The Secretary of Energy
Washington, DC 20585

March 7, 1991

The Honorable John T. Conway
Chairman
Defense Nuclear Facilities Safety Board
625 Indiana Avenue, N.W.
Washington, D.C. 20004

Dear Mr. Chairman:

Enclosed for your use is an Implementation Plan addressing a safety concern with ferrocyanide in single-shell tanks at the Hanford Site (Enclosure 1). This Implementation Plan is consistent with my December 3, 1990, responses to Recommendation 90-7. We understand that there was no public comment on my responses, which were published in the Federal Register on December 11, 1990 (55FR50875).

This Implementation Plan has been developed based on a Program Plan generated by the Hanford Ferrocyanide Task Team. It replaces an Implementation Plan submitted to you on August 10, 1990, that responded to your Recommendation 90-3, and is responsive to your Recommendation 90-7. Actions are ongoing and generally on schedule with the plans given in this Implementation Plan. We will provide quarterly reports on status of actions listed in this Implementation Plan.

As indicated in my responses to Recommendation 90-7, the Department of Energy has taken many actions to aggressively address the high-level radioactive waste (HLW) safety issues, including both unreviewed safety questions on hydrogen accumulation and ferrocyanide. Although we are in the early stages of implementing initiatives, preliminary results received to date will be helpful in guiding our future actions.

In response to the ferrocyanide issue, specifically Recommendation 90-7, the Hanford Ferrocyanide Task Team has systematically reviewed historical waste transfer records. This review identified two more single-shell tanks having the potential for a significant accumulation of ferrocyanide, bringing the total number of tanks in question to 24 tanks.

Hanford is implementing an Action Plan responding to abnormal conditions in ferrocyanide tanks (Enclosure 2) and has also developed a draft recovery plan addressing actions after an emergency (Enclosure 3). The HLW Tanks Advisory Panel's review of the ferrocyanide process flow sheets, and chemistry of waste storage and transfers resulted in the preliminary conclusion that ferrocyanide might have been redissolved and transferred to other HLW tanks.

Preliminary results from a reanalysis of the postulated ferrocyanide accident by the Los Alamos National Laboratory (LANL) confirm the Hanford analysis and show that the likelihood is low for hot spots at the temperature of concern, which is about 370°F; the highest temperature for a single-shell tank with ferrocyanide is less than 140°F. The results also confirm that the probability for a ferrocyanide explosion is low. Preliminary results such as these are being used to review the Ferrocyanide Program Plan that was issued in January 1991 (Enclosure 4), to ensure that critical data are being collected on a priority basis, and that needed program modifications are being planned and implemented.

As for the hydrogen issue, I am providing for your information a copy of the draft Hydrogen Program Plan (Enclosure 5), which is undergoing DOE review for technical adequacy, for appropriateness of the proposed schedules, and of its focus on mitigation and remediation. The Department has collected some crust samples from three level detectors removed from Tank 101-SY in November 1990. Even though these limited samples may not provide representative information about the composition of the crust, they provide preliminary indications that (1) considerable moisture may be present in the crust just beneath the surface that would act to significantly retard a secondary reaction; (2) total organic content of the crust might be too low to support a secondary reaction; and (3) synthetic crust materials are reasonably representative of the crust that was sampled. Based on these preliminary indications and laboratory studies performed with synthetic waste, the possibility of a secondary crust reaction appears to be low. This subjective conclusion requires considerably more sampling and further study to support a quantitative risk assessment.

Venting of Tank 101-SY was anticipated during the February 1991, time frame, and I approved a request to collect more crust samples and to install improved instrumentation in this tank (Enclosure 6). However, crust level drop, hydrogen concentration, temperature changes, and pressure history indicated a venting that would be smaller in magnitude than several previous events. The Department is working with Hanford staff to determine (1) if the venting that occurred was sufficient in magnitude to open a sampling window, and (2) what activities could have been conducted safely. We will keep you and your staff informed of our decisions. A detailed discussion will be provided when you and your Board members and staff visit the Hanford Site on March 12-13, 1991.

Resolution of the Hanford HLW safety issues is one of my top priority actions in the Department of Energy. All actions will be conducted in accordance with all applicable requirements. Internal safety oversight organizations are being kept informed so that they can discharge their independent review functions. We continue to work closely with the State of Washington and the U.S. Environmental Protection Agency to implement programs that may affect regulatory compliance with Federal and state environmental requirements at the Hanford Site.

Problems such as the Hanford HLW safety issues took decades to develop and will require more than one year to resolve. We will make the appropriate notification to Congress that it will take more than one year for the Department to complete actions given in this Implementation Plan. The Department is committed to working closely with the Defense Nuclear Facilities Safety Board members and staff to address these safety issues in an expeditious manner. Please contact me or Leo Duffy if we can be of assistance.

Sincerely,

James D. Watkins
Admiral, U.S. Navy (Retired)

Enclosures

ENCLOSURE 1

91:633

WHC-EP-0415

Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7

Prepared for the U.S. Department of Energy
Assistant Secretary for Environment, Safety and Health

Westinghouse Hanford Company Richland, Washington

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

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WHC-EP-0415

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Implementation Plan for the Defense Nuclear Facilities Safety Board Recommendation 90-7

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Approved for Public Release

IMPLEMENTATION PLAN FOR DEFENSE NUCLEAR FACILITIES SAFETY BOARD RECOMMENDATION 90-7

R. J. Cash

ABSTRACT

This document describes the plan for implementing the recommendations made by the Defense Nuclear Facilities Safety Board in their Recommendation 90-7 to the U.S. Department of Energy. Recommendation 90-7 addresses safety issues of concern for 24 single-shell, high-level radioactive waste tanks containing ferrocyanide compounds at the Hanford Site. These tanks are a potential safety concern because under certain conditions involving elevated temperatures ferrocyanide compounds in the presence of oxidizing materials can be made to explode. Activities underway by the responsible Hanford Site contractor that address each of the six parts of Defense Nuclear Facilities Safety Board Recommendation 90-7 are described. Schedules are also included with the plan.

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1.0 INTRODUCTION

In March 1990, the Defense Nuclear Facilities Safety Board (DNFSB) gave the U.S. Department of Energy (DOE) its Recommendation 90-3 (FR 1990a) regarding the safety of single-shell high-level radioactive waste (HLW) tanks at the Hanford Site. The tanks of interest are those containing significant amounts of ferrocyanide that under certain abnormal conditions might increase in temperature to a value where explosive ferrocyanide reactions could occur.

The DOE submitted an implementation plan to the DNFSB in August 1990 addressing the four parts of Recommendation 90-3 (FR 1990b). The DNFSB reviewed this implementation plan and believed the plan was not adequately responsive to Recommendation 90-3. To strengthen their concerns, the DNFSB reiterated their position in Recommendation 90-7, consisting of six parts (FR 1990c). The DOE accepted the six recommendations (FR 1990d), and agreed with the need to accelerate and expand its programs dealing with the HLW safety issues at the Hanford Site. The Implementation Plan for Recommendation 90-3 has been expanded and program elements accelerated to be responsive to DNFSB Recommendation 90-7.

2.0 BACKGROUND

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 1984; Burger and Scheele 1988). In 1987, the environmental impact statement (EIS), *Final Environmental Impact Statement - Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes* (DOE 1987), was issued. The EIS 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 recently completed General Accounting Office (GAO) study (Peach 1990) postulates a greater "worst-case" accident with independently calculated doses of one to two orders of magnitude greater than DOE (1987). Coupling the ferrocyanide concerns with potential hydrogen accumulating in some Hanford Site HLW tanks, the DOE established the High-Level Radioactive Waste Tanks Task Force and Technical Advisory Panel in August 1990. These two groups were formed to ensure that all safety concerns with HLW tanks at DOE sites are identified and addressed in a systematic and timely manner. The initial focus of the task force and Technical Advisory Panel is on the Hanford Site hydrogen and ferrocyanide safety issues. In September 1990, a special Hanford Site

Ferrocyanide Task Team was commissioned by the Westinghouse Hanford Company to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident.

Using process knowledge and transfer records, an evaluation process that is still ongoing, 24 tanks[1] have been identified at the Hanford Site as containing 1,000 g-mole (465 lb) or more of ferrocyanide as the $Fe(CN)_6$ radical. In October 1990, the ferrocyanide issue was declared an Unreviewed Safety Question[2] because the safety envelope for these tanks may no longer be bounded by the existing safety analysis report (WHC 1986). Work in and around any of the ferrocyanide tanks requires detailed planning with the preparation of supporting safety and environmental documentation and approval by DOE top management. These restrictions are required for safety purposes; however, they do increase the time required to complete work or install equipment in the tanks.

Five of the ferrocyanide tanks (104-BY, 105-BY, 106-BY, 108-BY, and 110-BY) have temperature readings above 38 °C (100 °F), but below 60 °C (140 °F). These tanks each contain from 30,000 g-moles (13,950 lb) to 200,000 g-moles (93,000 lb) of ferrocyanide and are the highest priority for installation of expanded tank monitoring capabilities. Tank 104-BY is the first choice for expanded tank monitoring because it contains the most ferrocyanide and is the reference "worst-case" tank for safety purposes. Temperatures in the remaining 19 tanks are below 38 °C (100 °F), and many contain less than 10,000 g-moles (4,650 lb) of ferrocyanide. Table 1 lists significant data on the 24 ferrocyanide tanks.

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[1] Two more tanks potentially containing ferrocyanide were identified since DOE responded to Recommendation 90-7 in November 1990.

[2] Unreviewed Safety Question as defined by DOE Order 5480.5 (DOE 1986).

"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."

Table 1. Significant Data on Ferrocyanide Tanks.

Tank	Ferrocyanide (1,000 g-moles)	Heat load (Btu/h)	Maximum temperature (°F) (January 1991)	Assumed leaker	Interim stabilized
102-BX	0 - 3	<10,000	65	1971	11/78
106-BX	0 - 1	<10,000	64	No	NA
110-BX	0 - 1	<10,000	65	1976	8/85
111-BX	0 - 1	<10,000	69	1984	NA
101-BY	0 - 1	8,200	75	No	5/84
103-BY	0 - 1	8,600	80[a]	1973	NA
104-BY	100 - 200	17,000	129	No	1/85
105-BY	70 - 100	37,700	114	1978	12/84
106-BY	30	12,200	132	1984	NA
107-BY	30 - 80	14,500	79	1984	7/79
108-BY	30 - 70	23,000	102	1972	2/85
110-BY	50 - 90	25,200	122	No	1/85
111-BY	0 - 3	34,200	84[a]	No	1/85
112-BY	2 - 3	<10,000	66[a]	No	5/85
108-C	9 - 20	<10,000	74	No	3/84
109-C	30 - 50	<10,000	77	No	11/83
111-C	10 - 30	<10,000	72	1968	3/84
112-C	50 - 70	<10,000	81	No	9/90
101-T	0 - 10	<10,000	68	No	NA
107-T	0 - 5	<10,000	60[b]	1984	NA
118-TX	0 - 3	4,900	73	No	4/83
101-TY	0 - 30	<10,000	67	1973	8/83
103-TY	0 - 30	<10,000	63[a]	1973	2/83
104-TY	0 - 20	<10,000	72[b]	No	NA
24 tanks					

NOTE: To convert °F to °C, use the formula (°F - 32)/1.8.

[a] Temperature data from liquid observation well.

[b] Historical data suspect.

NA = Not applicable.

3.0 OBJECTIVES

The objective of this implementation plan is to specifically show how each of the six parts of DNFSB Recommendation 90-7 (FR 1990c) is being addressed and to describe the associated program activities for that part of the recommendation.

The overall approach taken to address the ferrocyanide issues includes short- and long-term safety analyses, management and control of tank storage operations, collection and analysis of tank historical information, interim waste tank stabilization, and, ultimately, waste remediation and/or disposal. The principal objective of the work is to gain a thorough understanding of ferrocyanide tank waste and the reactive behavior of its constituents so that (1) the ferrocyanide tanks can be maintained in a safe condition with minimal risk of an incident, (2) one or more strategies can be selected to implement interim stabilization, and (3) ultimate disposal options can be identified and developed.

To gain a thorough understanding of the ferrocyanide tank waste and the reactive behavior of its constituents, chemical reaction studies are underway using synthetic compounds believed to be in the ferrocyanide waste tanks. These tests are described in more detail in Section 4.5. Aerosol tests are also planned in the Hanford Site Containment Systems Test Facility to experimentally validate dose consequence release models that bound the "worst-case" accident scenario.

Instrumentation presently on many of the ferrocyanide tanks consists only of equipment originally installed when the tanks were constructed. Although some new capability, such as liquid observation wells (LOWs), was installed on some of the tanks, obtainable tank data are limited and sometimes suspect. In addition, the physical properties and exact chemical makeup of the waste are not well known because so many additions and transfers occurred since the original ferrocyanide scavenging campaigns in the mid-1950's. Chemical and physical changes may have occurred within the waste over the 30-plus yr of storage. To learn what is in the tanks and to monitor continuously their conditions, it is necessary to provide an accelerated program to upgrade the databases for these tanks. The purpose of the ferrocyanide program is to provide these databases by the end of fiscal year 1993, so that the principal objective stated previously can be achieved.

Activities underway addressing each part of DNFSB Recommendation 90-7 are detailed and discussed separately in Section 4.0. A schedule for these activities is shown in Section 5.0.

4.0 IMPLEMENTATION TASK ACTIVITIES

4.1 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."*

4.1.1 Discussion

An "Expanded Tank Monitoring and Modeling" task activity was set up to respond to this recommendation and Recommendations 90-7.2 and 90-7.3. Four of the subtasks for this activity apply to this recommendation:

1. Installation of new multifunctional instrument trees
2. Application of alternative tank monitoring technologies, such as infrared imaging
3. Upgrades to existing tank temperature monitoring instrumentation
4. Development and analyses of a thermal model for ferrocyanide tank temperatures and hot spots.

The first two activities specifically respond to Recommendation 90-7.1.

4.1.2 Multifunctional Instrument Trees

The existing thermocouple trees in the 24 ferrocyanide tanks are the original trees installed when the tanks were constructed. In at least four tanks, the thermocouple trees are inoperative, and individual thermocouples in certain remaining trees are also not functional. In some cases, the historical data are suspect.

To comply with this recommendation, new trees must be fabricated and installed. Because the number of available openings (risers) in the single-shell tanks is limited and three or more trees are needed in the ferrocyanide tanks at statistically significant locations, it is prudent to incorporate into the design as many monitoring capabilities as possible.

The multifunctional tree will have, as a minimum, 12 thermocouples; guide tube to be used for calibrating the thermocouples in place or for measuring temperature at selected elevations; and 3 dome space gas sampling tubes. The gas sampling tubes are discussed under Section 4.3, which responds to Recommendation 90-7.3. The thermocouples will be protected from contamination by the tank contents and spaced at set elevations from the bottom of the tree; at least two thermocouples, near the top of the tank, will measure temperatures in the dome space above the waste.

The design engineers for the multifunctional tree are evaluating the possibility of adding one or more tubes for deployment of fiber optic cables for sensing waste and dome space gas compositions. The feasibility is still being determined. A generic design applicable for all tanks (both single-shell and double-shell tanks) has been specified. Because there are different waste levels in each tank and the length of the tree has to vary depending upon riser location and tank design, placement of the sampling tubes and the thermocouples are tank dependent.

