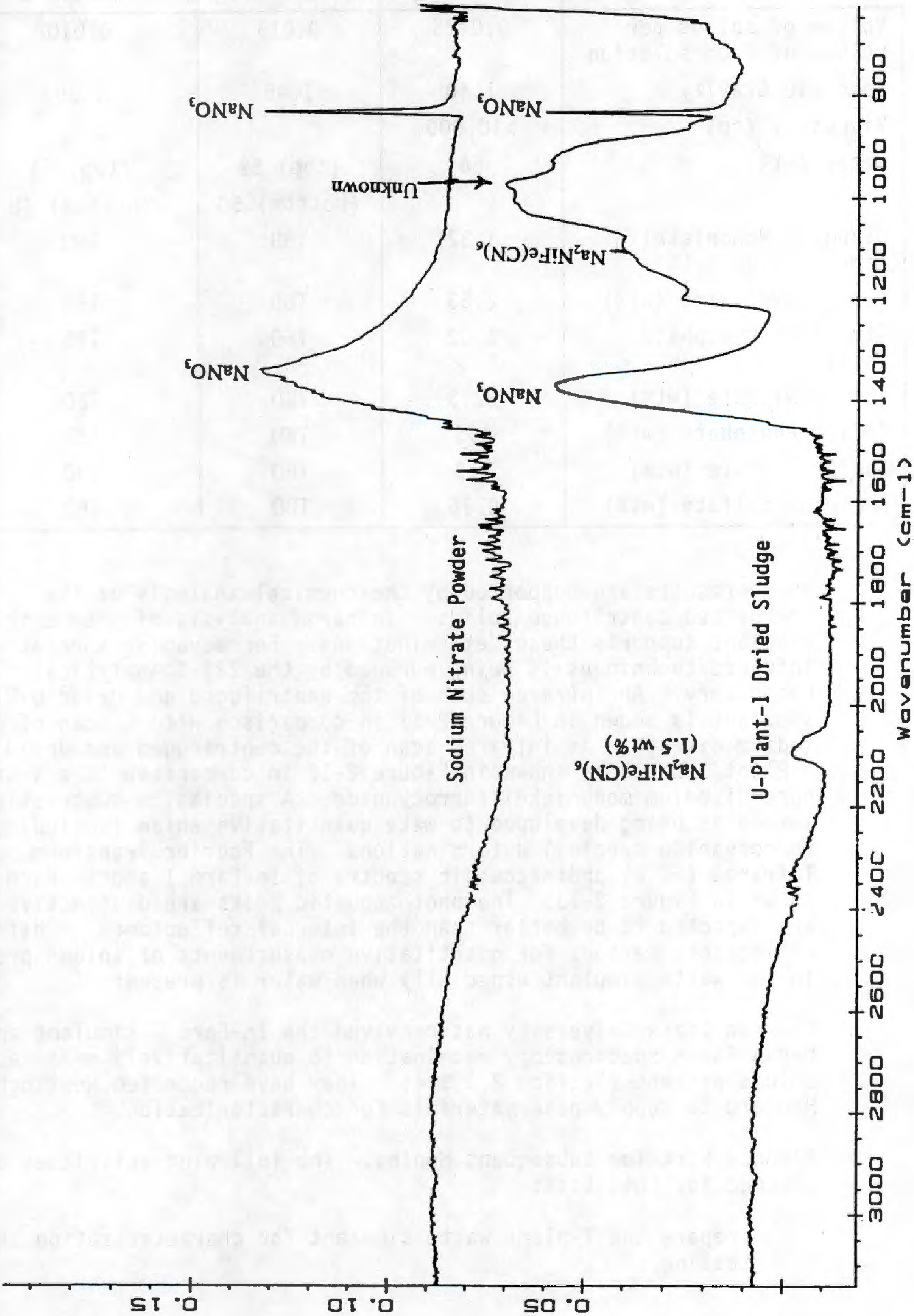


Figure 2-12. Attenuated Total Reflectance Infrared Scans of Centrifuged and Dried U-Plant 1 (Bottom Fraction) Simulant and Pure Disodium Mononickel Ferrocyanide.

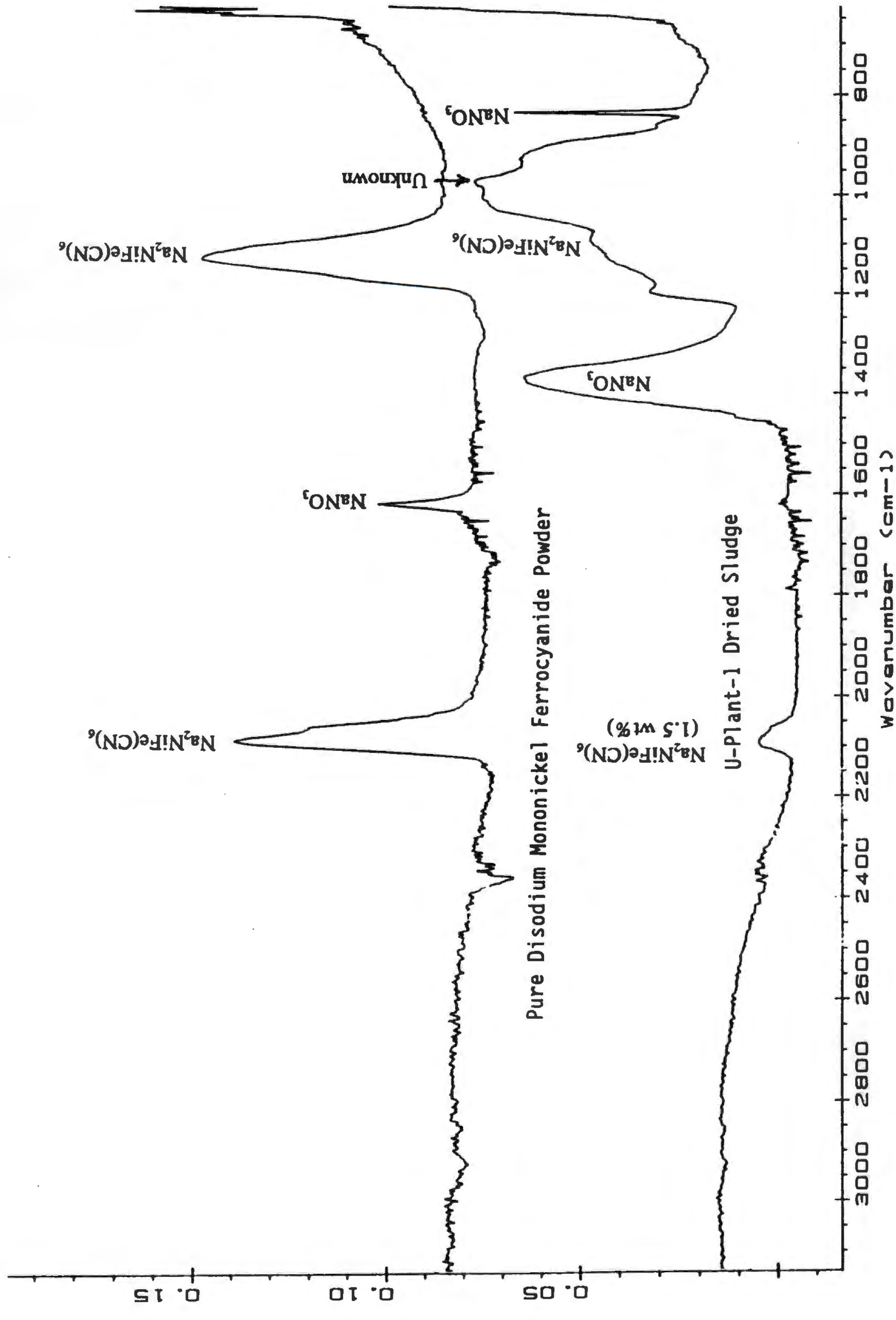


Figure 2-13. Photoacoustic Infrared Scan of In-Farm-1 (Top Fraction), In-Farm-1 (Bottom Fraction), In-Farm-2 (Top Fraction), and In-Farm-2 (Bottom Fraction) Sludge as Centrifuged. (approximately 50 wt% water present)