The schedule for installation of multifunctional instrument trees in the ferrocyanide tanks shows two trees being installed by December 1991. During fiscal year 1992, trees should be installed in the ferrocyanide tanks at the rate of two trees per month. Priority will be given to those tanks of greatest interest and that have had pumpable liquid waste removed as part of the Hanford Site single-shell tank interim stabilization program. Considerable field work will be necessary for some tanks because they have been interim isolated and stabilized. The risers were foamed in and sealed for protection against water intrusion. It may also be necessary to remove some hardware now installed in some risers before new trees can be inserted. These issues are being investigated by a special riser task force created for this purpose.

4.1.3 Alternate Tank Monitoring Technologies

Infrared Imaging System -- Infrared (IR) imaging systems are commercially available from numerous vendors. An IR system was used at the Hanford Site in the recent past to perform in-tank surface temperature mapping. Because these systems are sensitive to changes of +/- 0.5 °C (+/- 41 °F), they should prove very beneficial for mapping the surface temperature profiles in the ferrocyanide waste tanks. Thermal modeling performed on Tank 104-BY shows that hot spots with temperatures of concern would produce surface differences easily detectable by IR imaging.

One drawback of an IR imaging system is the limited life caused by gamma radiation exposure to the semiconductor components within the scanner. Assuming an average radiation level within the single-shell tanks of 400 R/h, the useful life of an IR scanner is approximately 25 to 50 h. Deployment for surface monitoring, therefore, will have to be done periodically, perhaps weekly or monthly, unless tank anomalies dictate otherwise.

The IR emitted from a surface is a function of both its temperature and emissivity. The emissivity of the surface is its ability to emit IR radiation; this property changes with variations in surface composition, texture, and moisture content. Because the waste surface in the tanks is not uniform, accurate temperature measurement is probably not possible; however, temperature mapping is useful to detect potential hot spots and for historical comparison when one scan is compared with another taken at a different time. Evidence of a change in temperature at a particular location should be noticeable, although results of recent thermal modeling show that the time constant for surface temperature changes because of a hot spot at the bottom of the tank may be on the order of 1 to 2 mo.

Procurement, delivery, testing, and deployment of an IR imaging system in one of the five highest priority tanks is scheduled for August 1991. Assuming laboratory IR test results are favorable, several IR imaging systems would be procured and deployed in the field for monitoring the 24 ferrocyanide tanks. A routine IR scanning program should be in place for all 24 tanks by April 1992, as shown in the schedule (Figure 1).

Other Tank Monitoring Techniques -- Other monitoring now done on applicable ferrocyanide tanks at the Hanford Site include gamma scans and neutron probe scans to monitor interstitial liquid levels. These techniques can only be applied for tanks that have LOWs. The LOW is a closed-end nonmetallic (sometimes fiberglass) tube approximately 10.2 cm (4 in.) in diameter that enters the tank through a riser and extends to the tank bottom. Eleven ferrocyanide tanks have LOWs. The LOWs are also being used in some cases for measuring the waste temperature by placing a thermocouple into the well in tanks without an operable thermocouple tree.

Gamma scans show gross radiation levels within a tank, while neutron scans show the moisture content, both as a function of elevation. The liquid level and the saltcake level are both discernable in the tank. Westinghouse Hanford Company scientists, with assistance from scientists at DOE national laboratories, are working on new gamma energy discrimination techniques that may allow characterization of various isotopes within the waste as a function of elevation. In addition, pulsed-neutron scans may be very effective for determining information on tank contents and moisture content as a function of elevation. Well-logging instrumentation, commercially available and widely used in oil fields, uses this technique.

Gamma and neutron scans will continue on a periodic basis for the 11 ferrocyanide tanks with LOWs. Pulsed-neutron technology is presently being investigated for applications in the tanks; the schedule for possible deployment in the tanks is not yet defined.

4.1.4 Upgrades to Existing Tank Temperature Monitoring Instrumentation

This subtask was started as part of the response to Recommendation 90-3 and is continuing. The activity will determine the accuracy of presently installed thermocouples on the 24 ferrocyanide tanks and other tanks of interest at the Hanford Site. Until new multifunctional instrument trees are installed, these thermocouples must be used to provide temperature measurements in the ferrocyanide tanks.

Field measurements are being taken on each thermocouple in the existing trees to determine resistance across the junction and across each lead to ground. The ends of each lead are being redressed and new plugs are being installed. The exact condition of each thermocouple is being determined using resistance and voltage measurements. The location (elevation) of each thermocouple is being verified by drawings and resistance measurements. The leads will be resealed within the tree and the coverbox weatherized to keep moisture out. It is expected that many suspect readings and most scatter in temperature data will be eliminated by these upgrades and the parallel effort to upgrade procedures to track unusual readings and new training for operations personnel involved with taking and surveying the data.

These upgrades are scheduled for completion on all ferrocyanide tanks by June 1991, with a report to follow by August 1991.

4.1.5 Hot Spot Thermal Modeling

The decay of radioactive materials in the waste tanks generates heat. Runaway chemical reactions within the waste could occur if the temperature in a tank reaches a value high enough to cause significant exothermic reaction rates. Because there is presently only one thermocouple tree per tank and the trees are not always at the same location, uneven heat generation could exist in these tanks and not be detected. This subtask provides for modeling and analysis of available temperature data from some of 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 hot spots that could theoretically exist within the waste.

State-of-the-art, validated computer codes are used in the modeling. They are benchmarked with existing data and employ two- and three-dimensional capabilities. Present work involves only steady-state modeling, but the activity calls for transient modeling later in the program.

Six subtasks are ongoing or planned:

1. Heat removal from tank dome by air infiltration/breathing. This will establish an upper bound for the tank heat load and thermal conductivities of the sludge and saltcake layers. Scheduled completion: April 1991.

2. Hot spot analyses. Using thermal properties obtained from subtask 1 the thermal loading necessary to achieve a 175 °C (350 °F) hot spot will be determined. Evaluate effects of low thermal conductivities (dryout) in the vicinity of a hot spot. This temperature is of interest because it is close to exothermic values observed in the laboratory. Scheduled completion: April 1991.

system. Monitoring will be continuous, with the capability of taking measurements in the range of every few seconds up to once per day. All thermocouple data will be collected automatically at the CASS operator control station. The monitoring system will be independent of CASS and be capable of displaying, to an operator, on request. Trend data on selected points will be available for display in numeric or graphic form.

The system will have the capability to assign alarms for change in level for any temperature point. Alarms will trigger an audible annunciator and be logged to hardcopy on occurrence. An alarm summary display will provide a list of the most recent alarms in order of occurrence. Each alarm will be identified by point and time of occurrence. Operator acknowledgement of the alarm will silence the audible annunciator.

Signal conditioning and multiplexing will be 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 interference and thermal gradients are thereby reduced.

Field installation of the continuous monitoring system is now underway for the BY Tank Farm. There are 10 ferrocyanide tanks in this farm, 5 of which are the highest priority tanks of interest. Continuous monitoring for these 5 tanks will be operational in August 1991, with completion of the remaining tanks by December 1991. The last 14 tanks, which are located in five other tank farms, will be linked to CASS by the end of fiscal year 1992. Installation in the field is a time-consuming process because all wires have to be placed in buried electrical conduit and several thousand feet of trenches must be dug by hand. Workers must wear special work permit clothing because of possible radioactive ground contamination.

To provide some near-term continuous monitoring, two strip-chart recorders are being installed on Tanks 106-BY and 110-BY. The recorders will be located in a building adjacent to the BY Tank Farm and will be monitored and maintained by Tank Farm Facility Operations. Initial screening of tank temperature data will also be performed by Facility Operations. Tank Farm Surveillance Analysis will receive the temperature data and be responsible for reviewing (trending), permanently logging (record keeping), and reporting the data on a weekly basis. This installation will be operational by March 1991.

Currently, abnormal readings are treated in accordance with *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide*, WHC-EP-0407 (Cash and Thurman 1991); see Section 4.6.

4.3 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."

4.3.1 Discussion

The multifunctional instrument trees discussed in Section 4.1 are being designed to have dome space gas sampling tubes incorporated within the body of the tree. These tubes will be located within each tree and will penetrate the side of the tree at elevations that allow gases from several levels within the tank dome space to be sampled.

The dome space gas sampling tubes will exit through the top of the instrument tree and can be cleaned if vapor deposits cause plugging. Gas drawn from these tubes will be monitored for gas composition and moisture (humidity) either on a continuous basis, if warranted, or on a periodic basis depending upon trending data, once the trees are installed and become operational. This method of dome space gas sampling will replace flammable gas sampling now done on an "as requested" basis using hand-held portable gas monitors.

4.3.2 Interim Flammable Gas Monitoring

An intensive effort is now underway to conduct flammable gas monitoring and analyses in the 24 ferrocyanide tanks, starting with the 5 highest priority BY tanks. Because the ferrocyanide tanks are listed as an Unreviewed Safety Question, this activity is directed at securing DOE approval to perform follow-on sampling activities within the tanks. Although sampling conducted in the past by Industrial Hygiene and Safety has indicated no flammable gas content above 6% of the lower flammability limit (LFL), no qualitative measurements for individual species were obtained.

All 24 ferrocyanide tanks are passively ventilated through individual breather filters. The air breathing is dependent upon changes in barometric pressure. 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. In addition, there is a potential for air flow through the dome space via natural circulation.

Tank dome space gas samples will be taken through different risers and at three elevations. The lowest elevation sample will be about 0.30 m (1 ft) above the waste surface, with one sample in the middle and one near the top. Gas sampling criteria have been defined and include identification of the chemicals to be monitored, detection limits, accuracy and precision of the analytical methods, sample positions inside the tank, and sample frequency. Sampling and analysis of the dome space in the first tank will be completed during June and July 1991, and subsequent tanks will be sampled at the rate of approximately two tanks per month. Analysis and comparison of the data may allow reduction in the number of samples taken per tank.

4.4 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."*

4.4.1 Discussion

Characterization of the tank contents is necessary to guide chemical reaction studies, to allow application of the study results to remediation of these tanks, and to provide a basis for estimating the consequences of an uncontrolled ferrocyanide reaction. Knowledge of the relative position of various waste constituents is also important to determine the proximity of potential reactants.

4.4.2 Ferrocyanide Tank Waste Sampling and Characterization

The important reaction materials present in the ferrocyanide tanks are fuel (ferrocyanides and reduced carbon species, such as organic complexants), oxidants (nitrates and nitrites), and inerts or diluents (phosphates, sulfates, carbonates, oxides, and hydroxides). The location of fission products, such as ^{137}Cs and ^{90}Sr, are important because they act as heat sources that can raise and maintain the temperature of the tank contents and because they are source terms in the event of a radiological release. The water content of the waste is very important because the high heat capacity and the heat of vaporization for water makes it an effective inerting material and prevents sustained combustion. Other materials may be important as potential catalysts (e.g., nickel, copper, lead, and the rare earths).

The waste characterization plan for the Hanford Site single-shell tanks (Winters et al. 1991) calls for obtaining two core samples from each single-shell tank by 1998, as part of the Environmental Restoration and Remediation Action (ERRA) program. Originally, the ferrocyanide tanks were not a high priority for sampling in this plan because the saltcake layer in several of these tanks was expected to make core sampling difficult. The priority for sampling ferrocyanide tanks has now been changed to reflect the need to determine reactive properties of the contents. This change in priority will not affect ERRA commitments, because core samples obtained from the ferrocyanide tanks are part of the same commitment. Ferrocyanide tank samples will undergo all analyses to satisfy ERRA requirements and those required to resolve safety issues.

The critical path for obtaining core samples is tied to the preparation and approval of safety assessment documentation and tank data that must be obtained to support this documentation. Because operations in and around the ferrocyanide tanks are severely restricted by DOE Order 5480.5 (DOE 1986) for Unreviewed Safety Questions, the task of eventually getting core samples must follow an orderly process. This process starts first with a safety assessment and DOE approval to obtain samples of the dome space gas (Section 4.3). The next step is to obtain samples of the saltcake to determine its composition and properties. This activity will also require a safety assessment and DOE approval. Because the saltcake may be difficult to core drill, surface samples up to 15.24 cm (6 in.) deep will be obtained by using a newly developed "surface (auger) sampler." Saltcake penetration resistance tests will be measured with a modified commercial soil penetrometer. The information obtained from these activities will feed into the safety assessment, plans, and approvals for core sampling. This process is now well underway for hydrogen-producing Tank 101-SY at the Hanford Site, and these activities will provide invaluable guidance for core sampling of the ferrocyanide tanks.

Again, priority is being given to obtaining core samples from the five tanks at the BY Tank Farm of greatest interest. Dome space gas samples from one of these tanks should be obtained in June and analyzed by July. Dome space gas sampling will continue on the other tanks thereafter. The present design for the "surface sampler" and the penetrometer use the same guide tube assembly and the two operations are normally done in concert. Saltcake samples would be taken first for determining chemical and physical properties in the laboratory followed immediately by a penetrometer test to measure saltcake resistance and thickness. At least three different locations will be sampled in the first ferrocyanide tank; this is scheduled for completion by September 1991. Obtaining one full-length core sample is planned by October 1991. The high priority now placed on Tank 101-SY sampling could possibly impact this schedule, as it already has for fiscal year 1991 core sampling of other non-ferrocyanide single-shell tanks. Three core samples will probably be taken from each of the five highest priority BY tanks. This could be reduced to two full-length core samples if results show layers and compositions are similar within the same tank. Once routine sampling is achieved, ferrocyanide tanks will be sampled at an average rate of two core samples per month until completed in fiscal year 1993. Additional surface sampling and penetrometer tests will continue in other ferrocyanide tanks to support core sampling of these tanks as necessary.

4.5 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."

4.5.1 Discussion

Determining the chemical reaction characteristics of possible ferrocyanide precipitates, their radiolysis, and aging progeny with nitrates and/or nitrites is central to determining the hazard associated with ferrocyanides in the single-shell tanks and to developing a strategy for rendering the wastes nonexplosive. Because it is so important, an aggressive program was started early in fiscal year 1991 that addresses the embodiment of Recommendation 90-7.5.

Understanding the chemistry and sensitivities of the ferrocyanide reactions will also provide tank farm management with knowledge essential for ensuring the safety of operations and selection of appropriate remediation or disposal strategies. Schedules for these activities are shown in Section 5.0.

4.5.2 Chemical Reaction Studies

In late 1988, the Pacific Northwest Laboratory (PNL) began an experimental program to investigate the effects of temperature on the oxidation reaction between ferrocyanide and nitrates and nitrites representative of materials present in the Hanford Site ferrocyanide tanks. Additional reaction studies were started at the Los Alamos National Laboratory (LANL) in fiscal year 1990. These studies involve measuring the reaction sensitivity to possible initiating events, such as impact, friction, or thermal events, in order to determine what conditions will initiate reactions.

<u>Initial Results</u> -- Testing to date indicates that both the reaction and explosion can be thermally initiated, are sensitive to the cation of the nitrate and/or nitrite, are sensitive to whether the oxidant is nitrate or nitrite, and are sensitive to EDTA (ethylenediaminetetraacetic acid), iron hydroxide, and nickel hydroxide catalysts or initiators. The lowest exothermic reaction and explosion temperatures observed by PNL during their fiscal year 1990 test program were 220 °C (430 °F) and 280 °C (540 °F), respectively, for an oxidant mixture of 47.5 mol% sodium nitrate, 47.5 mol% sodium nitrite, and 5 mol% EDTA (Burger and Scheele 1990).

Testing conducted at LANL in fiscal year 1990 shows that a mixture made from nearly equimolar amounts of ferrocyanide and 50 mol% sodium nitrate/50 mol% sodium nitrite was insensitive both to reaction initiation in impact and friction tests and to a spark with energy equivalent to a static discharge from a human. The LANL observed a minimum exothermic reaction temperature of 210 °C (410 °F) during their differential thermal analyses tests (Cady 1990). Preliminary work at Fauske and Associates (Fauske 1991) shows initial exothermic behavior for some ferrocyanide/oxidant mixtures at approximately 190 °C (370 °F).

In response to this recommendation, the Hanford Site Ferrocyanide Task Team has expanded the scope of the planned chemical reaction studies. The work described here will be conducted using waste simulants. If actual waste samples show the presence of different compounds, efforts will be refocused on determining the reaction properties of the compounds found in the actual waste.

4.5.3 Chemical Nature of Cyanide in Wastes

Based upon results of previous PNL studies, it was found that the chemical nature of the cyanide in the waste could have a dramatic impact on the reaction sensitivity and mechanism. Several cyanide-containing compounds, representative of those originally precipitated and those produced by radiolysis and long-term exposure to a highly alkaline environment, are being studied to understand what effect the chemical nature of the cyanide may have on the explosive properties of ferrocyanide in the tanks.

Exposure to a radiation field in a highly alkaline environment for 35 yr could have affected the chemical form of the cyanide in the tanks. The available literature suggests moderate instability of aqueous solutions of cyanide or ferrocyanide and identifies several different products. Limited testing at PNL on radiation effects on solid ferrocyanide indicates that cesium nickel ferrocyanide is quite resistant to radiation damage. Because radiolytic systems tend to be oxidative, radiolysis could also affect the possible conversion of ferrocyanide to ferricyanide. Although ferrocyanides are normally more stable, the ferricyanide may form in oxidizing alkaline media and further decompose to ferric hydroxide and oxidized carbon-nitrogen species. These issues are being investigated by duplicating the flowsheet conditions and compositions when the ferrocyanide was put into the tanks in the mid-1950's. The precipitates will be irradiated in a highly alkaline environment. These precipitates, their aging products, and pure compounds of nickel-, iron-, and mixed ferrocyanides, will be chemically characterized and species identified, and their solubilities, reactivities, sensitivities, and enthalpies of formation will be measured.

4.5.4 Reaction Mechanisms and Kinetics

The way the oxidation reactions of cyanide-containing compounds proceed (mechanism) will determine the amount of energy released. The speed with which the oxidation proceeds at any temperature, coupled with the enthalpy of the reaction and the thermal conductivity and heat capacity of the system, will determine the maximum point temperature at which the material can be safely stored. It is therefore important for predictive purposes to determine the mechanism by which ferrocyanide and its aging products are oxidized by nitrates and nitrites and the kinetic parameters for the reaction or reactions.

In this subtask, reactions between ferrocyanide and its aging products with nitrates and/or nitrites and other waste constituents such as water are being studied to determine pathways and Arrhenius constants for significant steps in the oxidation. To investigate the mechanism, isothermal and nonisothermal tests are being performed using differential scanning calorimetry (DSC), scanning thermogravimetry (STG), and accelerating rate calorimetry (ARC) allowing monitoring of various stages of the reactions.

A supplementary program is underway at Fauske and Associates where ferrocyanide reaction mechanisms, kinetics, reaction temperatures, pressures, and product gases are being studied in the Fauske Adiabatic Calorimeter. Propagation tests are planned for determining the burn velocity as a function of stoichiometry and moisture. Reaction temperatures, pressures, and gas compositions will be measured. As results are obtained, additional tests will be planned. Tests with various ferro- and ferricyanide compounds will be conducted.

4.5.5 Effects of Catalysts and Initiators

The ferrocyanide tanks contain a very broad range of materials that could act as catalysts or initiators for the ferrocyanide reaction with nitrates or nitrites. Studies by PNL have shown that potential waste constituents, such as 5 mol% EDTA and 5 mol% nickel hydroxide, can affect ferrocyanide oxidation by nitrate and nitrite. It is suspected, based on DSC and STG analyses, that metals are acting as catalysts, and the EDTA is acting as an initiator [additional fuel]. Potential catalysts that may also exist in the tanks include copper, lead, manganese, chlorine, and other organic agents.

Investigations to determine the effect of potential catalysts and initiators are using DSC, STG, time-to-explosion (TTX), and may use other isothermal and nonisothermal tests such as ARC and adiabatic scanning calorimetry (ASC). Analyses of the product gases and solids are also being performed.

4.5.6 Effects of Diluents

Ferrocyanides may be mixed intimately with other waste constituents that could serve as inert diluents and mitigate the effects of any ferrocyanide oxidation by nitrates and/or nitrites. Possible diluents include waste constituents such as bismuth phosphate, sodium aluminate, sodium carbonate, and water. Diluents increase the mass that must be heated by the reaction before a temperature is reached to initiate a runaway reaction. This investigation of dilution effects should indicate, among other things, whether a remediation technique such as mixing the ingredients in the tank, will render the wastes nonexplosive.

This activity will investigate the effect of solid diluents on the nitrate and nitrite oxidation of possible ferrocyanides and aging progeny using DSC, STG, TTX, ARC, ASC, and possibly impact, friction, and spark tests. Gases and solid products will be analyzed as necessary.

4.5.7 Effects of Increasing Mass

The explosivity of a material is dependent upon its mass, geometry, and confinement. The ability of a material to transfer reaction heat from the reaction zone to its outer boundaries will determine whether the reaction will reach the thermal runaway temperature. It is therefore important that tests be conducted using larger, kilogram quantities of material. If possible, geometries similar to those in the ferrocyanide tanks should be investigated.

The test mixtures will be chosen based upon results obtained from other subtasks. These mixtures (ferrocyanides and/or aging products, nitrates, nitrites, catalysts, initiators, and diluents) will be prepared by PNL and/or Westinghouse Hanford Company; testing will be conducted at the Hanford Site Containment Systems Test Facility and at LANL. Initially, 1-g (0.002-lb) to 10-g (0.02-lb) samples of selected mixtures will be tested for thermal initiation. Depending on the information obtained, larger samples (kilogram quantities) may then be thermally tested. Using larger quantities of material requires that sensitivity testing be conducted to ensure that the material can be handled safely. These sensitivity tests will be done at LANL.

4.6 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."*

4.6.1 Discussion

Waste temperature is a key safety control parameter for those tanks with potential for a rapid exothermic reaction if heated sufficiently. The ferrocyanide tanks (see Table 1) have heat generation rates less than 11.7 kW

(40,000 Btu/h) and dissipate their heat via natural circulation and conduction to the surrounding earth. Temperatures in these tanks are currently monitored weekly and the highest temperature observed in any of the tanks is less than 60 °C (140 °F). This is well below the minimum exothermic reaction temperature of 190 °C (370 °F) observed in the laboratory (Fauske 1991) for ferrocyanide tests conducted to date.

4.6.2 Action Plan for Response to Abnormal Conditions

The *Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide* (Cash and Thurman 1991) 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. Based upon the specific event, actions taken would likely include the following.

- Adjustments or modifications to tank ventilation systems, including the addition of active ventilation (i.e., portable exhausters). Tank Farm Facility Operations has spare portable exhausters available that can be moved to any tank farm and made operational within 24 h.

- Addition of a refrigerated cooling system into the tank or as a part of the ventilation system.

- Addition of water (even to a leaking tank) in minimum quantities necessary to prevent temperature increases and restore temperature control. Water will not be added unless dry cooling methods are ineffective at keeping the waste temperature below 93 °C (200 °F).

4.6.3 Response to a 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. All tank farms are equipped with these monitoring systems.

The Hanford Site plans for responding to a significant release are described in WHC-PRP-SD-0001, *Tank Farm Emergency Response Stabilization Plan* (WHC 1991); WHC-CM-4-1, *Westinghouse Hanford Company Emergency Plan* (WHC 1989); WHC-CM-4-43, *Westinghouse Hanford Company Emergency Management Procedures* (WHC 1990); and *U.S. Department of Energy--Richland Operations Office (DOE-RL) Emergency Response Plan and Emergency Procedures* (DOE-RL 1990).

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 Company 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). The plan includes predetermined mitigative actions for terminating the emergency phase and providing a transition to the recovery phase. Acknowledging that an event could range from minor to major releases, the plan addresses responses in four distinct and defined steps that will cover the range of consequences. The stabilization plan provides quick, preplanned actions that can be used to stabilize an emergency event at an underground radioactive waste storage tank.

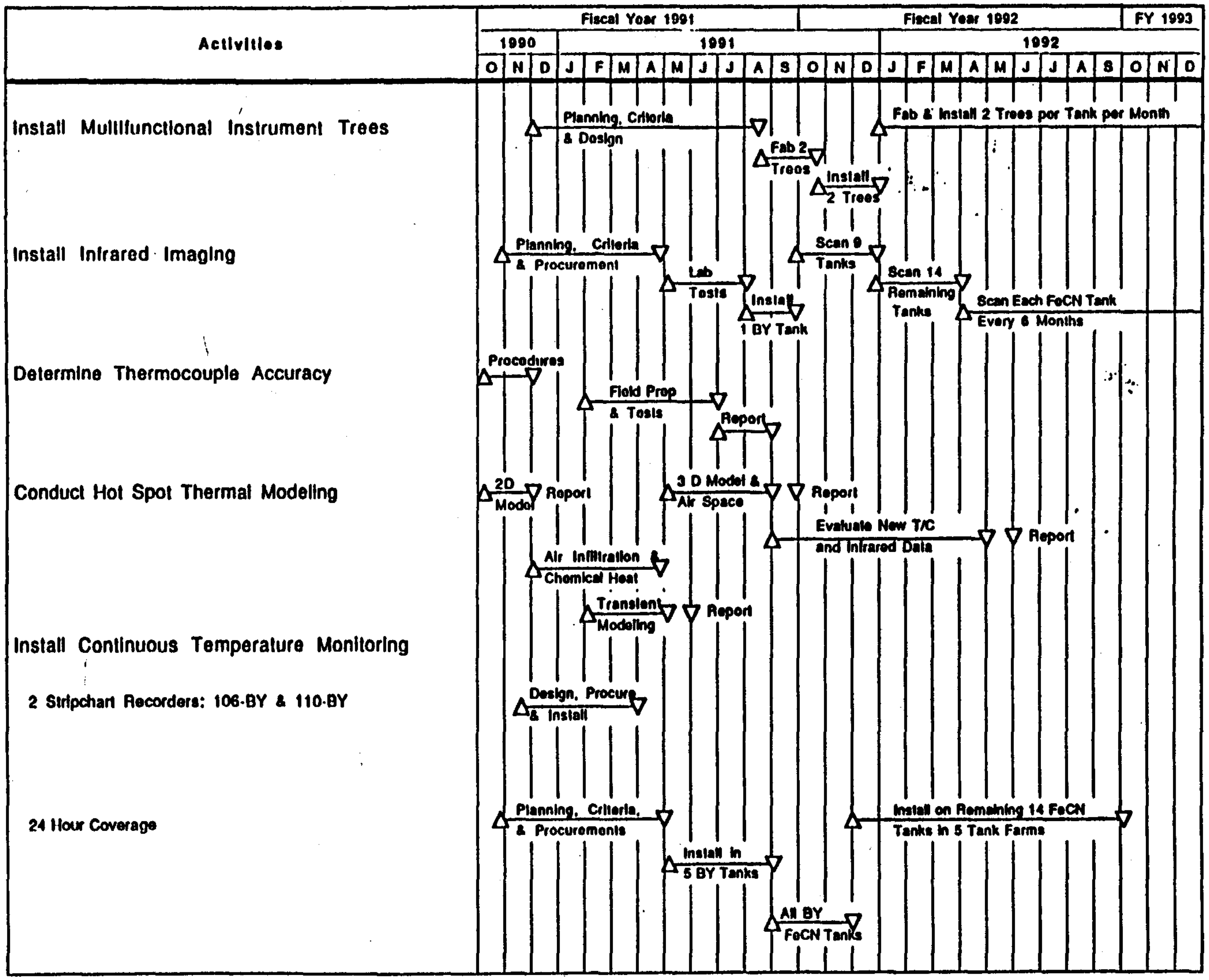
As part of the effort to upgrade the response plans for the Hanford Site to cover tank farm emergency events, two emergency exercises are currently planned and will be conducted during June and August of 1991. This first exercise will require activation and participation by Tank Farm Emergency Response organizations and Area Emergency Response organizations, because of an emergency situation at a tank farm facility. The second exercise will consist of an event requiring the highest level of response: a general emergency classification. This exercise will require full involvement and coordination with the DOE, the state, counties, local agencies, and the Hanford Site emergency organizations. At the conclusion of each exercise, a formal critique will be conducted of the exercise and a formal report issued that identifies all deficiencies and tracks their resolution to completion.

5.0 SCHEDULES

The schedules shown in Figure 1 reflect the level of effort required to be responsive to DNFSB recommendations. The schedules are dependent upon available funding. In preparing these schedules, it was assumed that the Westinghouse Hanford Company Waste Tank Safety Program would receive their requested level of funding for fiscal year 1991. If that funding is not made available, the schedule will be modified and stretched out as necessary.

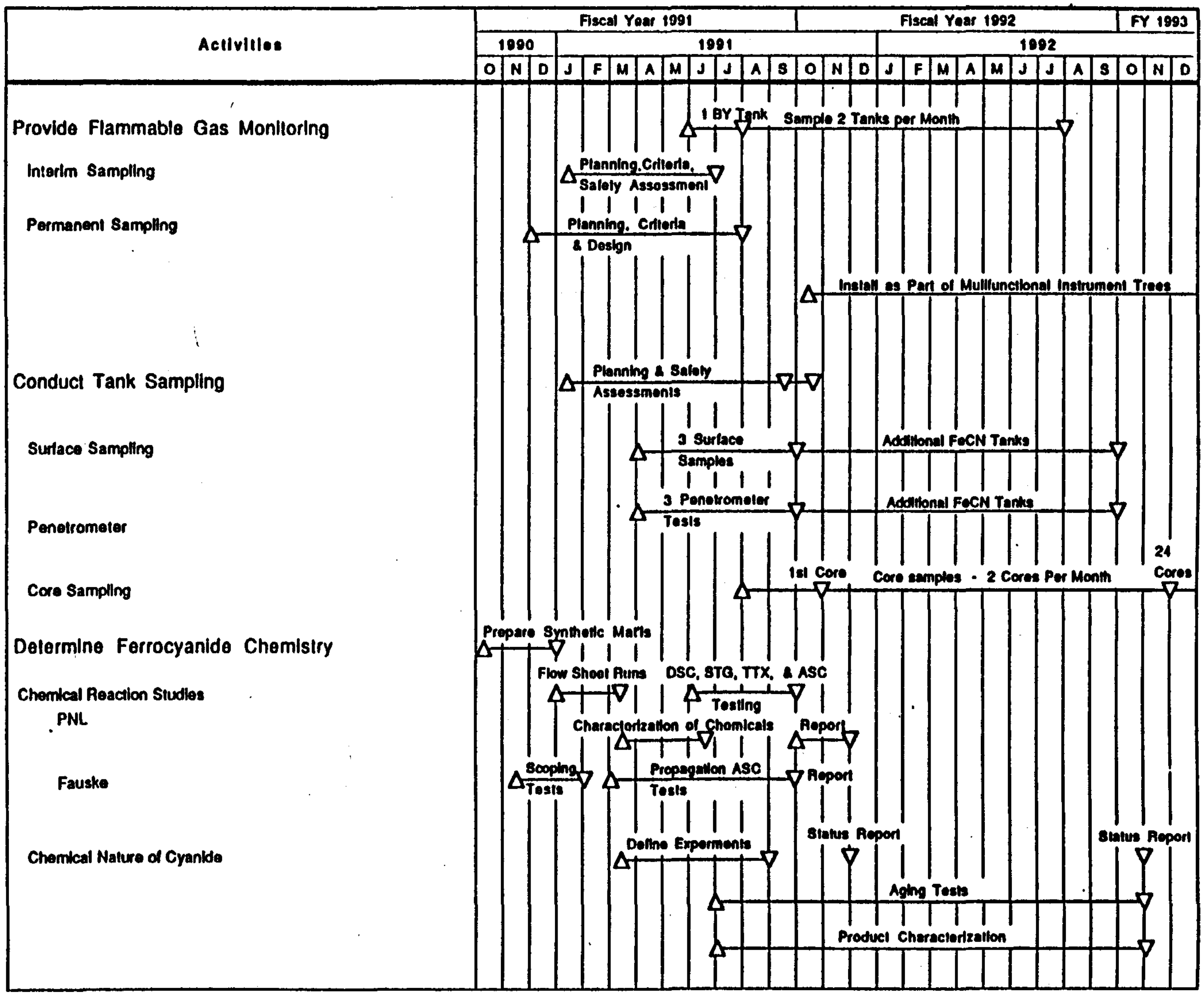
One other possible perturbation to these schedules is the availability of engineering and operations personnel for preparation of design, safety, and work control documentation and for conducting the field operations required for the ferrocyanide tanks. Safety issues associated with hydrogen-generating Tank 101-SY command the highest priority at the Hanford Site and available personnel and equipment resources may be assigned full time to the various "window" activities on a temporary basis. These assignments could potentially delay some ferrocyanide tank work for 1 to 2 mo.