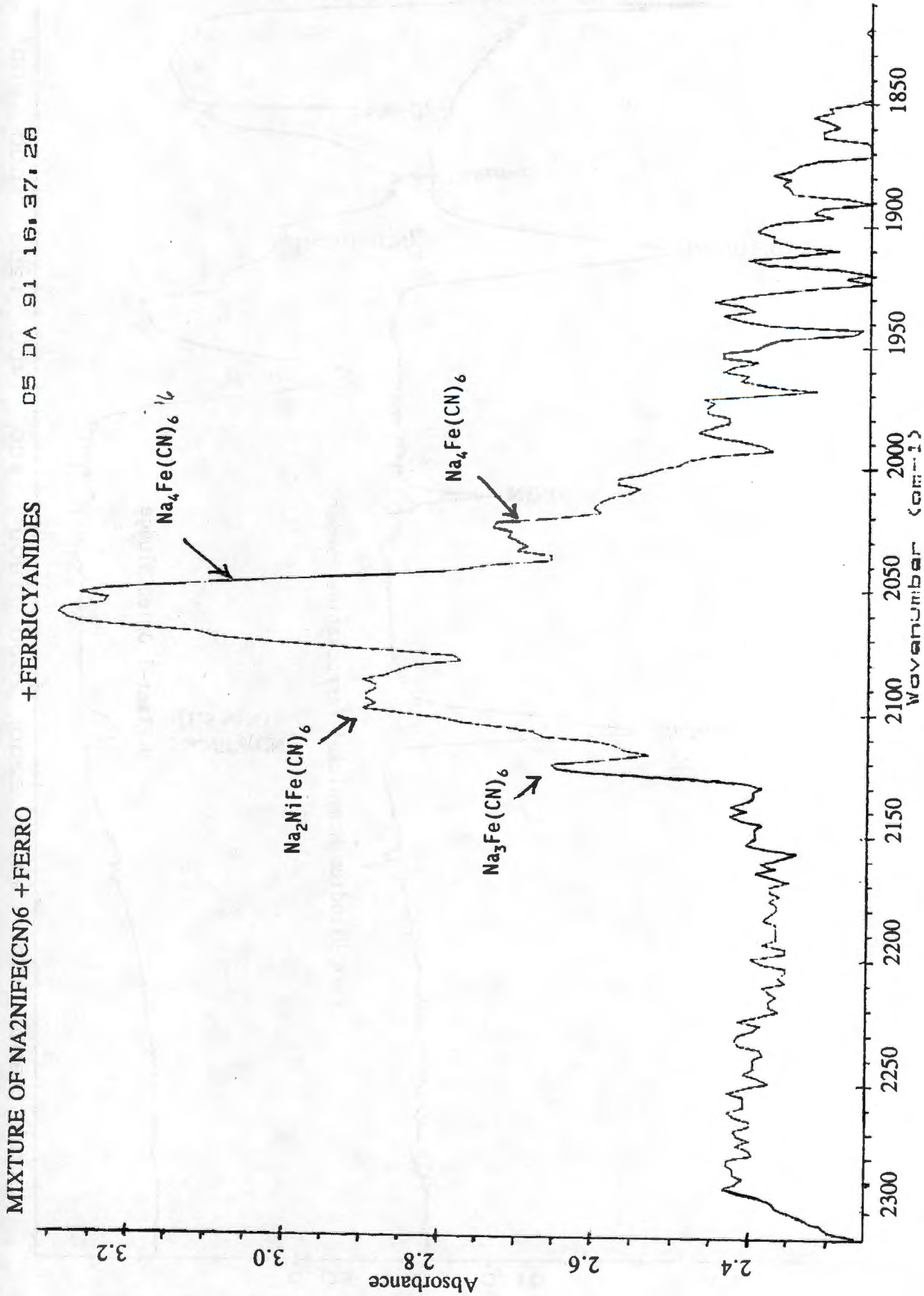
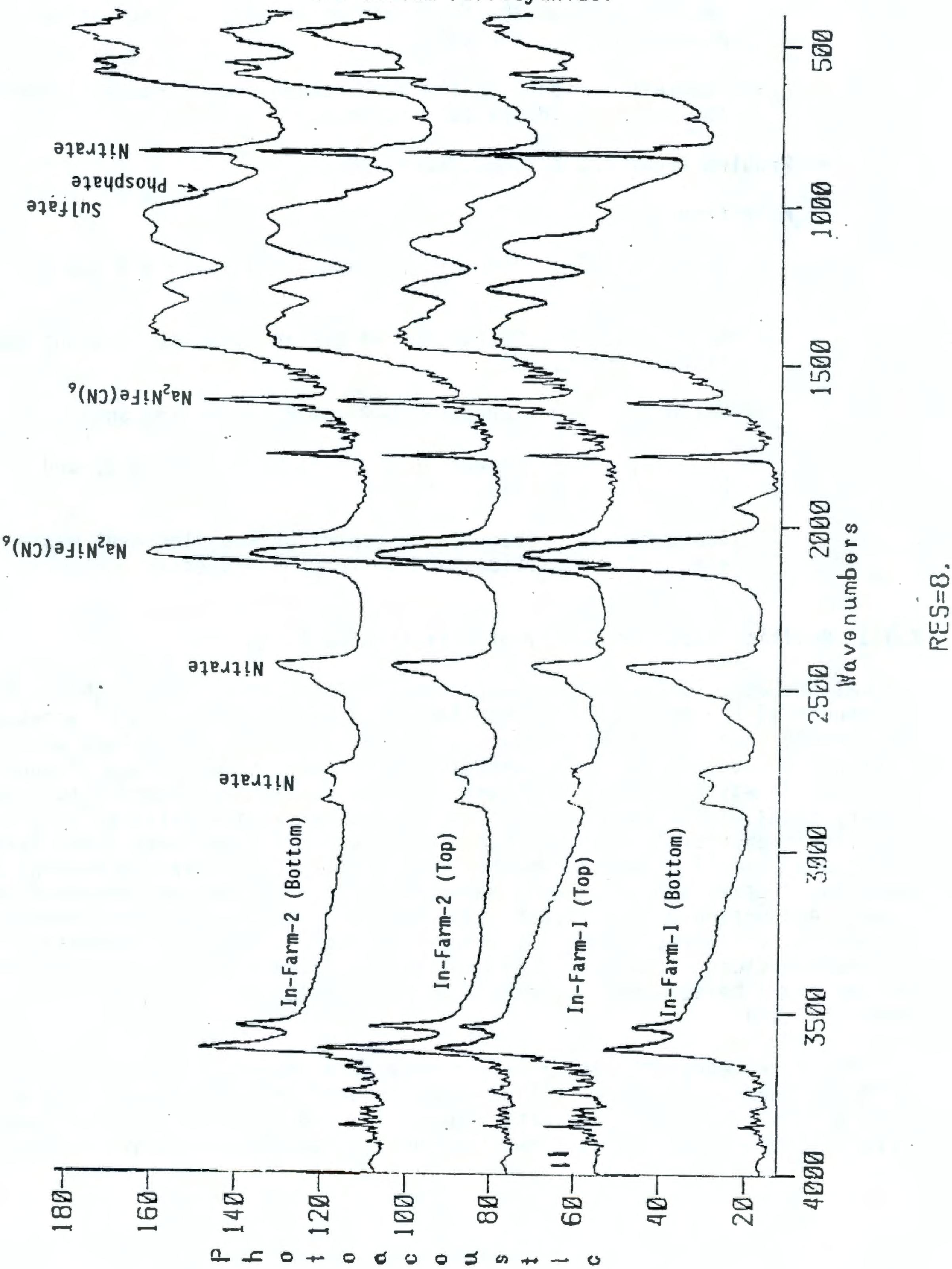


Figure 2-14. Photoacoustic Infrared Scan of a Mixture of Sodium Ferricyanide, Disodium Mononickel Ferrocyanide, and Sodium Ferrocyanide.



- Determine the chemical and physical properties of In-Farm 1, In-Farm 2, U-Plant 2 and T-Plant simulants.
- Make quantitative anion and ferrocyanide speciation measurements of the ferrocyanide waste simulants using FTIR photoacoustic methods.
- Complete a report on the preparation and characterization of the ferrocyanide waste simulants.

- **Problem Areas and Actions Taken.** None.
- **Milestone Status.**
  - March 6, 1992: Prepared In-Farm 1 and In-Farm 2 waste simulant.
  - March 9, 1992: Characterized U-Plant 1 waste simulant and issued report.
  - March 27, 1992: Prepared U-Plant 2 waste simulant.
  - July 17, 1992: Characterize In-Farm 1, In-Farm 2, and U-Plant 2 waste simulants.
  - September 30, 1992: Issue report on the flowsheet waste simulant compositions and ferrocyanide species.

2.4.3 Position Paper on Safety of Ferrocyanide Tanks

At the June 1991 Tanks Advisory Panel (TAP) meeting, Westinghouse Hanford was requested to prepare a position paper on the current state of knowledge on the ferrocyanide tank safety issue at a point in time. The intent of the paper was to document what is 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 reported 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 work represents an effort to provide a snapshot in time of what is currently known about ferrocyanide wastes stored in underground tanks at the Hanford Site, what this information means in terms of storage safety, what key uncertainties exist, and what must be done to resolve the Unreviewed Safety

Question. It is expected that periodic updates of this position paper will be issued as significant new information becomes available and results of core sample analyses are reported.

- **Progress During the Reporting Period.** A predecisional report on the current understanding of the safety of storing high-level waste containing ferrocyanide at the Hanford Site was issued on November 27, 1991, for review and comment. Comments were requested from the TAP, DOE, and RL before the first issue of the document is approved for release to the public. At the end of the quarter informal comments had been received from the requested parties. Formal receipt of these comments from the RL is expected in April, at which time the document will be revised to reflect these comments. A cleared document will be issued next quarter.

  The position paper is an overview document, with technical backup provided by the ferrocyanide hazards assessment document (Section 2.4.4). Although the contents of each tank are different, studies completed to date indicate that an uncontrolled, exothermic reaction in any ferrocyanide tank is an 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 support the current conclusions.

- **Planned Work for Subsequent Months.** Formal comments on the position paper from the selected reviewers are expected in April. 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 and temperatures of the waste. 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.

- **Problem Areas and Action Taken.** Comments were not received from the reviewers on the schedule expected. This has delayed issuance of the cleared report until next quarter.

- **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. Delayed because review comments were not received as scheduled. Revised date: May 1992.

2.4.4 Ferrocyanide Waste Tank Hazards Assessment

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

- **Progress During the Reporting Period.** A predecisional report assessing ferrocyanide waste tank hazards was issued on December 4, 1991, for review and comment by the TAP, DOE, and RL. Informal comments were received at the end of the quarter. Formal receipt of these comments from the RL is expected in April.

  The next phase of the hazards assessment was initiated, including development of a refined hazards identification approach using fault tree logic. The refined hazards identification will better define the specific conditions that would be necessary for an uncontrolled release of material from these tanks. These specific potentially hazardous conditions will then be investigated through testing, experiments, and analytical modeling in a focused and prioritized fashion.

  Accident consequence method development continued. A preliminary model was developed to describe the mechanical effects and the temperature and pressure transients resulting from a ferrocyanide burn in a waste tank both in a subsurface cavity and in the head space.

  A meeting of the Aerosol Experts Panel was held on March 2, 1992, to obtain recommendations on the approach to be used in estimating the release of radioactive aerosols from a hypothetical ferrocyanide reaction in a high-level waste storage tank. The panel focused its attention on aerosols produced at the relatively low burn velocities suggested by the preliminary tests by FAI. Under these conditions, aerosol generation by the mechanical breakup of surrounding material is minor compared to that produced at the burning fuel surface.

  Written recommendations of the panel, dated March 18, 1992, were received. These may be summarized as follows:

  - The major uncertainty regarding aerosol behavior is the fraction of the radioactive material contained in the fuel (dry ferrocyanide) burned that would initially be converted to aerosol. The panel was not aware of existing data which would allow aerosolization to be predicted accurately.

  - Tests should therefore be conducted to measure the fraction of Cs, Sr, and TRU simulant that are initially converted to aerosol form from ferrocyanide-nitrate and nitrite mixtures of interest, as well as the particle size distribution of such

aerosols. These tests should be so designed that measurements are made before excessive aerosol agglomeration or depletion occur. Non-radioactive materials will be used.

- The agglomeration and depletion of the aerosol between its initial formation and its release to the environment should be predicted by use of an existing multi-species aerosol code using the results of the above tests as input.

- The need for large-scale integrated aerosol tests, suggested earlier in the Ferrocyanide Stabilization Program for the Containment Systems Test Facility at Westinghouse Hanford, was discounted as not necessary if, as presently expected, rapid explosive reactions will not occur.

- **Planned Work for Subsequent Months.** After formal receipt of comments on the hazards assessment, the document will be revised to reflect these comments. A cleared document available to the public will be issued next quarter.

  Hazards identification using the fault tree logic approach will be continued. Test requirements for small-scale testing to determine aerosol generation for a postulated ferrocyanide event will be developed. Existing aerosol computer codes and models will be reviewed and one appropriate for this tank will be selected for use in analyzing aerosol behavior following postulated ferrocyanide events. Activities to refine ferrocyanide tank inventory models and to develop models to predict how the ferrocyanide was laid down in the tanks will be planned and pursued. The calculation of dose consequences for postulated events will be performed after accident scenarios are better defined (including refined hazard identification) and accident analysis models (e.g., burn effects models, aerosol models, and structural models) are developed. The hazards assessment report will be updated when significant new information is available.

- **Problem Areas and Action Taken.** Change Control Board actions were taken in March 1992 to significantly reduce funding cost account. Funding will be transferred to the Single-Shell Tank Stabilization Program which did not have sufficient budget in FY 1992 to meet Tri-Party Agreement milestones. This action impacts two milestones in this tank.

- **Milestone Status.**

  - March 31, 1992: A recommendation letter and report from the Aerosol Experts Panel on small-scale aerosol testing was issued on March 30, 1992.

  - May 29, 1992: Issue hazards assessment document as a cleared report.