The schedules will be updated on a quarterly basis to reflect available resources and changing conditions.



Thursday, February 28, 1991

Figure 1. Schedule. (sheet 1 of 3)



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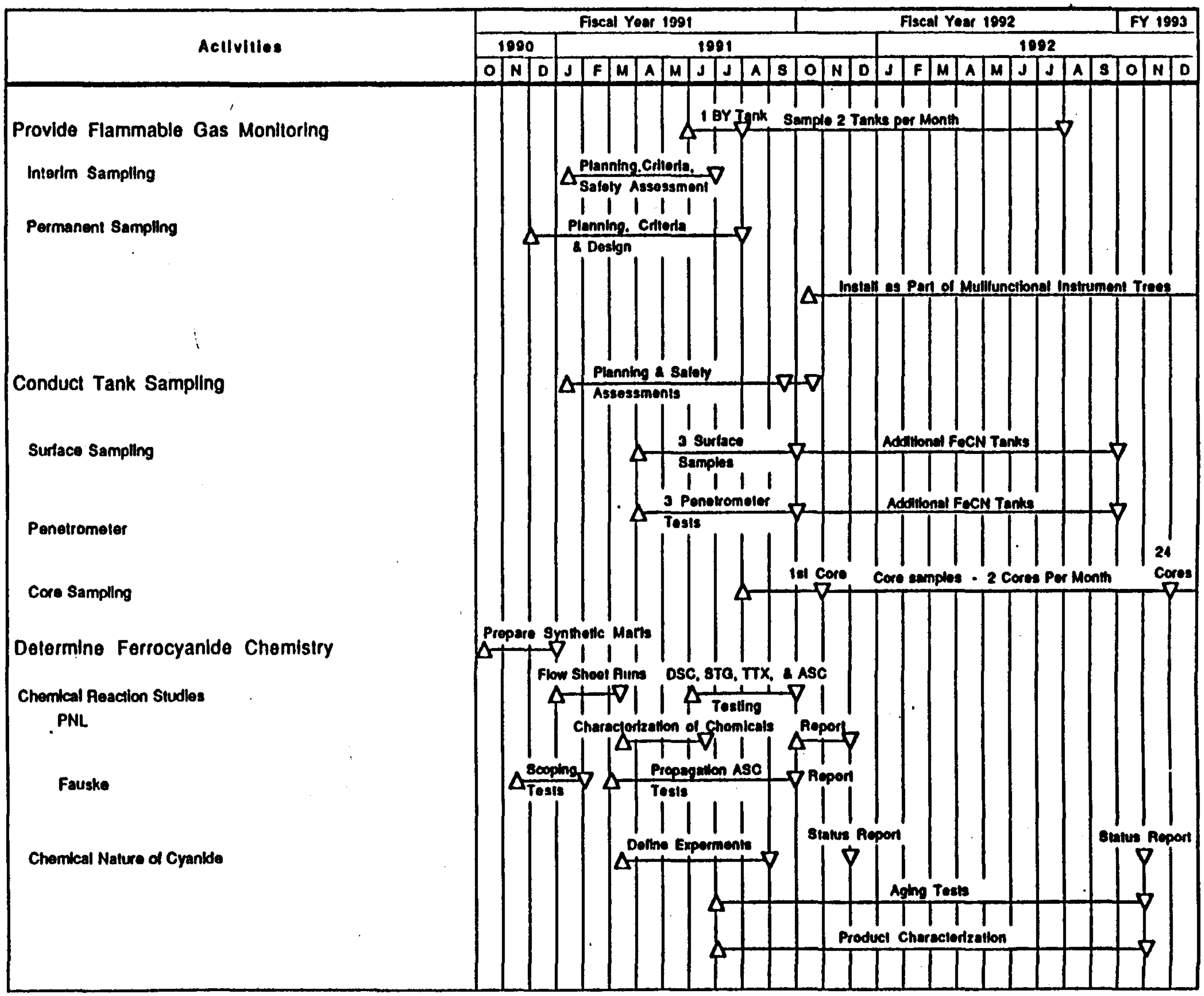

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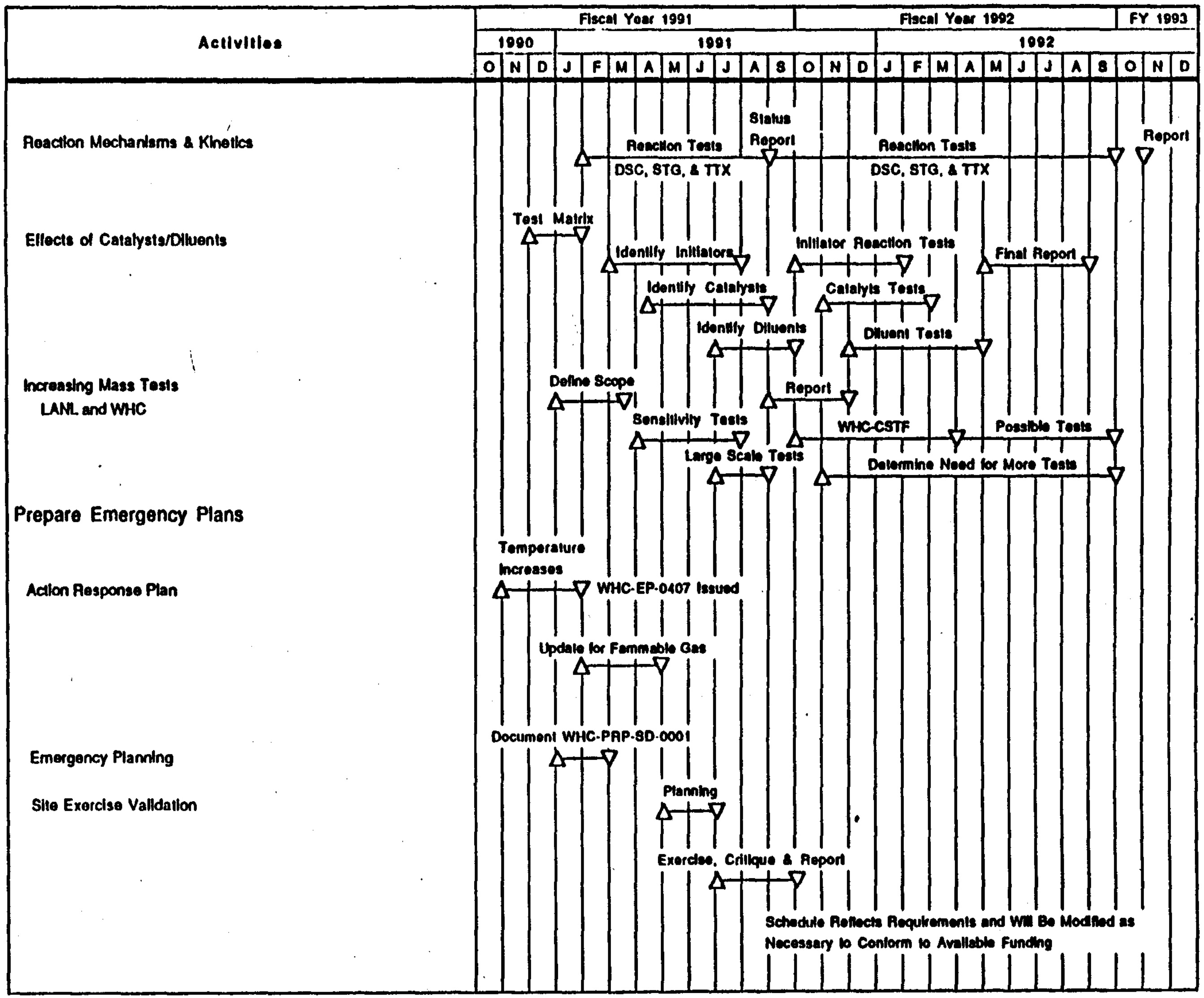

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Figure 1. Schedule. (sheet 3 of 3)

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ENCLOSURE 2

WHC-EP-0407

UC-610/UC-630

Action Plan for Response to Abnormal Conditions in Hanford Site Radioactive Waste Tanks Containing Ferrocyanide

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ACTION PLAN FOR RESPONSE TO ABNORMAL CONDITIONS IN HANFORD SITE RADIOACTIVE WASTE TANKS CONTAINING FERROCYANIDE

R. J. Cash
J. Thurman

ABSTRACT

This document defines the responses that shall be implemented when anomalies in temperature measurements or flammable gas contents are observed in single-shell waste tanks containing ferrocyanide. This plan defines (1) the criteria and specification limits required for ensuring that the tanks are maintained in a safe condition, (2) the responsible organizations, and (3) the response actions to prevent or mitigate temperature excursions.

CONTENTS

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1.0 INTRODUCTION

1.1 BACKGROUND

The Defense Nuclear Facilities Safety Board (DNFSB) (FR 1990) made six recommendations (90-7) concerning the Hanford Site single-shell, high-level waste tanks that contain ferrocyanide compounds. The sixth recommendation (90-7.6) states "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: those that respond to unexpected degradation of a tank or its contents and those that respond in the event of an explosion. The reference to "alarms" was part of DNFSB Recommendation 90-7.2, which states that temperature sensors should have continuous recorded readouts and alarms should be installed at a permanently manned location to signal any abnormally high temperatures and any failed temperature instrumentation.

DNFSB Recommendation 90-7.1 requests that "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 . . ." Recommendation 90-7.3 states that "Instrumentation should also be installed to monitor the composition of cover gas in the tanks, to establish if flammable gas is present."

Instruments currently in use at Westinghouse Hanford Company (Westinghouse Hanford) for monitoring ferrocyanide tanks consist of thermocouple trees located inside the waste tanks, thermocouples in dry wells below the waste level in several tanks containing such wells, and periodic flammable gas monitoring equipment using a portable flammable gas instrument. Work responding to all the DNFSB recommendations is underway. One activity provides continuous temperature monitoring and alarms on all ferrocyanide tanks using the existing thermocouples and new thermocouples that will be installed within the next 24 months. Currently, selected data in ferrocyanide tanks are being recorded and interpreted weekly for signs of anomalies by a special surveillance working group (Tank Farm Surveillance Analysis). This group records, statistically analyzes, and reports on trends in selected Hanford Site waste tank surveillance data.

Processing facilities at the Hanford Site have produced various radioactive liquid and slurry wastes that are stored in 149 underground single-shell tanks. Twenty-four of these tanks may contain ferrocyanide in quantities sufficient to present a potential for exothermic or explosive reactions between ferrocyanide precipitates, and nitrate or nitrite compounds. This document applies to the 24 tanks listed in Table 1.

Table 1. Significant Data on Ferrocyanide Tanks.

Tank	Ferrocyanide (1,000 g-moles)	Heat load (Btu/h)	Maximum temperature (°F) (January 1991)	Assumed leaker	Interim stabilized
102-BX	0 - 3	<10,000	65	1971	11/78
106-BX	0 - 1	<10,000	64	No	NA
110-BX	0 - 1	<10,000	65	1976	8/85
111-BX	0 - 1	<10,000	69	1984	NA
101-BY	0 - 1	8,200	75	No	5/84
103-BY	0 - 1	8,600	80[a]	1973	NA
104-BY	100 - 200	17,000	129	No	1/85
105-BY	70 - 100	37,700	114	1978	12/84
106-BY	30	12,200	132	1984	NA
107-BY	30 - 80	14,500	79	1984	7/79
108-BY	30 - 70	23,000	102	1972	2/85
110-BY	50 - 90	25,200	122	No	1/85
111-BY	0 - 3	34,200	84[a]	No	1/85
112-BY	2 - 3	<10,000	66[a]	No	5/85
108-C	9 - 20	<10,000	74	No	3/84
109-C	30 - 50	<10,000	77	No	11/83
111-C	10 - 30	<10,000	72	1968	3/84
112-C	50 - 70	<10,000	81	No	9/90
101-T	0 - 10	<10,000	68	No	NA
107-T	0 - 5	<10,000	60[b]	1984	NA
118-TX	0 - 3	4,900	73	No	4/83
101-TY	0 - 30	<10,000	67	1973	8/83
103-TY	0 - 30	<10,000	63[a]	1973	2/83
104-TY	0 - 20	<10,000	72[b]	No	NA
24 tanks					

NOTE: To convert °F to °C, use the formula (°F - 32)/1.8.
[a] Temperature data from liquid observation well.
[b] Historical data suspect.
NA = Not applicable.

Single-shell tanks contain radioactive waste that generates heat from radioactive decay. For a runaway exothermic reaction to occur in the waste, a sufficient amount and concentration of reactant material and a minimum reaction temperature must exist. A sufficient energy source could also initiate the reaction.

None of the ferrocyanide tanks are high-heat tanks (≥ 11.7 kW [40,000 Btu/h]). Over the past several years, temperatures in the ferrocyanide tanks have shown a steady, typical temperature decrease of approximately 2 °C/yr (3 °F/yr), which corresponds to the radioactive decay of the principal heat-generating isotope, ^{137}Cs. Single-shell tanks are inactive (i.e., wastes are no longer added to the tanks), and the heat generation rates continue to decrease as a result of radioactive decay. Based upon these factors and tank thermal modeling, no significant temperature rise is expected. The highest temperature currently measured in any ferrocyanide tank is approximately 56 °C (132 °F). This is considerably lower than the lowest exothermic reaction temperature of 220 °C (430 °F) and explosive temperature of 280 °C (540 °F) respectively, for an oxidant mixture of 47.5 mol% sodium nitrate, 47.5 mol% sodium nitrite, and 5 mol% EDTA (ethylenediaminetetraacetic acid) measured in the laboratory (Burger and Scheele 1990).