- September 30, 1992: Complete update to ferrocyanide hazards assessment document. This milestone is deferred to FY 1993 because of reduced funding.

- September 30, 1992: Complete report on dose consequence recalculation. This milestone is deferred to FY 1993 because of reduced funding.

2.4.5 Mitigation/Remediation Concepts for Ferrocyanide Waste

A portion of the June 1991 TAP meeting was devoted to brainstorming possible concepts that might be developed for mitigation and/or remediation of the ferrocyanide tank safety issue. As a result of that session Westinghouse Hanford established three ferrocyanide working groups at the end of July 1991 to address in more detail the following concepts:

- **Zero Action Option:** No actions would be made to change the waste form. Assuring a safe condition for the waste would depend upon improved characterization, in situ monitoring and operational safety requirement, supported by technical data and safety documentation. This option would undoubtedly require installation of additional surveillance and control equipment.

- **Mitigation:** Actions would be taken on the waste to reduce the intensity or severity of the safety hazard. These actions may be periodic and repetitive. Mitigation would probably require installation of additional equipment. Concepts considered were mixing, waste cooling or dilution with barriers to isolate the tank from the environment.

- **Remediation:** Actions would be taken to modify the waste form to eliminate the safety hazard; treatments such as chemical reaction or selective ion exchange removal would be examples. Remediation would probably require installation of additional equipment to remove the waste from the tanks and treat it in a special facility.

A total of nine different mitigation and remediation ideas, including pursuit of a zero action option, were explored during the period of July through October 1991. A predecisional report was prepared and issued on November 1, 1991, for review and comment by TAP members, DOE, and RL. Comments were requested by the end of November 1991.

Two basic options were identified by the working groups: (1) Continued in situ safe storage without further treatment and (2) remediation by chemical subcategories recommended for study in conjunction with the HWVP pretreatment activities.

- Removal of major radionuclides by solvent extraction or ion exchange.

- Removal of oxidant from ferrocyanide waste by aqueous washing of soluble components.

- Controlled high temperature oxidation of the cyanide components.

Continued in situ safe storage without further treatment shows viability because preliminary laboratory information and engineering reviews of flowsheet data indicate that the waste parameters have a significant margin of safety. This is discussed in more detail in the position paper and the hazards assessment reports (Sections 2.4.3 and 2.4.4).

Concepts for in-tank mitigation or remediation were severely restricted because the ferrocyanide waste at the present time is limited to single-shell tanks. The *Hanford Federal Facility Agreement and Consent Order*, also known as the Tri-Party Agreement (Ecoloyg et al. 1990), stabilization program and the fact that the single-shell tanks are approaching 50 yr in age are limiting factors for restricting in-tank options.

- **Planned Work for Subsequent Months.** Verbal comments on the mitigation/remediation report from selected reviewers were received at the January TAP meeting in January and from other reviewers in February. Written comments will be received and incorporated next quarter, and the document will be cleared for public release.

  Engineering studies on the recommended options will be conducted to provide specific technical details for design, development, performance requirements, implementation, and risk assessment.

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

- **Milestone Status.**

  - November 1, 1991: Issue predecisional report on mitigation/ remediation concepts for ferrocyanide waste tanks. Completed on schedule.

  - March 31, 1992: Issue mitigation/remediation concept recommendations as a cleared report. Milestone delayed to allow more time for reviewers to provide written comments. Revised date: May 30, 1992.

2.4.6 Safety Assessments for Ferrocyanide Tank Activities

Because the "watchlist" ferrocyanide waste tanks involve an Unreviewed Safety Question, the performance of tank-intrusive activities requires special authorization based upon the risk involved in the proposed activity. The risk evaluations of these activities, mainly waste sampling or intrusions and vapor space sampling, are documented in SA reports. These reports are used in the activity authorization process.

- **Progress During the Reporting Period.** A draft SA for the installation of an infrared imaging camera in one of the ferrocyanide tanks was completed. The SA was put on hold pending

proof of concept testing and a decision on installing the infrared camera in a ferrocyanide tank.

The SA of installing new TC trees was expanded at the beginning of the quarter from 4 tanks to all 24 ferrocyanide tanks.

The SA for installation of MITs in ferrocyanide tanks was put on hold pending design completion and the decision to install MITs only in hydrogen gas generating tanks.

Work commenced this quarter on the SA for saltwell pumping of the remaining seven ferrocyanide tanks that are scheduled for stabilization in FY 1993 as part of the Tri-Party Agreement. This SA would also apply to a ferrocyanide tank that might start leaking. Progress on this SA was interrupted at the beginning of March to concentrate on safety documentation requested by DOE for continued saltwell pumping of non-watchlist tanks scheduled for pumping in FY 1992. Resumption of work on the ferrocyanide SA is not expected until about mid-May.

The SA for core sampling of ferrocyanide tanks that contain a hard waste type (e.g., saltcake) was initiated. This type of sampling will be performed with a rotary drill sampling system. The rotary sampling rig is not expected to be ready for deployment in the field until March 1993.

- **Planned Work for Subsequent Months.** The SA for installation of TC trees in ferrocyanide tanks will be completed. The rotary drill sampling SA will be completed in conjunction with the completion of design and testing activities now underway at the 305 Building.

- **Problem Areas and Action Taken.** Expanding the scope of the TC tree effort from the first 4 tanks (all sound) to all 24 ferrocyanide tanks raised issues about adding sluicing water to assumed leaker tanks (13 of the 24 ferrocyanide tanks). This issue has been discussed with DOE. Alternate methods for installing TC trees will be considered for these 13 tanks.

- **Milestone Status.**

  - April 15, 1992: The Safety Assessment for TC tree installation in ferrocyanide tanks will be issued to DOE.

  - May 29, 1992: Issue Safety Assessment for saltwell pumping (stabilization) of ferrocyanide tanks to DOE. This milestone will be delayed. Revised date: August 31, 1992.

2.5 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.5

"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."

2.5.1 Chemical Reaction Studies at Pacific Northwest Laboratory

A recent set of experiments has reconfirmed the dissolution and hydrolysis of vendor-prepared sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] in 0.1 N NaOH reported earlier. In the latest experiments, which were conducted in 0.1 N NaOH at room temperature using teflonware, the iron concentration in solution increased with time but leveled off after about 96 h. The $Na_4Fe(CN)_6$ formed under these conditions remained in solution while analyses of the solids indicated the formation of insoluble $Ni(OH)_2$.

Other experimental work produced evidence that a reaction occurs with dried In-Farm flowsheet-produced ferrocyanide waste (containing sodium nickel ferrocyanide and nitrate/nitrite) at temperatures as low as 130 °C (265 °F). The reaction appears to be endothermic but may be a necessary precursor to the explosive thermal reaction known to occur with stoichiometric mixtures of ferrocyanides and nitrates/nitrites at high temperatures [~290 °C (550 °F)]. The reaction was not observed when dry sodium nickel ferrocyanide was mixed with dry sodium nitrate and nitrite. Sodium nickel ferrocyanide precipitated and dried in the presence of sodium nitrate/nitrite in general begins to react exothermically at a lower temperature and faster than when the separate dried salts are mixed together. This suggests that the nitrate and/or nitrite are intimately bound or mixed with the ferrocyanide when they are dried together.

Infrared spectrophotometry, scanning electron microscopy (SEM), and X-ray diffraction (XRD) were evaluated to determine the detection limits of these techniques for sodium ferrocyanide in a mixture of single-shell tank salts. Preliminary results indicate that $Na_4Fe(CN)_6$ was detectable at the 0.1 wt% level by the infrared technique but that SEM and XRD analysis were inconsistent at the 1 percent level.

A statistical analysis was completed on time-to-explosion (TTX) data obtained in a scoping study in which various potential catalysts or initiators were added to mixtures of sodium ferrocyanide and nitrate and/or nitrite. Mixtures containing added EDTA only, EDTA + iron + chromium, and EDTA + iron + nickel + chromium had shorter mean explosion times at 380 °C (715 °F) than the ferrocyanide and oxidant mixture itself.

- **Progress During Reporting Period.**

  Chemical Nature of Cyanide in Wastes. Experiments to study the dissolution of vendor-prepared sodium nickel ferrocyanide were continued during the quarter. Initial dissolution experiments had been suspended to wait for the delivery of teflonware because the basic solutions were dissolving the glassware. Dissolution experiments have been run in 1.0 N NaOH, 0.1 N NaOH, and 0.01 N NaOH at room temperature. Reactions are followed by using inductively

coupled plasma atomic absorption spectroscopy to monitor the [Fe] in the solution as a function of time. The [Fe] increases and levels off after about 96 h under these conditions as shown in Figure 2-15 for the dissolution of FeCN in 0.1 N NaOH. Analysis of samples from the dissolution experiments in 1.0 N NaOH and 0.01 N NaOH are currently being analyzed and will be reported in the next quarterly report. Analyses of the solids indicates the formation of $Ni(OH)_2$ as reported before. The $Na_4Fe(CN)_6$ then appears in the solution as a soluble species.

Preparation and Characterization of Ferrocyanide Waste Simulants. During January, PNL began characterizing samples of simulated ferrocyanide wastes prepared by PNL using the U-Plant flowsheet coupled with strontium scavenging, an In-Farm flowsheet using the dilute option (3 M $NaNO_3$), and a large batch of sodium nickel ferrocyanide. For the In-Farm waste simulant, samples were recovered for characterization by settling and centrifuging for 0.23 and 30 g-y.

Analyses being performed on the samples include determination of the total cyanide content, total organic carbon, anions, elemental content by inductively coupled plasma/atomic emission spectroscopy, and identification of the chemical species by XRD analysis. The thermal sensitivities of the samples have been and will be determined using differential scanning calorimetry (DSC), scanning thermogravimetry (STG), and PNL's TTX test.

Table 2-3 provides the calculated overall compositions for dry In-Farm B* samples prepared using the dilute flowsheet. Table 2-3 also provides the measured ferrocyanide content for comparison.

The compositions in Table 2-3 were calculated using the amount of resulting solids, wt% water, and the concentrations of the parent solutions. The excellent correlation between the measured ferrocyanide and calculated ferrocyanide content provides a great deal of confidence in the accuracy of the calculated concentrations.

Table 2-4 provides the enthalpy changes measured by DSC for In-Farm B and an in-farm sample prepared from a solution having a total nitrate and nitrite concentration of 6 M (In-Farm A), the concentrated flowsheet.

The enthalpy releases measured by DSC for In-Farm A and the three In-Farm B samples, presented in Table 2-4, are much less than predicted, but may be a function of the analytical method.
A measurement using an adiabatic calorimeter or an accelerating rate calorimeter (ARC) is needed to assure total enthalpy change

*The compositions of PNL In-Farm-A and In-Farm-B flowsheet ferrocyanide simulants are slightly different from the In-Farm-1 and In-Farm-2 ferrocyanide simulants produced in larger quantities by Westinghouse Hanford and reported in Section 2.4.2 and in WHC-EP-0474-3 (Cash et al. 1992).

Figure 2-15. Plot of [Fe] vs Time; Hydrolysis of Vendor FeCN in 0.1 N NaOH.

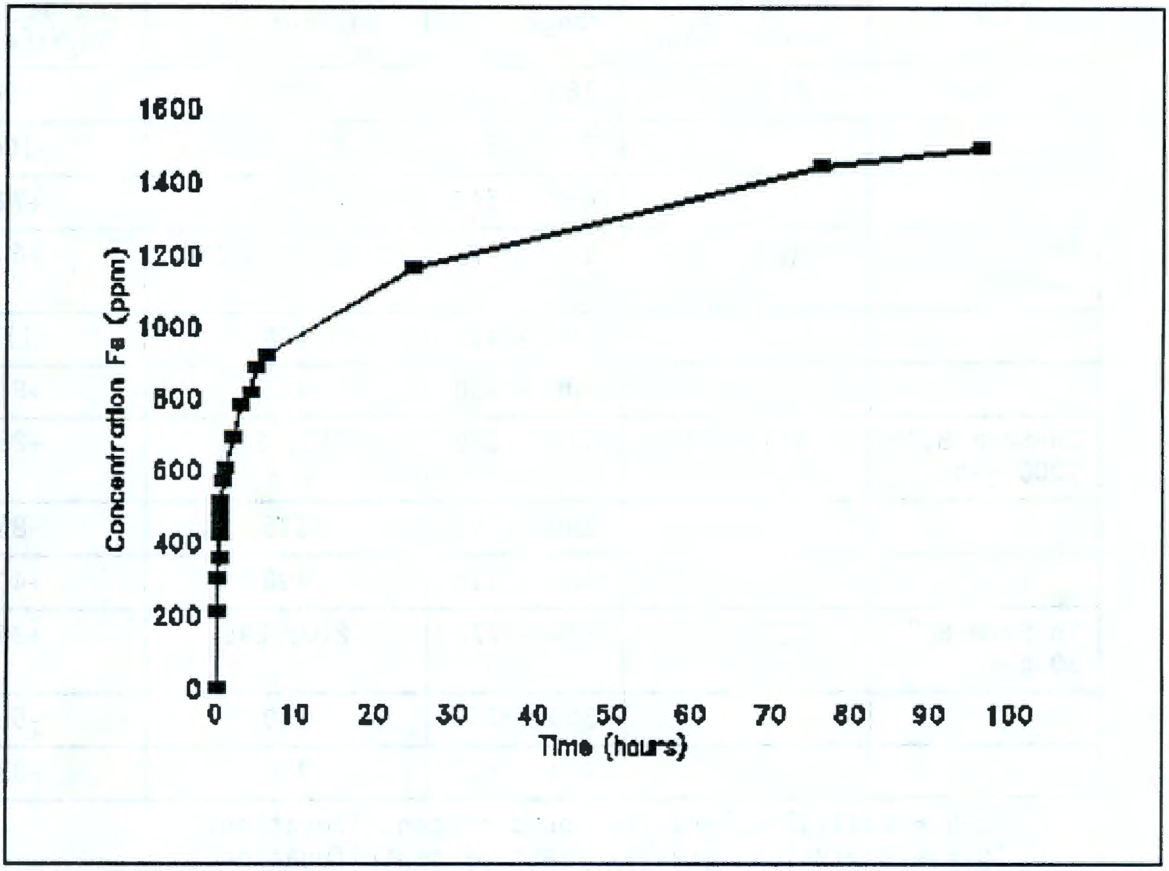


Table 2-3. Calculated Compositions of Dry In-Farm B Samples.

Constituent	Concentration (wt%)		
	Settled solids	Centrifuged 0.23 g-y[a]	Centrifuged 30 g-y[a]
Na_2SO_4	8.6	5.3	4.7
Na_3PO_4	7.5	4.6	4.1
$NaNO_3$	52	32	28
$NaNO_2$	21	13	11
NaCl	0.2	0.1	0.1
KNO_3	0.3	0.2	0.2
NH_4NO_3	0.5	0.3	0.3
$Na_2NiFe(CN)_6$[b]	10(11)[c]	45(44)[c]	51(44)[c]

[a]g-y = equivalent gravity years of centrifugation.
[b]Assumed nominal nickel ferrocyanide composition.
[c]Measured by total cyanide analysis.

Table 2-4. Measured Enthalpy Changes for In-Farm A and In-Farm B Samples.

Sample	Mole ratio of $NO_3 + NO_2$ to ferrocyanide	Reaction range (°C)	Peak minimum or maximum (°C)	Enthalpy change (kJ/mol $Na_2NiFe(CN)_6$)
In-Farm A	6(4 + 2)	180 - 250	220	+90
		275 - 360	310, 340	-1060
		460 - 540	509	+790
In-Farm B, settled	30(20 + 10)	170 - 270	210, 220, 260	+645
		300 - 400	360	-1150
		400 - 480	445	+815
In-Farm B,[a] 2000 g-h	4(3 + 1)	170 - 270	210, 240	+258
		280 - 405	335	-851
		460 - 510	490	+405
In-Farm B,[b] 30 g-y	3(2 + 1)	170 - 270	210, 245	+360
		300 - 360	330	-560
		470 - 510	490	+330

[a]g-h = equivalent gravity hours of centrifugation.
[b]g-y = equivalent gravity years of centrifugation.

measurement. ARC tests will be done next quarter. The maximum measured exothermic enthalpy change was -1,100 kJ/mole of ferrocyanide or roughly an energy yield of 30 percent of the nominal predicted maximum of -3,200 kJ/mole of ferrocyanide for a 2:1 nitrate to nitrite mole ratio mixture. Expected energy yields for good explosives are usually about 80 percent.

Cyanide Species Analytical Development. Experiments were performed during the quarter to evaluate the detection limits for sodium ferrocyanide [$Na_4Fe(CN)_6 \bullet 10\ H_2O$] in mixture of single-shell tank salts by infrared, SEM, and XRD analytical techniques. The $Na_4Fe(CN)_6 \bullet 10\ H_2O$ was blended with a simulated mixture of single-shell tank salts to 1 percent and 0.1 percent levels (wt. $Na_4Fe(CN)_6$/wt. of single-shell tank salts).

The infrared analyses were performed in the transmission mode. The samples were mixed with KBr (3 percent sample/KBr) and pressed into a pellet. The infrared analyses indicate that $Na_4Fe(CN)_6$ was detectable at the 0.1 percent level by this technique. It is

believed that the limit of detection would be much lower if the analyses were performed in the reflectance mode using a zinc selenide internal reflectance cell.

Preliminary SEM and XRD analyses were unable to consistently detect the presence of $Na_4Fe(CN)_6$ in the single-shell tank salts at the 1 percent level. Additional samples containing 2 percent and 5 percent $Na_4Fe(CN)_6$ are being analyzed by SEM and XRD.

The necessary materials are being assembled to begin development of a method to determine cyanide species in Hanford Site wastes using ion chromatography (IC). In addition to these activities, an evaluation of the suitability of the micro-distillation method for the determination of total cyanide in Hanford wastes is also underway.

Effects of Catalysts and Initiators. A statistical analysis was completed on TTX data obtained in a scoping study to determine if sodium EDTA, nickel hydroxide, iron hydroxide, and chromium (III) hydroxide act as catalysts or initiators for the oxidation of sodium nickel ferrocyanide by equimolar sodium nitrate/nitrite. In the TTX tests, the catalysts and initiators were added individually at 0.03 mole per mole of ferrocyanide in the mixture of equimolar sodium nitrate/nitrite oxidant and sodium nickel ferrocyanide. In some cases a combined mixture was prepared with each added at the 0.3 mole fraction level. The oxidant to ferrocyanide ratio was a factor of 1.1 of stoichiometry. The four temperatures used were nominally 295 °C (560 °F), 320 °C (610 °F), 350 °C (660 °F), and 380 °C (715 °F).

The statistical analysis indicates that only EDTA, EDTA + iron + chromium, and EDTA + iron + nickel + chromium had shorter mean explosion times at 380 °C (715 °F) than the ferrocyanide and oxidant mixture by itself. For example, for the oxidant mixture containing only EDTA, the TTX was 2.4 s compared to 2.9 s for a mixture without a catalyst or initiator added. At the lower temperatures, there was no statistical significant indication of an effect.

Graphical analysis of the log of the mean explosion times at various temperatures indicate that, in general, addition of any of the tested catalysts or initiators reduces the TTX. Because cobalt scavenging was often combined with the cesium scavenging process when treating in-farm wastes, nickel sulfide may be present in the ferrocyanide-bearing wastes. The In-Farm 2 simulant prepared by Westinghouse Hanford will be tested to determine the effect of nickel sulfide on the reaction(s) between nitrate/nitrite with ferrocyanide.

Laboratory experiments using DSC, STG, and temperature programmed pyrolysis coupled with mass spectrometry (pyrolysis/MS) continue to indicate that the reactions of ferrocyanides with nitrates/nitrites is very complex. Most of the evidence is from thermal analysis using DSC and STG. These experiments show shifts of the different

exothermic peaks and the shape of the peaks themselves as ferrocyanide samples precipitated in slightly different ways were tested.

Interesting information also comes from on-line limited gas analyses during programmed heating of the in-farm simulants. Evidence of a reaction between ferrocyanide and nitrate/nitrite occurs at temperatures as low as 130 °C (265 °F). The reaction is endothermic but may be a necessary precursor to the explosive thermal reaction known to occur with stoichiometric mixtures of ferrocyanides and nitrates/nitrites at high temperatures. In the absence of this information, the endothermic behavior observed at this low temperature was attributed to water loss but the on-line gas analyses show the presence of carbon monoxide and nitrogen. This latter observation shows the importance of gas analysis as an important complementary method to DSC and STG in characterizing these chemical reactions.

The pyrolysis/MS experiments coupled with the DSC and STG analyses also showed that sodium nickel ferrocyanide precipitated and dried in the presence of the nitrate/nitrite begin reacting earlier than mixtures prepared from washed and dried sodium nickel ferrocyanide mixed with dried nitrate/nitrite. This suggests that the nitrate and/or nitrite is intimately bound or mixed with the ferrocyanide. In fact, the oxidant may be held within the cage structure of the alkali nickel ferrocyanides.

To further pursue this observation, several preparations were made using stoichiometric mixes of mixed nitrate-nitrite, pure sodium nitrate, and pure sodium nitrite. The aqueous slurries were dried, ground, and tested. Preliminary results are summarized below:

1. Ferrocyanide samples dried with the oxidant in place tend to begin reacting at a lower temperature and complete the first exothermic reaction earlier than observed with carefully washed and dried ferrocyanide preparations to which dry oxidant is added. The DSC experiments at 5 °C/min (9 °F/min) show the first major exotherm at about 250 °C (480 °F).

2. The oxidation path is multi-step as discussed previously, but it appears that the nitrite reaction is different from the nitrate reaction and that much of the complexity of the DSC curves observed may result from the way the oxidants and ferrocyanides are prepared or mixed.

3. Rate of heating experiments with sodium nickel ferrocyanide using DSC and STG indicate a lower activation energy for the oxidation reaction than was found for cesium nickel ferrocyanide.