Testing indicates that the exothermic reaction and the explosion can be thermally initiated, as discussed in the previous paragraph. The reaction and possibility of explosion are also sensitive to the following:

- Nitrate and/or nitrite cations
- Type of oxidant (nitrate or nitrite)
- EDTA catalyst or initiator
- Iron hydroxide catalyst or initiator
- Nickel hydroxide catalyst or initiator.

Testing at Los Alamos National Laboratory in fiscal year 1990 shows that a mixture on nearly equimolar amounts of ferrocyanide and 50 mol% sodium nitrate/50 mol% sodium nitrite was insensitive to reaction initiation in impact and friction tests and to a spark with the energy equivalent of a static discharge from a human. Los Alamos National Laboratory also observed a minimum exothermic reaction temperature of 210 °C (410 °F) during their differential thermal analyses tests (Cady 1990). Preliminary work by Fauske and Associates (Fauske 1991) shows initial exothermic behavior for some ferrocyanide/oxidant mixtures at approximately 190 °C (370 °F).

Waste temperature is the key safety control parameter for the 24 tanks with the potential for a rapid exothermic reaction if heated sufficiently. The tanks dissipate their heat via natural circulation and conduction to the surrounding ground. The temperatures in these tanks are monitored weekly, and the highest temperature observed in any of the tanks is less than 60 °C (140 °F). This is well below the minimum exothermic reaction temperature of 190 °C (370 °F) observed in the laboratory for ferrocyanide tests conducted to date.

However, if temperature monitoring indicates that a significant increase above a tank baseline temperature has occurred, then appropriate corrective responses shall be taken.

1.2 PURPOSE

The purpose of this action plan is to define the responses that shall be taken if anomalies in temperature measurements or flammable gas contents are observed for single-shell tanks containing ferrocyanide. This plan defines (1) the criteria and specification limits required for ensuring the tanks are maintained in a safe condition, (2) the responsible organizations, and (3) the response actions to prevent or mitigate temperature excursions.

1.3 SCOPE

The information contained within this document applies to all single-shell tanks at the Hanford Site identified as being potentially capable of ferrocyanide reactions (Table 1) and defines the points at which corrective action responses shall be initiated.

This action plan does not include emergency preparedness for the Hanford Site. The *Westinghouse Hanford Company Emergency Plan*, WHC-CM-4-1 (WHC 1989a), and its companion document, *Westinghouse Hanford Company Emergency Management Procedures*, WHC-CM-4-43 (WHC 1990a), are adequately responsive to possible accidents that result in a release from the tank.

2.0 DISCUSSION

2.1 TEMPERATURE MONITORING AND RESPONSE

2.1.1 Administrative Controls

Administrative documents and procedures are in place to ensure that corrective responses take place before temperatures exceed single-shell tank temperature specifications for ferrocyanide tanks. These documents and procedures are administered in the following hierarchial order.

- The primary administrative control documents for single-shell tanks are the safety analysis reports (WHC 1986a, 1986b, 1989b).
- The Westinghouse Hanford *Management Requirements and Procedures* (WHC-CM-1-3) implements administrative controls derived from U.S. Department of Energy (DOE) directives (WHC 1990b).
- Basic single-shell tank surveillance limits are detailed within the *Operating Specifications for Single-Shell Waste Storage Tanks* (WHC 1990c).
- Occurrence reporting system requirements are specified within the occurrence reporting and processing of operations information procedures (WHC 1990d, 1990e).
- Specific single-shell tank technical criteria limits and controls are contained within the *Waste Storage Tank Status and Leak Detection Criteria* (WHC 1991).
- Specific ferrocyanide tank temperature criteria limits and controls are listed in Table 2 of this document.

Criteria and response actions that are specific only to single-shell tanks containing ferrocyanide are listed in this document. Changes to this document shall reflect the requirements of the upper-level documents listed previously.

2.1.2 Tank Temperature Criteria

Ferrocyanide temperature criteria are specified in *Waste Storage Tank Status and Leak Detection Criteria*, WHC-SD-WM-TI-357 (WHC 1991). Table 2 shows the temperature monitoring action values for the 24 Hanford Site ferrocyanide tanks specified in that document.

Table 2. Ferrocyanide Tanks Temperature Monitoring Baseline and Threshold Values (WHC 1991).

Tank	Monitoring frequency	Baseline temperature (°F)	Surveillance alert	Maximum temperature criteria	Instrument type
			10 °F above baseline	18 °F above baseline	
102-BX	Weekly	69	79	87	J
106-BX	Weekly	68	78	86	J
110-BX	Weekly	71	81	89	J
111-BX	Weekly	75	85	93	J
101-BY	Weekly	75	85	93	J
103-BY	Weekly	78[a]	88	96	K
104-BY	Weekly	132	142	150	J
105-BY	Weekly	116	126	134	J
106-BY	Weekly	133	143	151	J
107-BY	Weekly	85	95	103	J
108-BY	Weekly	104	114	122	J
110-BY	Weekly	124	134	142	E
111-BY	Weekly	84[a]	94	102	K
112-BY	Weekly	75[a]	85	93	K
108-C	Weekly	78	88	96	J
109-C	Weekly	80	90	98	J
111-C	Weekly	77	87	95	J
112-C	Weekly	89	99	107	J
101-T	Weekly	71	81	89	J
107-T[b]	Weekly	65[c]	75	83	J
118-TX	Weekly	79	89	97	J
101-TY	Weekly	70	80	88	J
103-TY	Weekly	69[a]	79	87	J
104-TY[b]	Weekly	72[c]	83	91	J

NOTE: To convert °F to °C, use the formula (°F - 32)/1.8.

[a] LOW means temperatures measured in liquid observation wells.

[b] Tanks 107-T and 104-TY added.

[c] Historical data suspect.

2.1.3 Monitoring Frequencies

All ferrocyanide tanks shall be monitored for temperature on a weekly basis. "Weekly" is defined as 7 days, not to exceed 12 days, between any successive thermocouple readings for an individual tank.

2.1.4 Reporting Requirements

- Any temperature reading that exceeds the surveillance alert criteria (~12 °C [10 °F] above baseline) as specified in Table 2, after recheck verification, will result in an off-normal occurrence report (WHC 1990d, 1990e) being issued by Tank Farm Surveillance Analysis.
- Failure to monitor a ferrocyanide tank temperature within the prescribed frequency period will result in an off-normal occurrence report being issued by Tank Farm Surveillance Analysis.
- Any temperature reading that exceeds the maximum temperature criteria (~8 °C [18 °F] above baseline) as specified in Table 2, after recheck verification, will result in an unusual occurrence report (WHC 1990d, 1990e) being issued by Tank Farm Surveillance Analysis.
- Any ferrocyanide tank temperature that reaches 93 °C (200 °F), after recheck verification, will result in the declaration of an "unusual event" (WHC 1990a).

2.2 FLAMMABLE GAS MONITORING AND RESPONSE

2.2.1 Administrative Controls

Currently, flammable gas monitoring is performed before any work is conducted in or around an area connected with a tank vapor space. Administrative documents and procedures are in place to ensure that corrective responses take place should any flammable gas readings exceed the criteria in Section 2.2.2. These documents and procedures are administered in the following hierarchial order.

- The primary administrative control documents for single-shell tanks are the safety analysis reports (WHC 1986a, 1986b, 1989b).
- The Westinghouse Hanford *Management Requirements and Procedures* (WHC-CM-1-3) implements administrative controls derived from DOE directives (WHC 1990b).
- Occurrence reporting system requirements are specified within the occurrence reporting and processing of operations information procedures (WHC 1990d, 1990e).

As additional monitoring systems are added to the ferrocyanide waste tanks, this action plan will be revised to reflect the latest configurations, criteria, and controls.

2.2.2 Flammable Gas Monitoring Criteria

- Interim operating safety requirements are in place for all ferrocyanide tanks. These requirements state that hydrogen/flammable gas monitoring is required before opening the primary tank air space or the associated ventilation/exhaust system. If flammable gases are detected above 20% of the lower flammability limit, approval must be received from the Manager of the Tank Farm Project Facility Operations and from Safety Assurance to proceed with work.
- Criteria for flammable gases of interest will be specified and documented as part of the flammable gas monitoring program that is currently being defined.

2.2.3 Monitoring Frequencies

A flammable gas monitoring program for the ferrocyanide tanks is currently being defined. The required monitoring frequencies are "to be determined."

2.2.4 Reporting Requirements

Off-normal occurrence reporting (WHC 1990d, 1990e), unusual occurrence reporting (WHC 1990d, 1990e), and unusual event reporting (WHC 1990a) requirements for flammable gases in ferrocyanide tanks are "to be provided."

3.0 RESPONSIBILITIES

The Waste Tank Safety, Operations, and Remediation division is responsible for all tank farm operations. The responsibilities (WHC 1990f) associated with response to a temperature or flammable gas content increase in a ferrocyanide tank are assigned as follows.

- Tank Farm Project Facility Operations shall be responsible for the safety of the facility and for both routine and nonroutine temperature monitoring of all single-shell tanks containing ferrocyanide. Industrial Hygiene and Safety shall be responsible for performing the flammable gas monitoring. Initial screening of tank temperature data shall also be performed by Facility Operations. The initial screening of flammable gas data shall be performed by Industrial Hygiene and Safety.
- Tank Farm Surveillance Analysis receives temperature data and shall be responsible for reviewing (trending), permanently logging (record keeping), and reporting the data. Additionally, Tank Farm Surveillance Analysis shall have the responsibility for reporting data anomalies and initiating response actions in accordance with WHC (1990e).
- The Director, Tank Farm Project, shall be responsible for conducting assessment activities and determining appropriate corrective actions.
- Corrective actions shall be defined by Tank Farm Project Engineering, and implemented in the field by Tank Farm Project Facility Operations.

4.0 CORRECTIVE ACTION

4.1 TEMPERATURE INCREASES

For temperature increases in a ferrocyanide tank, corrective actions may include the following:

- Adjustments or modifications to tank ventilation systems, including the addition of active ventilation systems (i.e., portable exhausters)
- Addition of a refrigerated cooling system into the tank or as a part of the ventilation system
- Addition of water (even to a leaking tank) in minimum quantities necessary to prevent temperature increases and restore temperature control. Water will not be added unless dry cooling methods are ineffective at keeping the waste temperature below 93 °C (200 °F).

4.2 FLAMMABLE GAS INCREASES

The corrective actions for excessive flammable gases in ferrocyanide tanks will be provided as part of the flammable gas program currently being defined.

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ENCLOSURE 3

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DRAFT

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7. Abstract

This plan is provided to respond to stabilize an emergency event in a 200 Area Underground Waste Storage tank, and transcend from the emergency phase to the recovery phase.

8. PURPOSE AND USE OF DOCUMENT - This document was prepared for use within the U.S. Department of Energy and its contractors. It is to be used only to perform, direct, or integrate work under U.S. Department of Energy contracts. This document is not approved for public release until reviewed.

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9. Impact Level

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1.0 INTRODUCTION

A WHC task team consisting of Industrial Safety, Radiological Safety, and Safety Analysis and Regulation, Tank Farms Operations, Emergency Preparedness, and Engineering was established to develop a set of stabilization plans which identify pre-planned responses to postulated emergency events associated with core sampling at the 101-SY Tank, in 200 West Area.

A review of the eleven postulated events from the safety evaluation, resulted in 4 situations or resultant conditions from an explosion or fire in an underground waste storage tank, which are representative of the post event conditions of all of the Hanford underground waste storage tanks.

Condition 1:	Quick but small explosion resulting in breach of the HEPA filtration system, with no sustained release.
Condition 2:	Quick but small explosion resulting in breach of the HEPA filtration system, with a sustained release.
Condition 3:	Large explosion resulting in breach of the HEPA filtration system, and rupture of the inner tank, with potential leaks to the annulus and surrounding soils, but the tank dome remains intact.
Condition 4:	Large explosion resulting in breach of the HEPA filtration system, and rupture of the inner tank, with total dome collapse.

Based on the four tank conditions described, this stabilization plan was developed which can be used for each condition.

2.0 PURPOSE

The purpose of the plan is to stabilize a release and terminate the emergency situation in preparation for recovery. Once an emergency condition is identified and is categorized as an emergency and classified as either an Unusual Event, Alert, Site or General Emergency, one of the initial actions is to activate emergency response facilities including an Incident Command Post, and area Emergency Control Center, and other supporting emergency centers as are deemed necessary.

3.0 SCOPE

This plan will be used to provide guidance for the Emergency Response Organization (Building Emergency Director, Area Emergency Director), to respond to an emergency situation in one of the 200 Area underground waste storage tanks. The actions taken by the emergency response organization, must be based on the existing conditions during the event and the technical recommendations made by the Emergency Control Center Staff.

NOTE: This plan is not intended to address recovery. A recovery plan would be developed by a designated team following termination of the release and termination of the emergency phase.

4.0 STABILIZATION PLAN

The following information is provided to respond to stabilize the emergency event and transcend from the emergency phase to the recovery phase.

4.1 Condition 1 Response (**ALERT LEVEL EMERGENCY**):

1. Establish a resource staging area and an incident command post in a safe location.

2. Restore filtered ventilation to the tank
   a. evaluate condition of primary filtration system and attempt to restart primary exhauster if operable
   b. if primary not operable, seal off exhauster
   c. hookup electric power source from power grid to backup exhauster
   d. startup alternate/backup exhauster
   e. insure ventilation for tanks on common exhaust systems is provided, this can be provided through the common ductwork

Note: Most tanks currently on active ventilation can exist without active ventilation for approximately 24 hours without adverse effects

3. For tanks which are not on active ventilation systems, evaluate the condition of the breather filters and establish containment as necessary and replace/repair breather filters.

4. Evaluate riser availability for tank access and if possible open riser and establish water spray to suspected area of fire/burn (supplied by tank truck, or water spray system) if evidence of continued release/fire/burn

Note: Limit water addition to tank to absolute minimum required to extinguish any fire of tank material.

5. Survey area to determine extent of radioactive contamination levels
6. Evaluate samples for indication of non-radiological hazardous materials release of ammonia, hydrazine, or nitrous oxide, or other hazardous materials, for habitability
7. Spray surface contamination with Aerospray 70 TM, or water to fix contamination in place.

4.2 Condition 2 Response (**ALERT LEVEL EMERGENCY**):

1. Establish a resource staging area and Incident Command Post
   a. contact meteorological station on 3-2716, or 3-2710 and request information relative to current and predicted wind conditions, considering wind direction, and extent of

  contamination establish a resource staging area in a safe location
  - b. consider access to the affected area or Tank Farm
  - c. consider establishment of resource staging area at a safe location for personnel and equipment with adequate communications capabilities, technical information, etc.
  - d. consider establishment of a "Regulated Corridor" for use in transporting contaminated equipment, soils from affected Tank Farm to burial grounds for disposal, decontamination; this can be accomplished by designating a roadway as a surface contamination area
  - e. notify T-Plant of possible use of decontamination facility for equipment decontamination

2. Restore filtered ventilation to the tank
   - a. evaluate condition of primary filtration system and attempt to restart primary exhauster if available/operable
   - b. if primary not operable/available, seal off exhauster
   - c. startup alternate/backup exhauster
   - d. hookup electric power source to backup exhauster
   - e. insure ventilation for tanks on common exhaust systems is provided, this can be provided through the common ductwork

3. For tanks which are not on active ventilation systems, evaluate the condition of the breather filters and establish containment as necessary and replace/repair breather filters.