These results support the hypothesis that the nitrate is intimately bound to the ferrocyanide and can reduce the exothermic reaction temperature; whether the nitrate is in the cage structure of the ferrocyanide has not yet been confirmed.

Sensitivity Tests with Simulated Ferrocyanide Wastes. The report describing the results of the LANL small-scale testing of cesium nickel ferrocyanide was issued this quarter as PNL-7928.

Westinghouse Hanford and PNL personnel held further discussions on the desired tests and waste simulants to be tested. Consistent with the DOE Tank Advisory Panel's expressed belief that all testing should be performed with materials representative of wastes precipitated during scavenging campaigns, plans were changed and four simulant waste mixtures instead of two will now be tested for their sensitivities to mechanical impact, friction, and electrical spark and their thermal behavior under selected conditions. An extension of the previous contract with LANL for these additional small-scale sensitivity studies is under negotiation with agreement yet to be reached on quality assurance (QA) procedures. When agreement is reached, samples of three ferrocyanide waste simulants prepared by Westinghouse Hanford's Chemical Engineering Laboratory (In-Farm 1, In-Farm 2, and U-Plant 2) and the vendor-produced sodium nickel ferrocyanide will be shipped to LANL for testing.

- **Planned Work For Subsequent Months.**

  Ferrocyanide dissolution/hydrolysis experiments using constant ionic strength [Na] solutions will continue. A series of hydrolysis experiments where the [Na] is increased to 2<u>M</u> and 6<u>M</u> will be performed.

  Infrared detection of solid ferrocyanides is proposed as a follow-on candidate for ferrocyanide speciation work. A method of standard addition will be used on flowsheet material in an effort to quantify the nickel ferrocyanide in the sample. A well characterized source of nickel ferrocyanide could be used as the standard addition reagent. Development of a method to determine cyanide species in Hanford Site tank wastes using IC is also proposed.

  Characterization of flowsheet simulant ferrocyanide wastes and iron nickel ferrocyanide will continue. The characterizations will include measurement of selected physical properties in addition to the chemical properties that have been measured for previous preparations. The effect of nickel and cobalt sulfides in the Westinghouse Hanford In-Farm 1 simulant will be investigated as catalysts and initiators. The interim report on catalysts and initiators will be issued.

  Final statistical analysis of the TTX tests to determine the effect of selected catalysts and initiators on the oxidation of sodium nickel ferricyanide by equimolar sodium nitrate/nitrite will be completed.

- **Problem Areas and Action Taken.** Delay in placing the contract with LANL on sensitivity tests will require Change Control Board action. The two milestones for completing these tests and issuing a report will be delayed.

- **Milestone Status.**

  - November 30, 1991: Issue annual report on FY 1991 PNL activities on ferrocyanide project. The predecisional copies of this report were issued November 27, 1991. The cleared document is now in final editing.

  - January 31, 1992: Issue interim report on catalyst, initiator, and diluent studies. Draft issued for review in February.

  - April 30, 1992: Issue topical report on reaction sensitivity studies conducted at LANL. Milestone will be delayed pending placement of subcontract; Change Control Board action is required. Tentative date: September 30, 1992.

  - August 31, 1992: Complete predecisional report on the effects of aging on ferrocyanide-containing wastes.

  - September 15, 1992: Complete predecisional report on methods development for ferrocyanide speciation.

  - September 30, 1992: Issue final report effects of aging on ferrocyanide-containing wastes.

  - October 30, 1992: Issue final report on catalyst, initiator, and diluent studies.

2.5.2 Ferrocyanide Propagation Studies

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

- **Progress During Reporting Period.** The ASC tests were completed by FAI for the upper and lower fractions of In-Farm 1 and In-Farm 2 centrifuged waste simulants. These simulants represent ferrocyanide waste stored in four tanks located in C Farm. The simulants were centrifuged for a 30 yr gravity-equivalent force (at 2,500 g) and then separated into an upper fraction and a lower fraction. The upper fraction of the In-Farm 1 material was blue and the lower fraction was black (the black fraction was larger in mass than the blue fraction). The upper and lower fractions (these fractions were about equal in mass) of the In-Farm 2 material were each blue.

  The test simulants were dried for 24 h at 50 °C (122 °F) and under 25 mm (1 in.) Hg vacuum to remove water. The simulants were then ground to less than 100 μm (0.004 in.) in diameter and loaded into

the Reactive Systems Screening Tool (RSST)*. About 12 to 16 g of test material were tested at a time. A summary of the results (FAI) are listed in Table 2-5.

Table 2-5. Summary of In-Farm Reactive Systems Screening Tool Tests.

Sample	Sample Mass (g)	Temperature °C			Moles of Gas Released
		Some exotherm	Onset	Peak	
In-Farm 1 Top	12.05	225	278	>500	~0.12
In-Farm 1 Bottom	12.98	190	250	>500	~0.15
In-Farm 2 Top	16.4	190	254	>500	~0.12
In-Farm 2 Bottom	13.65	190	244	>500	~0.16

The self heat rate, pressure buildup rate, temperature, and absolute pressure for the bottom half of the In-Farm 2 dried simulant RSST test are shown in Figures 2-16, 2-17, 2-18, and 2-19, respectively. Each of these materials when dried and heated to the indicated temperatures exhibited tendencies to propagate.

The propagating tendencies of these simulants sodium nickel ferrocyanide materials tested to date, and some to be tested in the near future are shown on the triangular diagram in Figure 2-20.

- **Planned Work for Subsequent Months.** Propagation tests will be conducted on ferrocyanide waste simulants (U-Plant 2, In-Farm 1, In-Farm 2, and T-Plant) for both as produced and dried material. A matrix of screening propagation tests will be conducted to determine the relative importance of eight variables on propagation rates. In addition, a series of variable moisture content tests will be conducted on the In-Farm 1 material to determine the minimum moisture concentrations that will preclude propagation.

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

- **Milestone Status.**

  - April 3, 1992: Shipped In-Farm 1, In-Farm 2, and U-Plant 1 waste simulants to FAI for propagation testing.

  - May 18, 1992: Complete RSST and propagation tests on In-Farm 1, In-Farm 2, and U-Plant 2 waste simulants.

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*RSST is the adiabatic scanning calorimeter used by Fauske and Associates, Inc., for small-scale screening tents.

Figure 2-16. Reactive Systems Screening Tool Measurements of Heat Generation Rates for Dry In-Farm-2 (Bottom Fraction).

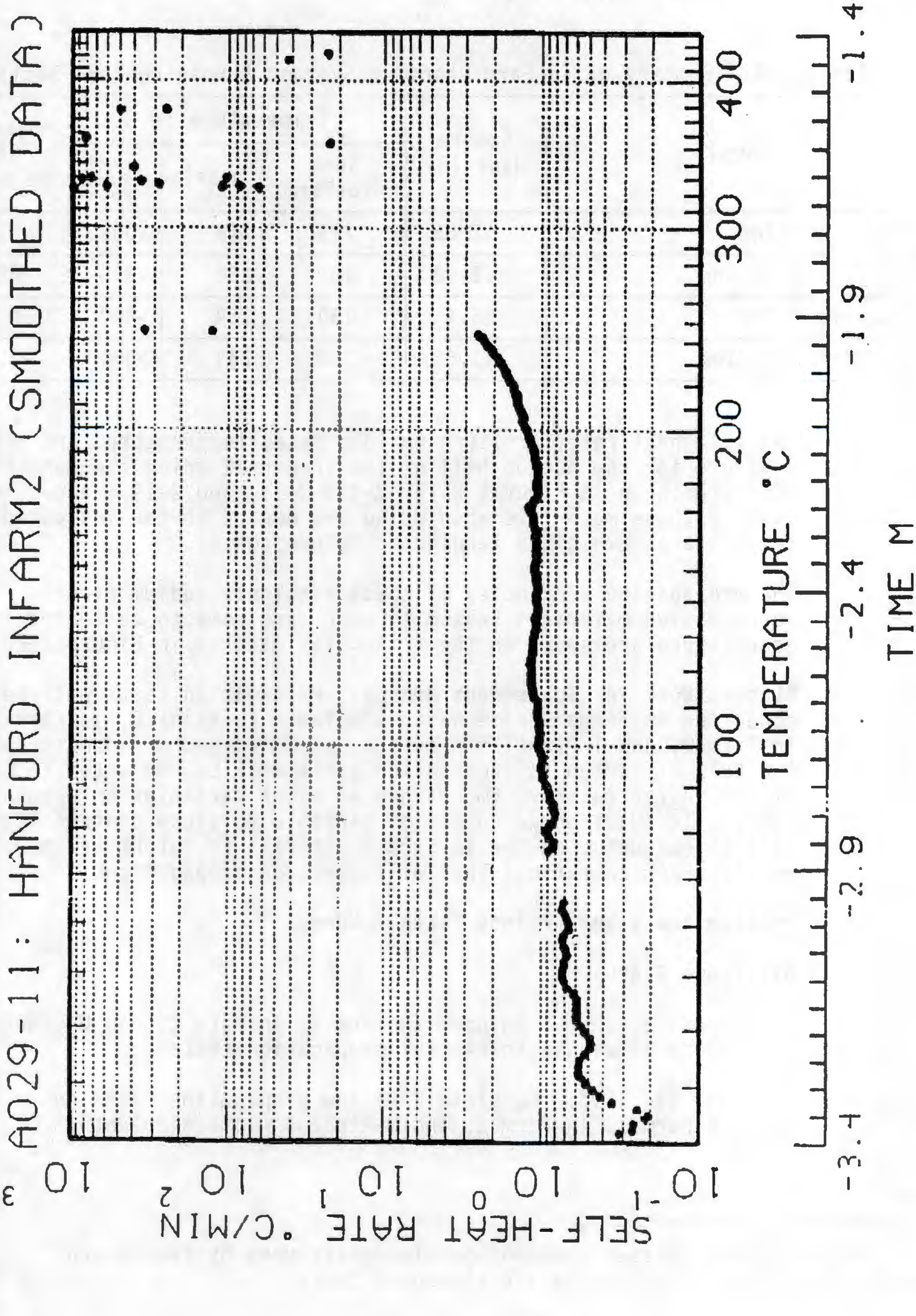


Figure 2-17. Reactive Systems Screening Tool Measurements of the Pressure Rise for Dried In-Farm-2 (Bottom Fraction).

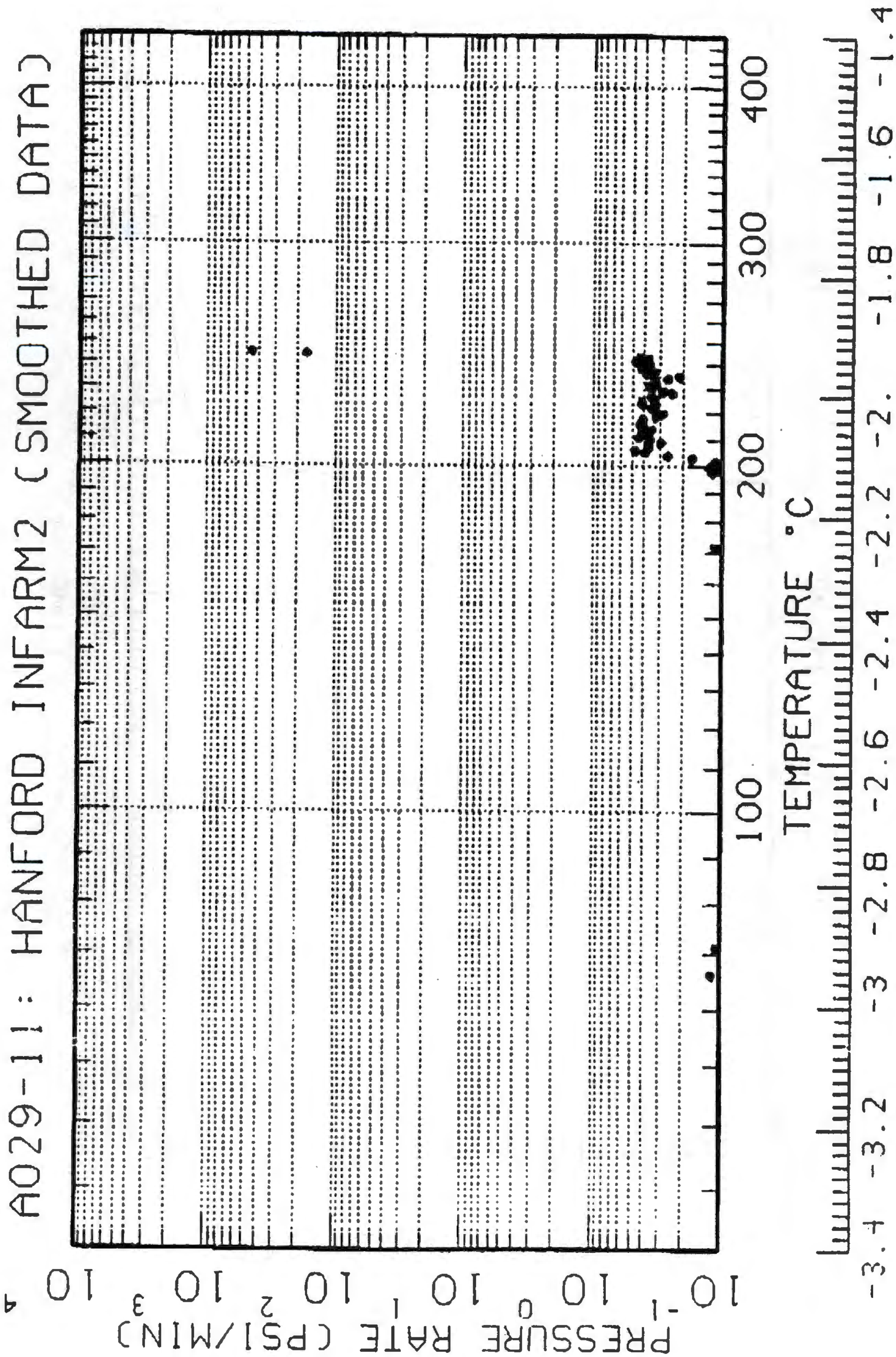


Figure 2-18. Reactive Systems Screening Tool Measurements of Pressure for Dried In-Farm-2 (Bottom Fraction).

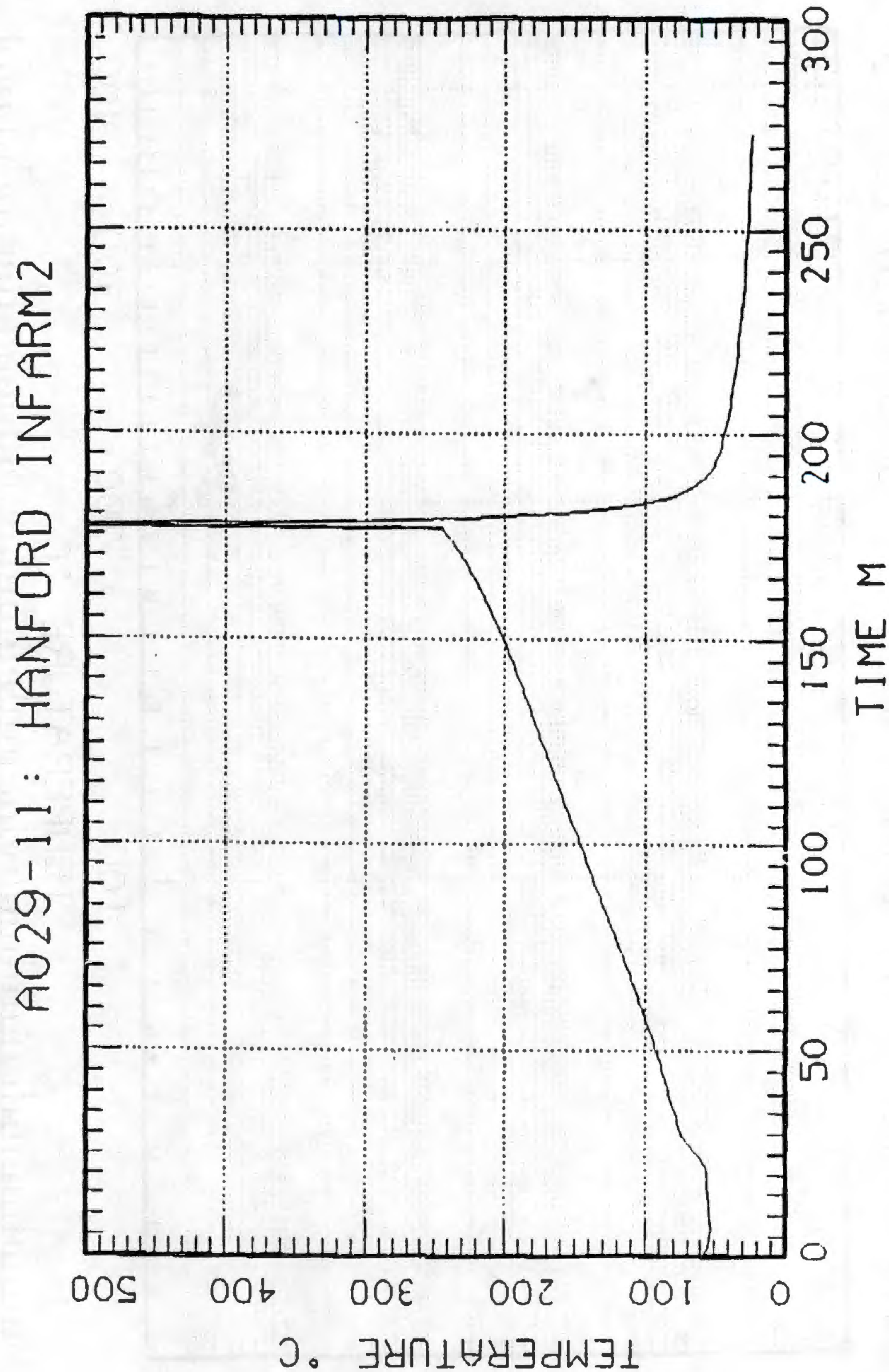


Figure 2-19. Reactive Systems Screening Tool Measurements of Temperature for Dried In-Farm-2 (Bottom Fraction).

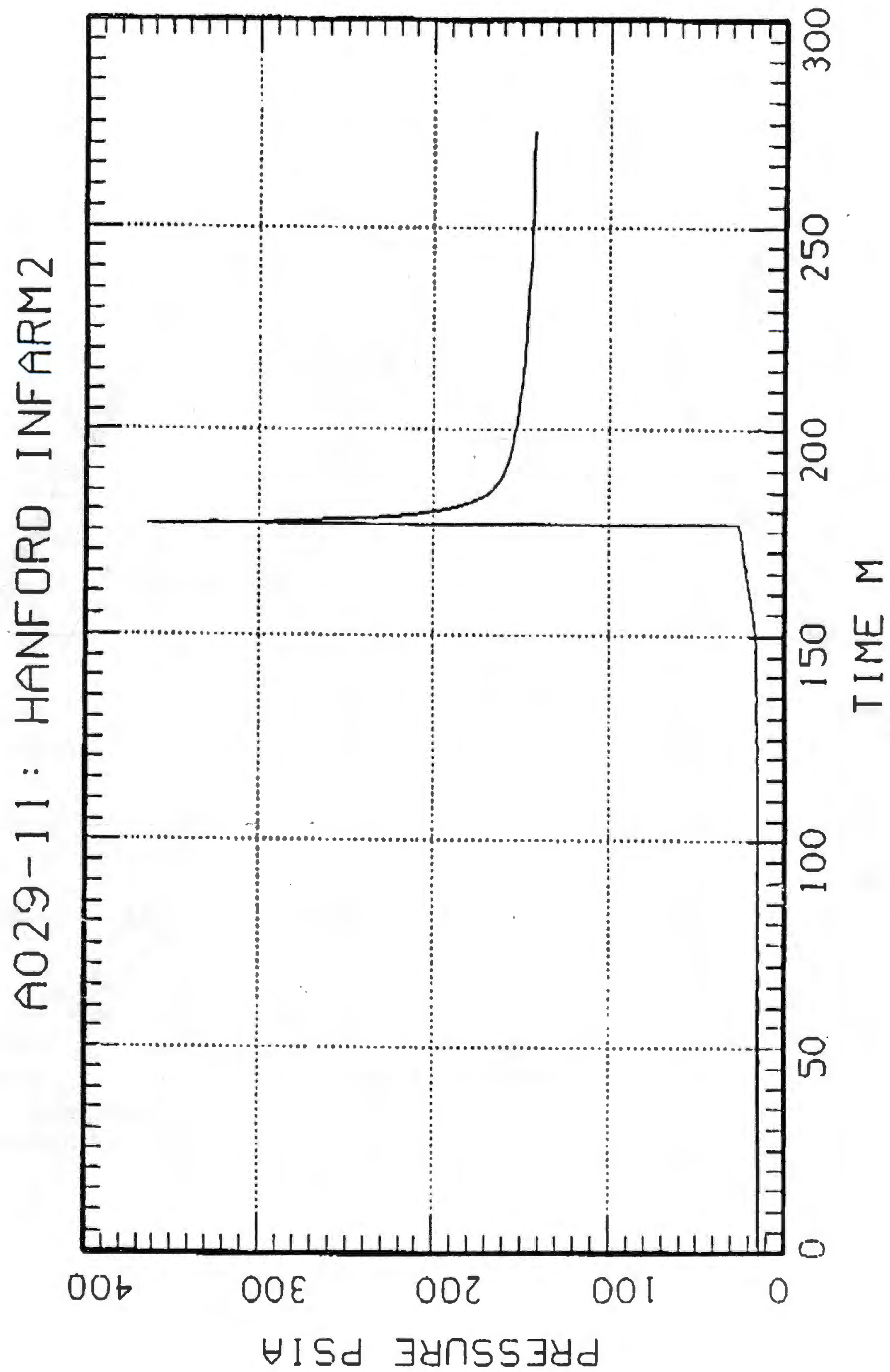
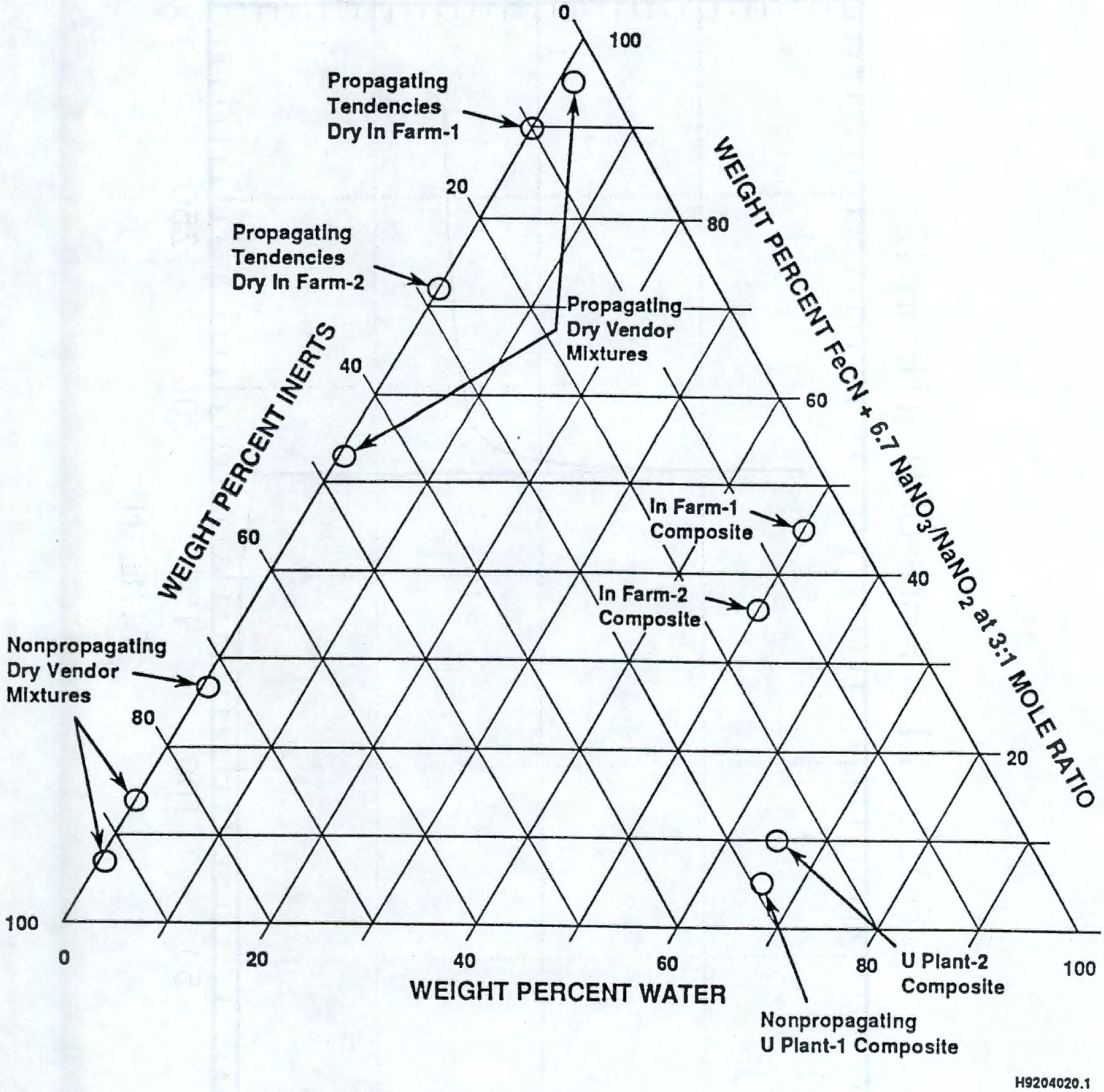