4. Reduce/eliminate effluent discharge from tank, in event exhauster(s) not operable
   - a. evaluate availability of risers to tank and if possible establish water spray to tank contents
   - b. establish a continuous flow of water to the water spray apparatus via connection to a fire hydrant or other permanent source of water
   - c. add water to the tank via the water spray apparatus (consider addition of A-FFF* foam or whetting agents)
   - d. consider addition/use of water fog/deluge spray via fire truck (Tele-squirt) on effluent stream from exhauster if unable to provide filtered exhaust

     * A-FFF: Aqueous Film Forming Foam

Note: Limit water addition to tank to absolute minimum required to extinguish any fire of tank material.

5. Stabilize surface contamination
   - a. spray contaminated metal and concrete surfaces with soil surfactant (AEROSPRAY 70) to "FIX" contamination in place
   - b. spray contaminated soil surfaces with soil surfactant (AEROSPRAY 70)

4.3 Condition 3 Response (**ALERT LEVEL EMERGENCY**):

1. Establish a resource staging area and Incident Command Post
   a. contact meteorological station on 3-2716, or 3-2710 and request information relative to current and predicted wind conditions, considering wind direction, and extent of contamination establish a resource staging area in a safe location
   b. consider access to the affected area or Tank Farm
   c. consider establishment of resource staging area at a safe location for personnel and equipment with adequate communications capabilities, technical information, etc.
   d. consider establishment of a "Regulated Corridor" for use in transporting contaminated equipment, soils from affected Tank Farm to burial grounds for disposal, decontamination; this can be accomplished by designating a roadway as a surface contamination area
   e. notify T-Plant of possible use of decontamination facility for equipment decontamination

2. Restore filtered ventilation to the tank
   a. evaluate condition of primary filtration system and attempt to restart primary exhauster if operable/available
   b. if primary not operable, seal off exhauster
   c. exhaust ducting may be damaged/dislodged; consider establishment of temporary repairs (flexible duct work) to reestablish exhauster flow
   d. startup alternate/backup exhauster
   e. hookup electric power source from power grid to backup exhauster
   f. insure ventilation for tanks on common exhaust systems is provided, this can be provided through the common ductwork

3. Reduce/eliminate effluent discharge from tank, in event exhauster(s) not operable
   a. turn on water spray apparatus to fire/burn area
   b. establish a continuous flow of water to the water spray apparatus via connection to a fire hydrant or other permanent source of water

Note: Limit water addition to tank to absolute minimum required to extinguish any fire of tank material.

   c. consider addition of A-FFF foam to water line and/or sprinkler system
   d. consider establishing a water fog/deluge spray on effluent stream from exhauster if unable to provide filtered exhaust

Note: Deluge/fog spray may discharge as much as 1000 gallons per minute therefore, consider runoff of water from spray area, therefor limit water spray to minimum amount required.

   e. cover blocks and/or ventilation system may be damaged; establish spray over open effluent streams (ie. cover blocks, damaged exhaust lines, etc.)
   f. if sustained "burn" or fire in tank evidenced by volume of smoke from exhaust points; consider adding A-FFF foam into tank through available access points, foam may be added via hose line from fire truck, or adding foam agent directly to water source

4. Stabilize surface contamination
   a. evaluate surface contamination levels and dose rates and establish radiation work permit for access and cleanup activities
   b. spray contaminated metal and concrete surfaces with water to wash
   c. spray contaminated soil surfaces with soil surfactant (AEROSPRAY 70)
   d. evaluate length of time necessary for fixant to be in place; consider if further applications may be necessary due to time, wind, heat, rain, snow, etc.

5. Mobilize heavy equipment as necessary for surface cleanup stabilization of contaminated soil
   a. contact WHC OSS for use of available scrapers, road graders, front loaders, dump trucks
   b. consider load on tank surface
   c. consider use of regulated vehicles
   d. consider dose rates to operators of heavy equipment
   e. contact KEH and consider placing available heavy equipment on standby or move to a staging area

4.4 Condition 4 Response (**SITE EMERGENCY for Hydrogen Tanks; GENERAL EMERGENCY for Ferrocyanide Tanks**):

1. Consider establishing a resource staging area and Incident Command Post at a safe location
   a. contact meteorological station on 3-2716, or 3-2710 and request information relative to current and predicted wind conditions, considering wind direction, and extent of contamination establish a resource staging area in a safe location
   b. consider access to affected Tank Farm
   c. consider establishment of resource staging area at a safe location for personnel and equipment with adequate communications capabilities, technical information, etc.

d. consider establishing a "clean" corridor, (reduced levels of contamination/dose rates) for access to the tank for stabilization and characterization purposes consider the following possibilities:
    - using road grader or front loader to "Windrow" contaminated soils for contamination reduction and cleanup
    - dumping clean soil over the contaminated areas to allow access to the tank or highly contaminated areas and reducing exposure

e. consider establishment of a "Regulated Corridor" for use in transporting contaminated equipment, soils from affected Tank Farm to burial grounds for disposal, decontamination

f. notify T-Plant of possible use of decontamination facility for equipment decontamination

2. Reduce/eliminate effluent discharge from affected tank, **IN THE EVENT OF TANK DOME COLLAPSE**

   a. cover blocks and/or ventilation system may be damaged or non existent; establish spray over open effluent streams (ie. cover blocks, damaged exhaust lines, etc.)

   b. if exhaust system intact or useable, use available exhausters to aid ventilation to tank, if operable

c. if sustained "burn" or fire in tank evidenced by volume of smoke from exhaust points; add A-FFF foam into tank directly to opening, considering exposure of personnel and equipment, via fire truck or fire hose lines, or other available water source
d. evaluate health physics on scene support and field team support and determine potential exposures to radioactive and non-radioactive contaminates, and insure capabilities exist for protection of responders

3. Reduce/eliminate effluent discharge from affected tank, **WITH TANK DOME INTACT**
   a. cover blocks and/or ventilation system may be damaged; establish spray over open effluent streams (ie. cover blocks, damaged exhaust lines, etc.)
   b. use available exhausters to aid ventilation to tank, if operable
   c. if sustained "burn" or fire in tank evidenced by volume of smoke from exhaust points; add A-FFF foam into tank through available access points via fire truck or fire hose lines, or other available water source
   d. evaluate health physics on scene support and field team support and determine potential exposures to radioactive and non-radioactive contaminates, and insure capabilities exist for protection of responders

4. Restore filtered ventilation to the other common ventilated tanks on common exhaust system
   a. evaluate condition of primary filtration system and attempt to restart primary exhauster if operable
   b. consider use of alternate/backup exhauster
   c. exhaust ducting may be damaged/dislodged; consider establishment of temporary repairs (flexible duct work) to reestablish exhauster flow and containment
   d. consider establishing a continuous power source to exhauster if operable

Note: Most tanks currently on active ventilation can exist without active ventilation for approximately 24 hours without adverse effects

5. Stabilize tank openings to reduce dose rates, and further discharge of contents.
   a. establish water spray apparatus over openings to tank(s)
   b. consider establishing a continuous flow of water to the spray apparatus via connection to a fire hydrant or other permanent source of water
   c. consider addition of A-FFF foam or other surfactant to water line and spray apparatus

   d. consider installation of a cover over exposed tank including integral HEPA filtered ventilation system (ie. Butler Type building, or other prefabricated type of building/structure.)

6. Stabilize surface contamination
   a. spray contaminated metal and concrete surfaces with soil surfactant (AEROSPRAY 70) to "FIX" contamination
   b. spray contaminated soil surfaces with soil surfactant (AEROSPRAY 70)
   c. evaluate length of time necessary for fixant to be in place; consider if further applications may be necessary due to time, wind, heat, rain, snow, etc.
   d. if plume "footprint" is over large area consider use of fire retardant and application by U.S. Forest Service air tankers as means of temporary stabilization, this should be a low priority option based on application concerns and availability.

Note: U.S. Forest Service air tankers can be summoned by contact to DOE-RL Facility Safety Representative.

7. Mobilize heavy equipment as necessary for surface cleanup stabilization of contaminated soil
   a. contact WHC OSS for use of available scrapers, road graders, front loaders, dump trucks
   b. consider load on tank surface
   c. consider use of regulated vehicles
   d. consider dose rates to operators of heavy equipment
   e. consider protective equipment for equipment operators
   f. contact KEH and consider placing available heavy equipment on standby or move to a staging area

5.0 GENERAL CONSIDERATIONS RELATIVE TO WORST CASE ACCIDENT

1. In the worst case accident assessment all of 200 E and 200 W would initially take cover until an assessment could be made to evacuate personnel if necessary. The emergency control center for the 200 Areas should be aware of the extent of the contamination prior to recommending other protective actions. The initial status would come from contact with the building emergency director and the incident command post wherever established. Contamination levels could be expected in the ranges which would exceed 5 R per hour within several hundred feet of the tank farm. Considerations include location of plume footprint, direction of travel of plume, egress points for 200 Area personnel, availability of evacuation buses, and time allowed to conduct evacuation.

2. The worst case event could potentially affect the continued operation of PFP, UO3, PUREX, B-Plant, Grout, and other 200 Area facilities, such as the power house, shops, 222-S labs, and T-

Plant. Considerations should be made for the shutdown of Operating facilities, or contingency plans for limited operation. The 222-S laboratory would be necessary for the purposes of evaluating radiological samples (air samples, soil samples, gas samples, etc) so consideration should be given to the use of an alternate facility for air sample counting and soil sample analysis such as PUREX labs.

3. T-Plant may be used to perform decontamination of heavy equipment used for cleanup and stabilization activities surrounding the tank farms facilities. If T-Plant becomes uninhabitable for use due to plume passage or deposits of high levels of contamination, an alternate solution should be considered. The capability to decontaminate equipment in burial grounds by washing of vehicles could provide a temporary solution to the concern.

4. The plume footprint could cause an evacuation and limited use of the laundry and mask cleaning station in 200 West area. This would require use of a temporary laundry facility, such as portable facilities which are available from offsite vendors during emergency situations.

6.0 BACKGROUND INFORMATION

The following is additional background information relative to methods and activities to support emergency response to a major tank farm emergency event.

1. WHC Emergency Preparedness contacted DOE-RL and the U.S. Forest Service in Redmond Oregon. The DOE-RL has an established agreement between the DOE-RL and the Wenatchee National Forest for request and dispatch of a retardant plane for use on range fires. This agreement can be implemented by the Hanford Fire Department by a request directly to the Wenatchee National Forest or through DOE-RL. The retardant is composed of several materials including primarily Ammonium Polyphosphate (a fertilizer), and iron oxide (for Color), and other lesser ingredients which are a "Trade Secret". The aircraft is available on a 24 hour per day basis, and requires about 15 minutes to load and prepare for a flight. The flight time from Wenatchee is approximately 30-45 minutes, and the flight time from Redmond Oregon is approximately 1 hour. Each plane can drop as many as 4 loads of about 600 to 750 gallons each dependant upon the type of plane used. The plane is however subject to availability, due to forest fire priority. <u>This application should be considered only as a backup resort to the application of fixant by Tank Farm Operations crews due to the availability, method and limits of application associated with area to cover, and density of the coverage.</u>

2. The Hanford Fire Department currently has the capability to establish a fog/deluge spray over an exhauster release point or open tank, The deluge spray would be accomplished by a request for support from the Hanford Fire Department (811). Hanford Fire would dispatch a "tele-squirt" fire truck which has the capability to connect to a continuous source of water (fire hydrant, or tank truck) and deliver a deluge spray from truck level to approximately 50 feet above ground, unattended. The truck is

capable of being set up to deliver 100 to 1000 gallons per minute in a fog spray fashion from an elevated position, and to run without operator attendance for approximately four hours until refueling is needed. This vehicle could be staged to spray over an exhauster or an open tank for long periods of time with only the need to supply a water source and fuel.

3. The Hanford Fire Department also indicated that the capability to use Aqueous Film Forming Foam (A-FFF) currently exists within the fire department, and is available. The A-FFF foam is generated by adding the foam concentrate to a source of water, and discharging the material onto the target. The foaming agent can be added directly to a tank truck, or added to a water hose line, or pumped directly from the container to the target. The fire department also has a "cellar" sprinkler which will deliver large volumes of water spray from a roof/ceiling to a "room", very similar to the inside of a waste tank. This sprinkler could be used to deliver the A-FFF foam or water to the tank vapor space in the event of a "burn" or continuous chemical reaction. The "cellar" sprinkler could be inserted into a riser and used to foam or spray the contents of the tank in the event of a continuous reaction.

4. High expansion foam is also available through the fire department, however the method of delivery requires a fairly large discharge duct (about 24 Inches in diameter) and a fan to blow the foam onto the target. This capability does currently exist, but it was not recommended for use on a tank due to the method of application. The high expansion foam would probably be used only in the event of a dome collapse and then used to cover the "open hole", as a temporary protective cover over the tank openings. Other considerations involve the characteristics of the foam: it is very light and would be blown by the wind possibly carrying contaminated material with it which may contribute to the problem rather than solve one.

5. The methodology for quickly responding to an emergency condition in any nuclear or radiological facility under WHC contract control is in place, and documented in WHC-CM-4-10. This is where WHC establishes policy implementation of the requirements found in DOE 5480.11 for occupational worker radiation protection during emergency response conditions. Conditions exceeding 5 rem/hr are defined as emergency facility radiological conditions and existing Radiation Work Permits are not applicable. Emergency provisions for granting approval for occupational workers being authorized to be exposed to conditions which are expected to result in doses greater than DOE annual dose limits require the concurrence of the manager of Health Physics and the manager of DOE-RL. See WHC-CM-4-10, Section 4.0, paragraph 5.7. RWPs are available electronically on the HLAN and also at each HP office.

6. WHC HP personnel are trained on use of SCBA apparatus, and have adequate access to portable field instrumentation and dosimetry necessary to respond to all accident scenarios. Accident responder doses will be controlled by use of appropriately ranged field instrumentation. PNL Calibrations has been contacted and is ready to support additional field instrumentation requests. High range dose rate instruments are currently in the field throughout Hanford facilities in pre-established emergency response kits. Additional resources are available through other Hanford contractors.

ENCLOSURE 4

91:633

WHC-EP-0399 DRAFT

PRE-DECISIONAL DRAFT

INTEGRATED PROGRAM PLAN FOR STABILITY OF HANFORD TANKS CONTAINING FERROCYANIDE WASTES

HANFORD FERROCYANIDE TASK TEAM

R. J. Cash, Chairman, WHC
G. B. Mellinger, PNL

January 10, 1991

Westinghouse Hanford Company
Pacific Northwest Laboratory

Richland, Washington 99352

PREDECISIONAL DRAFT

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INTEGRATED PROGRAM PLAN
HANFORD FERROCYANIDE TASK TEAM

1.0 INTRODUCTION

Efforts have been under way since the mid 1980s to evaluate the potential of a ferrocyanide explosion in Hanford Site single-shell tanks (SSTs) (Burger 1984; Burger and Scheele 1988). The 1987 Environmental Impact Statement (EIS), Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes (DOE 1987) for high-level waste storage tanks projected that a "worst-case" explosion in a ferrocyanide tank would result in a subsequent short-term radiation dose to the public of 200 mrem.