Figure 2-20. Sludge Composition Triangular Diagram Showing Propagating, Nonpropagating, and Mixtures to be Tested.



- July 31, 1992: Complete scanning matrix and variable moisture propagation tests.

- July 31, 1992: Define parametric and confined geometry tests.

2.6 DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7.6

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

2.6.1 Action Plan for Response to Abnormal Conditions

The *Action Plan for Response to Abnormal Conditions in Hanford Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991a) was prepared in response to DNFSB recommendations. The action plan describes the steps to be taken if a temperature increase trend above the tank temperature baseline is measured in any of the ferrocyanide tanks. The document was revised in December 1991 and reissued at 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.

- **Progress During Reporting Period.** Work was started this quarter on the safety assessment for stabilizing ferrocyanide tanks in support of the Tri-Party Agreement to stabilize all single-shell tanks by 1996, and to be able to saltwell pump a ferrocyanide tank if there are indications of a leak (see Section 2.4.6). Preparation of the safety assessment was redirected, however, to non-ferrocyanide tanks to satisfy a DOE verbal request to prepare safety documentation on non-watchlist tanks scheduled for near-term (FY 1992) stabilization. Instead, a SA was started for non-ferrocyanide tanks and that effort will lead into the assessment for ferrocyanide tanks.

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

- **Problem Areas and Action Taken.** During the April 11, 1991, meeting with the DNFSB, the question was posed, "What would Westinghouse Hanford do if there were a leak from a ferrocyanide tank?"

  Immediate actions have been defined that would include: assignment of initiating responsibilities, preparation and submittal of appropriate safety documentation, implementation of the readiness review process, and installation of external equipment to the tank. Upon approval to pump, final equipment would be installed and the tank pumped to established criteria.

- **Milestone Status.**

  - August 31, 1992: Issue 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.

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 event 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 will be able to 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 which 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.** Emergency event recognition and classification; protective action recommendations; and an emergency notification plan implementing procedures for response to tank farm emergencies have been completed and will be issued with an effective date of June 1, 1992. Concurrence and approval of these procedures by DOE is required. The procedures were approved and an initial

training has begun. Criteria that provides the basis for these procedures was submitted to DOE on September 19, 1991, and concurrence has not yet been received.

- **Planned Work For Subsequent Months.** The event recognition and classification emergency procedures to respond to tank farm emergencies will be forwarded to RL and DOE for concurrence and approval. Validation exercises of emergency response organizations will be conducted and a critique of the exercise results will be issued. A table top exercise is scheduled to be conducted at DOE by June 30, 1992.

- **Problem Areas and Action Taken.** Emergency Action Levels, which form the basis of the event recognition and classification procedures, and Emergency Planning Zones must have concurrence of DOE. The subject procedures for tank farm event recognition and classification have been approved by Westinghouse Hanford, and training has been initiated. Criteria submitted to DOE for approval have not been received and a potential change in the proposed criteria could result in procedure revisions.

- **Milestone Status.** The action to develop and issue Tank Farm emergency event recognition and classification procedures; protective action recommendations; and an emergency notification plan for implementing these procedures was originally scheduled for October 1, 1991. This activity was rescheduled for completion on May 15, 1992, and was just recently completed--ahead of schedule.

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3.0 SCHEDULES

The schedules shown in Figure 3-1 have been statused for the second quarter of FY 1992, ending March 31, 1992. Some milestones have been completed on or ahead of schedule, while others have slipped several months. Explanations for each slippage, where applicable, were described previously in Section 2.0 for each affected task activity.

Several additions were made to the schedules for this issue of the quarterly report. These additions are shown as solid and/or cross-hatched bars. The baseline schedule was not changed. Milestones started and/or completed on the baseline schedule are indicated by darkened triangles. Milestones on the projected (bar) schedules are also indicated by triangles, but their completion is indicated by a darkened triangle surrounded by a hexagon. The status line still refers to progress against the baseline schedule, as of March 31, 1992. A new schedule will be completed and issued next quarter as part of revision 1 to the implementation plan.

Delays were encountered this quarter in completing and approving SA and EA documentation required before the start of auger sampling and push-mode core sampling of scheduled ferrocyanide tanks. Sampling of tank 241-C-112 delayed from October was completed in March. Auger sampling of tank 241-BY-104, which had completed an earlier operational readiness review, has been delayed because access to all farms with ferrocyanide tanks now requires supplied respirator air. This restriction was imposed because of potential toxic vapors that might be present in the tanks. The restriction was precipitated by the January 28, 1992, release of noxious vapors near the BX and BY Tank Farms, that was later found to be unrelated to tank farm operations. At the end of the quarter, plans were proceeding with auger sampling of tank 241-BY-104 in early May and vapor sampling and push-mode core sampling of tank 241-C-109. Vapor sampling will then focus on 200 West Area ferrocyanide tanks in hopes of removing or reducing the supplied air restriction for T, TX, and TY Farms.

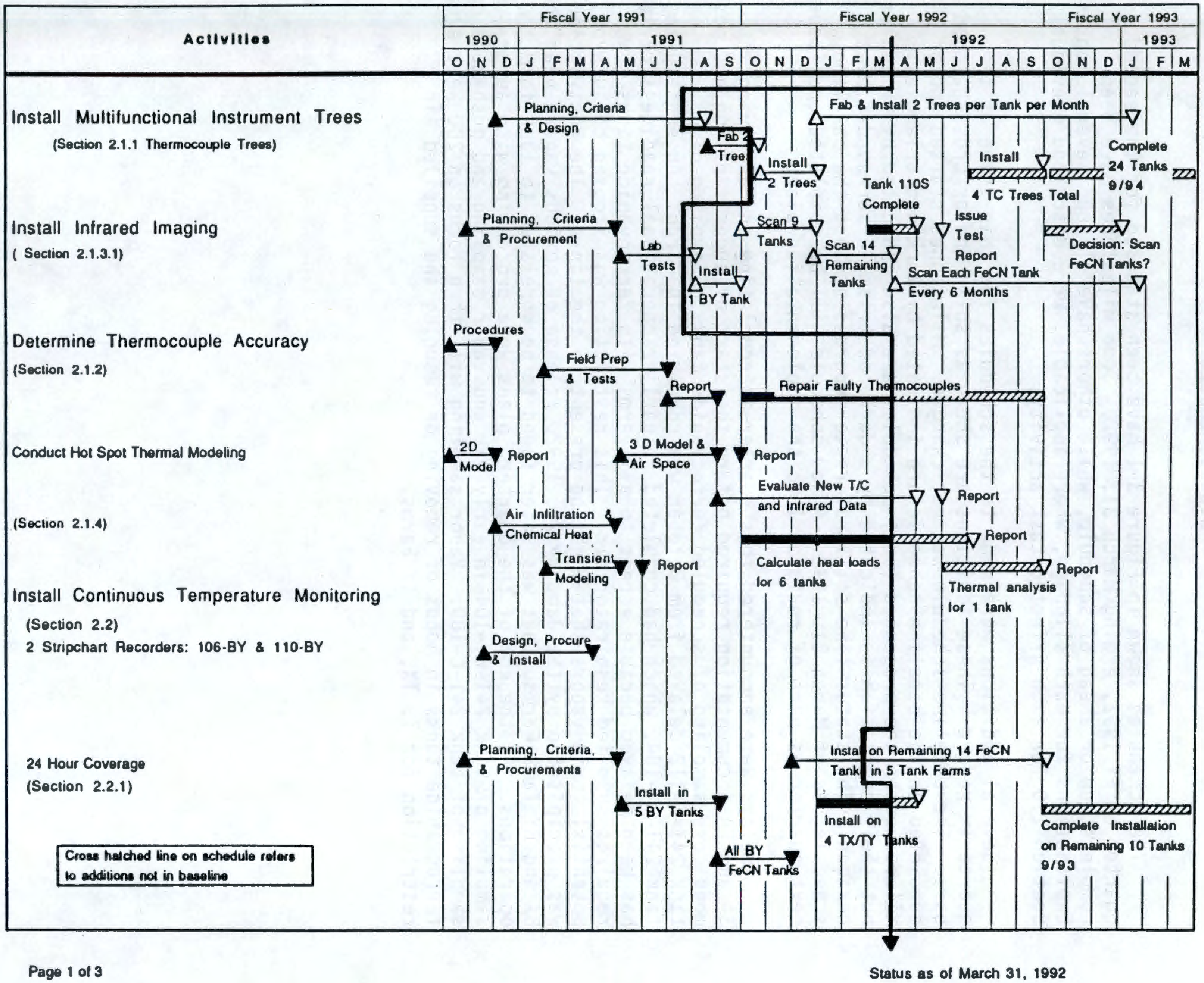

Figure 3-1. Schedule. (Sheet 1 of 3)