A recently completed General Accounting Office (GAO) study (Peach 1990) postulates a greater "worst-case" accident with independently calculated doses one to two orders of magnitude greater than the 1987 EIS. A special Hanford Ferrocyanide Task Team was commissioned in September 1990 to address all issues involving the ferrocyanide tanks, including the consequences of a potential accident. On October 9, 1990, Secretary of Energy James D. Watkins announced that a Supplemental EIS would be prepared that would contain an updated analysis of safety questions for the Hanford SSTs (including a ferrocyanide explosion) (DOE 1990). The efforts described in this Program Plan will provide the primary technical input required for the ferrocyanide explosion portion of the Supplemental EIS.

The Hanford Ferrocyanide Task Team is composed of technical experts from Westinghouse Hanford Company (WHC) and Pacific Northwest Laboratory (PNL). In addition, consultants to the Ferrocyanide Team will provide additional expertise in the fields of ferrocyanide chemistry, behavior of ferrocyanides as explosives, and behavior of aerosols formed from an explosion. Ferrocyanide Task team members are listed in Appendix B. The Hanford Ferrocyanide Task Team reports to the DOE-RL Tank Safety Project Office through the Waste Tank Ferrocyanide Stabilization function in the WHC Waste Tank Safety Program (Appendix A).

2.0 BACKGROUND

Radioactive wastes from defense operations have accumulated at the Hanford Site in underground waste tanks since the early 1940s. At present, there are 177 waste storage tanks at the Hanford Site; 149 are SSTs. Over the years, wastes have been distributed among tanks to segregate different types of waste and to reduce the need for additional tanks.

During the 1950s, 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 scientists developed a process to scavenge radiocesium from waste liquids stored in the tanks. This process involved the carrier precipitation of cesium nickel ferrocyanide, as shown in Figure 2.1. In implementing this process, the operating contractor added from 190 to 320 metric tons of ferrocyanide to the SSTs.

Records at Hanford show that there are 23 SSTs that contain 465 lb (1000 g-mol) or more of ferrocyanide precipitates. The ferrocyanide content of the 23 tanks ranges from 465 lb up to possibly 90,000 lb (in Tank BY-104) of ferrocyanide calculated as the $Fe(CN)_6^{4-}$ anion. Other wastes in these tanks probably include significant quantities of sodium nitrate, sodium nitrite, silicates, aluminates, hydroxides, phosphates, sulfates, carbonates, uranium, copper, and calcium in addition to the fission products present from the processing of irradiated fuel. A list of the 23 ferrocyanide tanks and available pertinent data are attached in Appendix C.

Ferrocyanide is a stable complex of ferrous ion and cyanide that is considered nontoxic because it does not dissociate in aqueous solutions. However, in the presence of oxidizing materials such as nitrates and/or nitrites, ferrocyanide can be made to explode in the laboratory by heating to high temperatures (above 280°C [540°F]) or by an electrical spark of sufficient energy. 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. Explosion propagation properties for large quantities of the

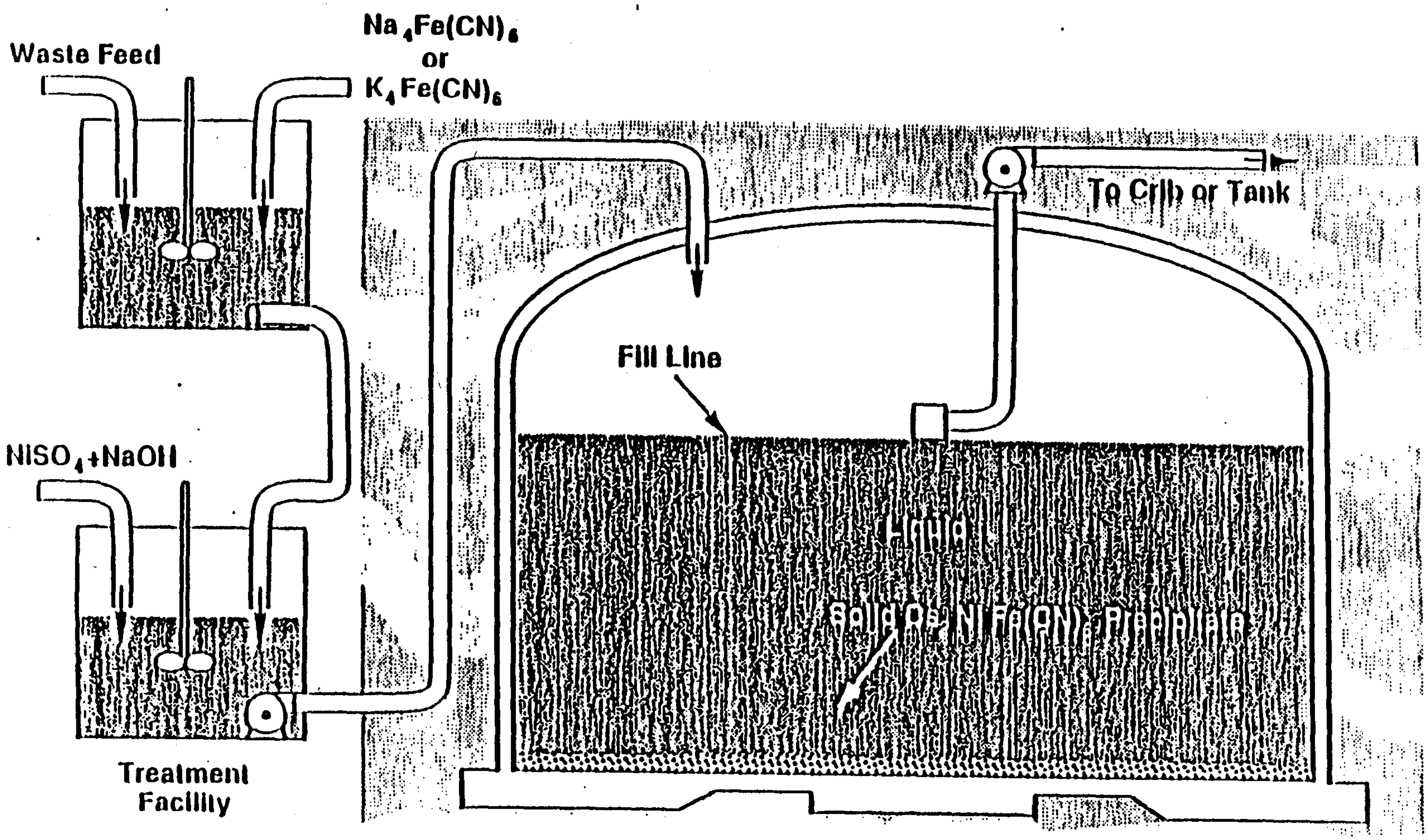

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FIGURE 2.1. Ferrocyanide Scavenging to Remove Cesium

material are unknown and the effects of moisture content and other diluents (or possible catalysts or initiators) that may be present are largely unidentified. Because the scavenging process involved precipitating ferrocyanide from solutions containing nitrate and nitrite, it is possible that an intimate mixture of ferrocyanides and nitrates/nitrites exists in parts of some of the SSTs.

3.0 SCOPE AND OBJECTIVES

The scope of work in this program plan includes the known safety and technical issues related to the SSTs at the Hanford Site that contain ferrocyanide. These issues include but are not limited to short- and long-term safety analyses, management and control of tank storage operations, collection and analysis of tank historical information, interim waste tank stabilization, and ultimately, waste remediation and/or disposal. The principal objective of this work is to gain a thorough understanding of ferrocyanide tank waste and the reactive behavior of the constituents so that 1) the tanks can be maintained in a safe condition with minimal risk of an explosion, 2) one or more strategies can be selected to implement interim stabilization, and 3) ultimate disposal options can be identified.

The Ferrocyanide Task Team shall consider and implement recommendations provided by internal and external agencies and oversight boards or committees, as appropriate. These agencies/boards include the Washington State Department of Ecology (WDOE and WDOH 1990), the Washington State Department of Health (WDOE and WDOH 1990), the Washington State Nuclear Waste Advisory Council, the Defense Nuclear Facility Safety Board,(a) the Advisory Committee for Nuclear Facility Safety,(b) the DOE High-Level Radioactive Waste Tanks Task Force and Technical Advisory Board, the General Accounting Office (Peach 1990), and other committees recognized by the U.S. Department of Energy (DOE).

3.1 FERROCYANIDE TASK TEAM APPROACH

A fundamental scientific understanding of the contents and chemical behavior of the waste in ferrocyanide SSTs is required if the tanks are to be maintained in safe condition until final treatment is implemented and to

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(a) Letters, J. T. Conway to J. D. Watkins, "Defense Nuclear Facility Safety Board Recommendation 90-3 to the Secretary of Energy [concerning susceptibility of Hanford's single-shell, high-level waste tanks to an explosion]," March 27, 1990. "Defense Nuclear Facility Safety Board Recommendation to the Secretary of Energy [concerning modification of the DOE implementation plan to be more responsive to Recommendation 90-3]," October 12, 1990.

(b) Transcription of Meeting, U.S. Department of Energy Advisory Committee on Nuclear Facility Safety (ACNFS), Pasco, Washington, June 22, 1990.

ensure that the methods chosen for final treatment can be safely accomplished. To meet these objectives, a number of issues must be addressed:

- The contents of the tanks must be known. This information must include not only the contents of the primary reactive species (ferro- and ferricyanides and nitrates/nitrites), but also the concentrations of catalysts and initiators that are determined to enhance the reactions and diluents that may impede the reactions. Certain of these analyses may be routine; other analyses will require development.
- Conditions required for initiating and suppressing the chemical reactions of concern must be known. Adequate monitoring of tank conditions (particularly temperature and moisture content of the waste layers) is required to ensure that the tanks remain safe. Installation of adequate and reliable instrumentation will be an important part of this tank monitoring. The use of a three-dimensional thermal model now being developed for the ferrocyanide tanks will ensure that accurate waste temperatures are determined.
- Experimental data and analyses are needed to accurately predict the consequences of an explosion in a ferrocyanide waste tank. Of particular interest are the fractions of Cs-137, Sr-90, and transuranic elements that would probably be discharged from the tank as respirable-size particles.
- Interim stabilization and potential final treatment and remediation methods need to be identified to allow selection of strategies that can be safely implemented. Finally, other issues that may apply to the ferrocyanide tanks, such as seismic factors and structural integrity, need to be identified and assessed for their impacts on tank safety.

Portions of the work identified in this plan will be performed by other DOE laboratories, universities, and/or private industry, as appropriate.

3.2 DESCRIPTION OF CESIUM/STRONTIUM SCAVENGING OPERATIONS

The following description of the ferrocyanide scavenging operations conducted between 1954 and 1957 at Hanford provides a brief history and background information to facilitate understanding the present ferrocyanide tank safety issues.

The bismuth phosphate extraction process used in the irradiated fuel chemical reprocessing plants during the 1940s and early 1950s did not recover uranium. The extraction waste or metal waste containing the uranium and approximately 90% of the fission products was stored in single-shell waste tanks. Waste from the first decontamination cycle, containing approximately 10% of the fission products, was stored in different waste tanks.

To recover the valuable uranium from the metal waste, a solvent-extraction uranium recovery process was installed. The metal waste solution was sluiced from the underground tanks, acidified in the tank farm vaults, and transferred to the uranium recovery plant. The uranium recovery process (also called the TBP Process since TBP [tributyl phosphate] was the active solvent extractant) began production in November 1952. While the process efficiently recovered uranium from the sluiced, acidified metal waste, the process generated almost 2 gallons of waste for every gallon of metal waste originally present. Ways to reduce the volume of stored waste were studied, resulting in development of the ferrocyanide scavenging process.

The objective of the ferrocyanide scavenging process was to remove the soluble Cs-137 from the uranium recovery waste as a precipitate. The other principal long-lived fission product, Sr-90, was already essentially insoluble in the neutralized waste. The cesium scavenging process consisted of adding $Fe(CN)_6^{-4}$ ion to the acid waste, adjusting the waste pH to 9 ± 1, and then adding an equal molar amount of Ni^{+2} ion to produce a $Cs_2NiFe(CN)_6$ precipitate and/or carry the cesium down along with other nickel ferrocyanide precipitates. It was not known then nor is it known today what the major ferrocyanide precipitate was. Since the major metal ion in the waste was sodium, the major precipitate is probably a compound approaching $Na_2NiFe(CN)_6$

The ferrocyanide scavenging flowsheet was tested in the U Plant in October 1953, and production scavenging of the uranium recovery wastes began in late September 1954. By that time, there was a total of approximately 21.2 millon gallons of unscavenged uranium recovery waste in the tank farms (approximately 13.1 million gallons in 200E Area and approximately 7.9 million gallons in 200W Area). The initial production flowsheet consisted of adding 0.005 $\underline{M}$ $K_4Fe(CN)_6$ to the acid waste and 0.005 $\underline{M}$ $NiSO_4$ to the waste after the pH was adjusted to 9 ± 1. In some campaigns, the pH-adjusted waste was partially concentrated before adding the $NiSO_4$.

The following flowsheet changes were made to the scavenging operation:

- replacing $K_4Fe(CN)_6$ with $Na_4Fe(CN)_6$ (April 18, 1955) to lower processing costs
- testing and routinely adding $Ca(NO_3)_2$ to improve strontium decontamination (April 21, 1955)
- testing and adding $Sr(NO_3)_2$ to replace $Ca(NO_3)_2$ for strontium decontamination as $Sr(NO_3)_2$ was available on plant (August 1955)
- testing and routinely using 0.0025 M $Fe(CN)_6^{-4}$ and Ni^{+2} instead of 0.005 M (August 1955 test, November 1955 routine) to reduce chemical costs.

The scavenged waste was routed to a receiver tank in the BY Farm in 200E Area (usually tank BY-106, 107, 108, or 110) at a maximum rate of approximately 50,000 gallons per day. When the tank was full, the waste stream was switched to another receiver tank. The filled tank was allowed to settle for a minimum of 1 week and was then sampled at several incremental depths and analyzed for pH, cesium, strontium, total ß, total α, and PO_4^{-3}. If the cesium and strontium were within applicable disposal limits at the time, the liquid content of the tank was pumped to a crib/trench using a floating suction pump. Grab samples were taken from the discharge line for every 50,000 gallons transferred (for every 100,000 gallons after June 1955). The samples were combined and analyzed for the components listed above plus several others. The combined samples showed dissolved solids in the range of 16 wt% to 35 wt% but low values for radioactive cesium and strontium. The accumulated sludge in the receiver tanks was periodically transferred to tanks BY-104 or BY-105.

Unscavenged waste already stored in 200E Area tanks before scavenging began in U Plant was routed to the 244-CR vault for scavenging. Much of this waste was first concentrated to approximately 60% of the original volume. The pH was then adjusted with nitric acid and/or NaOH to 9 ± 1 and $Fe(CN)_6^{-4}$ and Ni^{+2} ion added (generally to 0.005 M each). The scavenged waste was then routed to another tank for settling, sampling, and decanting. This procedure probably left many of the original alkaline insoluble solids (e.g., $Fe(OH)_3$)

in the original waste storage tanks. The primary receiver tanks for this "in-farm scavenged" waste were C-108, -109, -111, and -112.

Excess ferrocyanide, well above the stoichiometric amount of cesium present, was always added during the scavenging runs. This caused large quantities of sodium nickel ferrocyanide [$Na_2NiFe(CN)_6$] and possibly dinickel ferrocyanide [$Ni_2Fe(CN)_6$] to precipitate. From 1970 to 1977, evaporator bottoms were transferred to the ferrocyanide tanks and allowed to settle. After settling, the supernate was pumped back to the evaporators for further concentration. These bottoms did not contain ferrocyanide. An operational history of 200 Area tank farms is documented in WHC-MR-0132 (Anderson 1990).