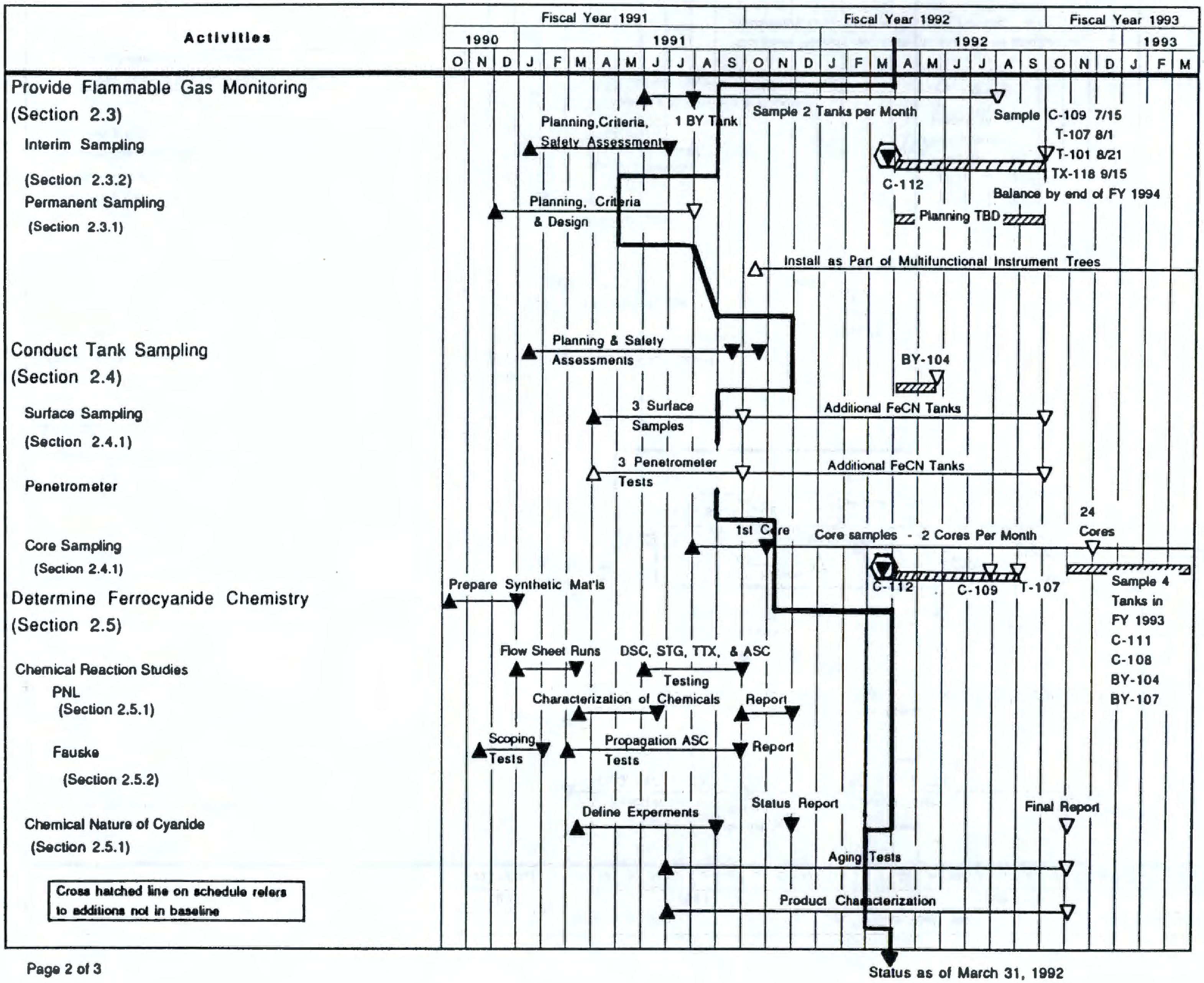

Figure 3-1. Schedule. (Sheet 2 of 3)

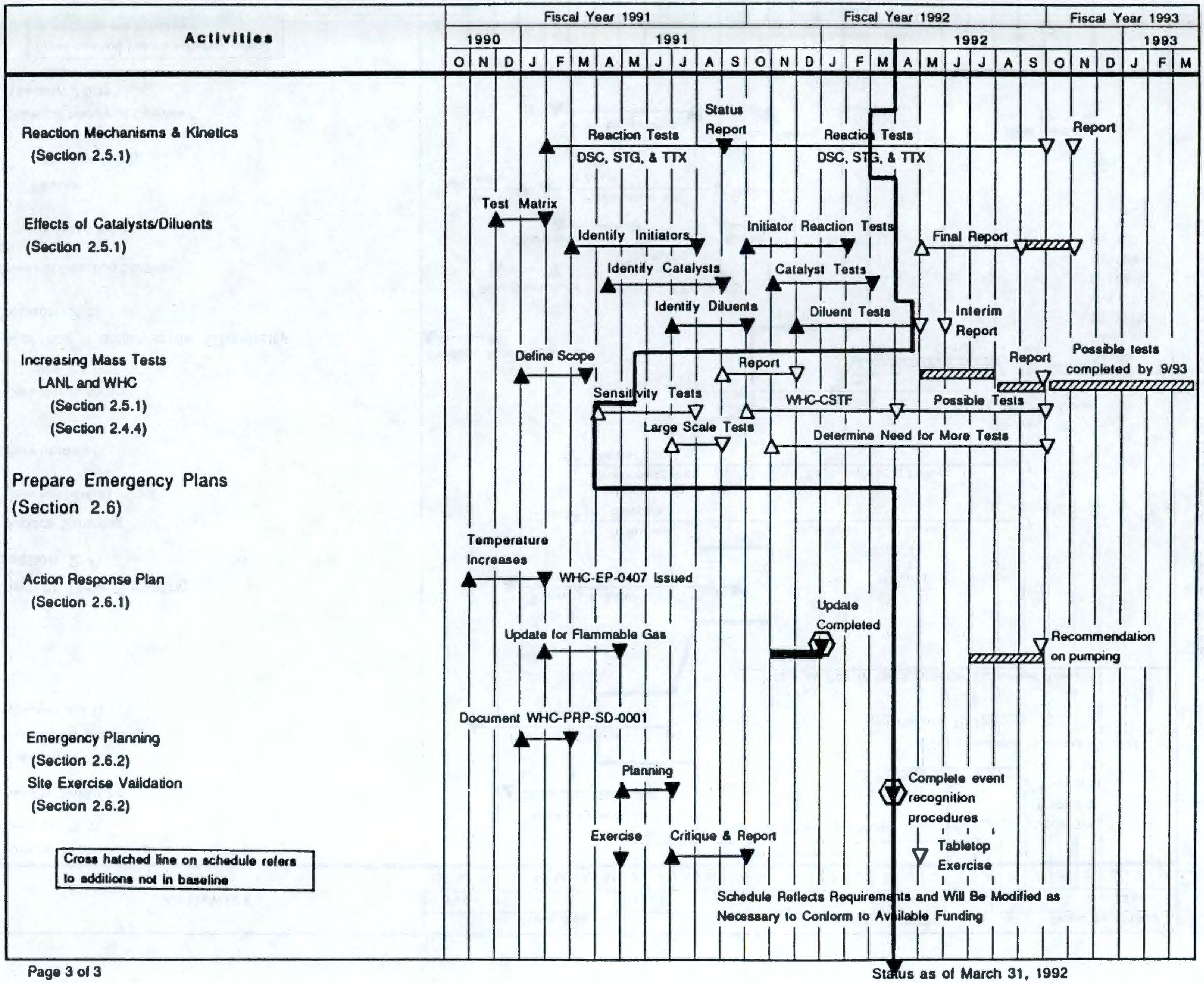

Figure 3-1. Schedule. (Sheet 3 of 3)

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APPENDIX A

LIST OF FERROCYANIDE TANKS

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

Tank	Total waste volume (1,000 gal)	FeCN[b] (1,000 g mol)	Heat load (Btu/h)[c]	Maximum temperature[d] (°C)	(°F)	Status
BX-102	96	< 1	10,000	18	65	Stabilized
BX-106	45	< 1	10,000	17	63	Not stabilized
BX-110	199	< 1	10,000	18	64	Stabilized
BX-111	230	< 1	10,000	21	69	Not stabilized
BY-101	387	< 1	8,200	23	74	Stabilized
BY-103	400	66	8,600	27	80	Not stabilized
BY-104	406	83	5,500[d]	54	129	Stabilized
BY-105	503	36	3,400[d]	46	114	Not stabilized
BY-106	642	70	3,300[d]	55	131	Not stabilized
BY-107	266	42	14,500	36	97	Stabilized
BY-108	228	58	23,000	33	92	Stabilized
BY-110	398	71	25,200	49	120	Stabilized
BY-111	459	6	34,200	31	87	Stabilized
BY-112	291	2	<10,000	28	83	Stabilized
C-108	66	25	10,000	22	71	Stabilized
C-109	66	30	3,800[d]	25	77	Stabilized
C-111	57	33	<10,000	21	69	Stabilized
C-112	109	31	<10,000	27	81	Stabilized
T-101	133	< 1	<10,000	23	74	Not stabilized
T-107	180	5	<10,000	19	66	Not stabilized
TX-118	347	< 3	4,900	24	75	Stabilized
TY-101	118	23	<10,000	20	68	Stabilized
TY-103	162	28	<10,000	19	67	Stabilized
TY-104	46	12	<10,000	21	69	Stabilized
Totals	5,834,000 gal	624,000 g-mol.				

[a]Based on information contained in monthly reports (WHC-EP-0182-XX) (Hanlon 1992).

[b]Inventories from Borsheim and Simpson, 1991.

[c]Heat load values are conservatively high; new values are being calculated (see Section 2.1.4).

[d]Data as of March 1992.

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APPENDIX B

METRIC CONVERSION CHART

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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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