3.3 RESULTS OF PNL/LANL STUDIES TO DATE

Several reactions can be postulated for the oxidation of cesium nickel ferrocyanide (FeCN) by nitrate and nitrite. Simple reactions with nitrate and nitrite salts are illustrated by Reactions (1) and (2). Other postulated reactions produce CO, NO, NO_2, carbonates, and hydroxides.

$$Cs_2NiFe(CN)_6 + 6NaNO_3 \rightleftarrows Cs_2O + 3Na_2O + NiO + FeO + 6CO_2 + 6N_2 \quad (1)$$

$$Cs_2NiFe(CN)_6 + 10NaNO_2 \rightleftarrows Cs_2O + 5Na_2O + NiO + FeO + 6CO_2 + 6N_2 \quad (2)$$

The calculated enthalpies of reaction for these two reactions are -1655 and -1704 kJ/mol, respectively. An uncertainty of ±300 kJ/mol is assumed based on the estimated heat of formation of ferrocyanide of 0 ±300 kJ/mol. The latter value is estimated from National Bureau of Standards (NBS) (Wagman et al. 1982) data for about a dozen metal ferrocyanides that have heats of formation ranging from about -99 kJ/mol CN^- to +115 kJ/mol CN^-, and these and others with free energies of formation from -2 to +10 kJ/mol CN^-. Using this value for ΔH_f for ferrocyanide, the heats of reactions for several reactions are given in Table 3.1.

Beginning in late 1988, the Pacific Northwest Laboratory (PNL) began an experimental program at the request of WHC to investigate the effects of temperature on the oxidation reaction between synthetic ferrocyanide and nitrates and nitrites representative of materials present in some of the Hanford SSTs.

TABLE 3.1. Heats of Reaction for Different Oxidation Reactions

Reactants	Products	Enthalpy, kJ/mol
$NaNO_3$, FeCN	FeO, NiO, CO_2, N_2, Na,Cs hydroxides	-2490
" "	" " " " Na,Cs carbonates	-3025
" "	" " " " Na,Cs oxides	-2088
$NaNO_2$, FeCN	FeO, NiO, CO_2, N_2, Na,Cs hydroxides	-2925
" "	" " " " Na,Cs carbonates	-3719
" "	" " " " Na,Cs oxides	-1704
$NaNO_3$, FeCN	" " " NO Na,Cs hydroxides	+ 624

PNL used differential scanning calorimetry (DSC), scanning thermogravimetry (STG), and small-scale (<100 mg) time-to-explosion (TTX) tests to investigate the relative effects of the oxidant melting point, the nitrate-to-nitrite ratio, the oxidant-to-ferrocyanide ratio, and several potential catalysts and/or initiators on the observed minimum reaction and explosion temperatures. In cooperation with PNL, the Los Alamos National Laboratory (LANL) has performed and will continue to perform a series of tests to determine the sensitivity of one mixture of ferrocyanide and oxidant to initiation by impact, spark, friction, increased temperature, and increasing mass.

The DSC, STG, and TTX methods show that the oxidation pathway for oxidant mixtures containing both nitrate and nitrite is not simple. In the TTX, even after slow degradation at a low temperature (about 250°C), the ferrocyanide and oxidant mixtures exploded when heated to 360 to 400°C. In addition, the characteristic brown color of NO_2 has been observed visually above the heated mixture prior to exploding.

The testing conducted at LANL to date showed that a mixture made from nearly equimolar amounts of ferrocyanide, 50 mol% sodium nitrate, and 50 mol% sodium nitrite was insensitive both to reaction initiation in impact and friction tests and to a spark with energy equivalent to a static discharge from a human.

The testing to date indicates that both the reaction and explosion can be thermally initiated, are sensitive to the cation of the nitrate and/or nitrite, are sensitive to whether the oxidant is nitrate or nitrite, and are sensitive to EDTA, iron hydroxide, and nickel hydroxide catalysts or initiators. The lowest observed reaction and explosion temperatures for ferrocyanide were 220°C (428°F) and 280°C (536°F), respectively, for an oxidant mixture of 47.5 mol% sodium nitrate, 47.5 mol% sodium nitrite, and 5 mol% EDTA.

These studies did not determine the reaction mechanism, the kinetic parameters of the Arrhenius equation, the behavior of other possible precipitated ferrocyanides, or the effect of inert diluents.

4.0 INTEGRATED PROGRAM PLAN TASKS

Seven tasks are covered in this joint WHC/PNL Program Plan. The tasks are described in detail in the following sections. Integration of the overall program will be conducted by WHC and PNL, and individual tasks will be managed by either WHC or PNL as described in task descriptions. Program reporting will be through WHC to the DOE-RL Tank Waste Safety Project Office.

To provide a representative bounding case for the safety analysis portions of this plan, Tank BY-104 has been selected as the "worst-case" ferrocyanide tank. This is the same tank cited in the 1987 EIS, and it is the tank with the largest quantity of ferrocyanide [possibly up to 90,000 lb as $Fe(CN)_6$]. Tank BY-104 is also one of four ferrocyanide tanks with the highest radionuclide content of Cs-137 and Sr-90. A multi-year effort will be required to complete the activities described in this proposal. The major near-term products of this work are described in Section 5 of this proposal, "Task Deliverables."

4.1 PROGRAM MANAGEMENT

Task Leaders - Robert J. Cash, WHC, George B. Mellinger, PNL

This task will provide program management and integration of the work described, including managing costs and schedules and ensuring that appropriate safety and quality assurance (QA) is applied. Data bases of all relevant information pertaining to the ferrocyanide tanks at Hanford will also be managed in this task. A monthly report will be prepared for DOE that contains a description of the previous month's technical progress, the status of milestones, and expenditure information. Also, it is assumed that quarterly program review meetings will be conducted in conjunction with the DOE Headquarters (DOE-HQ) High-Level Radioactive Waste Tanks Task Force/Technical Advisory Panel. Participation in periodic reviews by oversite committees and agencies is also part of this effort.

4.1.1 Peer Review

Because of the national importance and visibility of this program, it is critical that information generated by this program receive both internal and external technical peer review.

Internal peer review would be conducted within WHC and PNL, by DOE-RL, by the DOE-HQ High-Level Radioactive Waste Tanks Task Force and Technical Advisory Panel, by DOE-HQ Environment Safety and Health (EH), by the Advisory Committee for Nuclear Facility Safety (ACNFS), and possibly others. External review would be provided by external technical personnel identified by WHC and PNL, the Senior Science Panel, Washington State Departments of Ecology and Health, the Washington State Nuclear Waste Advisory Council and input from the public at quarterly meetings, the General Accounting Office, the Defense Nuclear Facility Safety Review Board, and the National Academy of Sciences.

4.1.2 Westinghouse Hanford Company Internal Control Management Systems

WHC, as the engineering and operations contractor at the Hanford Site, manages SST and double-shell tank (DST) farm operations. A bottom-up review of the current management control systems now in place will be conducted. This review will include, as a minimum, evaluating the recent Tiger Team findings relating to tank farm operations as they affect the ferrocyanide tanks, the way the tank farm management system has or is responding to these findings, responses to peer review and oversight committee/agencies findings and recommendations, the scope and adequacy of training required for tank farm operators and management, and contingency planning and emergency preparedness for emergency events. To complete this management systems review, the Hanford Ferrocyanide Task Team will perform an extensive management audit. Members of the audit team will include selected staff from WHC and PNL with audit experience who have a working knowledge of industrial safety practices, nuclear safety, quality assurance, and tank farm operations. The outcome of this audit would result in a set of recommendations to WHC senior management, including the possibility of a new organizational structure, if needed.

4.1.3 Interim Contingency Planning

A contingency plan for the engineering and operations contractor's response to unanticipated changes in the 23 ferrocyanide tanks is currently being developed in three phases and will be continued under this program plan. Phase I defines the criteria/specification limits required for ensuring that the tanks are maintained in a safe condition and identifies response actions required to prevent or mitigate temperature excursions that could result in an explosion. Phase II will incorporate the Phase I document into existing 200E and 200W Tank Farm Emergency Plan information, and Phase III will provide a comprehensive document that includes specific mitigation information for each ferrocyanide tank. All information from the first two phases will be included in this document.

4.2 FERROCYANIDE ACCIDENT MODELING, RISK ANALYSIS, AND SAFETY EVALUATIONS

Task Leader - Daniel D. Stepnewski, WHC

This task includes the aerosol test program, ferrocyanide accident analysis, and safety analysis documentation.

4.2.1 Aerosol Test Program

The radiological dose consequences from a ferrocyanide explosion in an SST depends largely upon the amount of radioactive material released as a respirable fraction. The respirable fraction, generally taken to be aerosol particles smaller than 10μm, is a major unknown in the prediction of potential accident consequences from a ferrocyanide energy release.

Existing experimental data on aerosol generation by explosions are inadequate because Cs-137 in the waste tanks could be present in the explosive itself and could be vaporized and later condense out as aerosol particles as the gas cools. Other radioactive materials may also be present within the explosive layer. Condensation from the vapor generally produces smaller aerosol particles than mechanical dispersion. However, turbulent effects associated with a high energy release may promote agglomeration.

The aerosol test program task will use the Containment Systems Test Facility (CSTF), a 30,000 ft^3 pressure vessel located at the Hanford Site. Tests will be conducted on explosive ferrocyanide mixtures using quantities of up to 1 kg. Following source characterization to determine energy utilization and source scaling, measurements of suspended aerosol mass and particle size distribution will be made under conditions which model a rapid energy release from a ferrocyanide waste storage tank. Test data will be obtained on dependence of reaction rate on scale, and on the inertial confinement produced by the earthen overburden of the tank.

Mathematical modeling will permit scaling up of test results to the actual-size waste tanks. A team of recognized aerosol experts will be convened periodically to evaluate the program plans and results and to recommend additional studies required to obtain the needed information.

4.2.2 Ferrocyanide Accident Analysis

Energy release accidents postulated to occur in a waste tank containing ferrocyanides will undergo both deterministic and probabilistic analyses. These analyses will determine the magnitude of consequences from bounding accidents and more realistic worst-case events. These results will improve current estimates of risk and can be used to guide remediation plans.

The analyses will depend on actual tank conditions and will rely, in part, on other data gathering programs. The thermocalorimetric tests are particularly important. Calorimetry will be performed on synthetic tank materials initially and on actual tank samples at a later date. These tests will determine the reaction initiation temperatures and burn propagation parameters. The effect of moisture on burn propagation is of particular interest. The tests will be performed at Fauske and Associates, Inc. and at WHC. Testing with radioactive samples will be done in WHC facilities. These test results will be used in conjunction with thermal testing to be performed at PNL and LANL. These tests are necessary because of the complex composition of the waste tank inventory and uncertainties in chemical reaction sequences. Mathematical models will be developed to scale up the chemical burning process to actual tank boundary conditions.

Deterministic calculations of the consequences of hypothetical ferrocyanide energy releases will be made (if such events cannot be precluded). Approved radiation-dose-consequence codes will be used. The dose calculations will utilize the aerosol performance predictions discussed earlier.

A probabilistic hazards analysis will be performed for the waste tanks. This evaluation will include a determination of initiating conditions during passive operations that could result in off-normal events with the potential for dispersing radionuclides both on and off site. The evaluation will also consider operations or changes in tank status or configuration that could result in similar off-normal events.

The approach will include assessing existing or potential hazardous conditions in the tanks and will determine how those hazardous conditions could contribute to potential energy releases.

The products of the study will be a set of accident sequences, quantified if possible, and organized into bins or classes of similar consequences from which risk values could be estimated. An uncertainty and sensitivity analysis will be included to evaluate how unknowns in tank contents and materials will affect the calculated risk values.

The foregoing studies will identify the inherent hazards associated with the waste tanks and will serve as a basis for the safety evaluations of tank sampling and remediation activities as discussed in the next section.

4.2.3 Safety Analysis Documentation

Personnel contributing to this task will prepare a report on the tanks' inherent hazards, and addenda to that report addressing tank-intrusive activities such as sampling. The initial report will include burn modeling, dose consequence analyses, and probabilistic risk assessment. Addenda will provide safety evaluations for specific activities; these evaluations will serve as the safety basis for management authorization of a given activity. The activity safety evaluations will be performed in the order of increasing risk or uncertainty. The initial addendum will address nonintrusive or limited activities such as adding instrumentation within a tank, and later addenda would evaluate tank sampling by core drilling and remediation activities such as sluicing and pumping.

The material generated in this safety analysis task will also be used in producing Chapter 9 in the safety analysis report upgrades and in developing operational safety requirements (OSRs) as needed.

4.3 CHEMICAL REACTION STUDIES

Task Leader - Randall D. Scheele, PNL

Determining the nitrate and nitrite oxidation chemistry of possible ferrocyanide precipitates, their radiolysis, and aging progeny is central to determining the hazard associated with the presence of ferrocyanides in the SSTs and to developing a strategy for rendering the wastes nonexplosive. Understanding the chemistry and sensitivities of the system will provide the tank operators with knowledge that is essential to ensure the safety of their operations and selection of appropriate remediation or disposal strategies.

This study involves measuring the reaction sensitivity to possible initiating events, such as impact, friction, or thermal events, to determine what conditions will initiate the reaction(s) of concern. The study will also recommend maximum safe operating temperatures for the ferrocyanide SSTs. The study will also determine the chemical pathway for oxidation to determine the energy produced by the reaction and to allow development of methods for identifying and detecting reaction products. Detecting reaction products in the SSTs on a real-time basis, particularly in the gas phase, could provide an early detection system for the reaction that would indicate when an emergency response procedure should be implemented.

The required experimental program involves investigating a number of interrelated and overlapping areas that are described in detail in Sections 4.3.1 through 4.3.6. It should be noted that the work in these areas will be conducted in parallel. The initial work will be scoping studies, which will provide direction for follow-on work that will focus on gaining a more fundamental understanding of the chemistry and reactivity of the wastes in the ferrocyanide-containing tanks. Results from the scoping studies will also provide data that may be used in preparing the supplement to the Hanford Defense Waste Environmental Impact Statement (HDW EIS) (DOE 1990).

Results from any one of the research areas may influence what portions of another area may be important. In fact, not all of the experimental program described herein may be needed, but decisions on the direction of the experimentation will have to be made as test results are obtained.

In the proposed experimental program, the hazards associated with the presence of ferrocyanides in the tanks will be ascertained by investigating the reaction chemistry (mechanism and kinetics) and sensitivity of synthetic mixtures of nitrates and/or nitrites and possible ferrocyanide precipitates, and their progeny created by radiolysis, oxidation, and hydrolysis. The effects of dilution by other potential waste constituents; the effects of potential catalysts and initiators (such as organic complexants); the effect of water; and the effects of increased mass on the chemistry, reactivity, sensitivity, and explosivity will be included in these studies.

Once samples of ferrocyanide-bearing waste have been obtained from an SST, samples of this material will be tested using the methods developed through use of synthetic ferrocyanide-containing wastes.

4.3.1 Chemical Nature of Cyanide in Wastes

Based upon results of previous PNL studies, it has been found that the chemical nature of the cyanide in the SST waste could have a dramatic impact on the reaction sensitivity and mechanism. Several cyanide-containing compounds, representative of those originally precipitated and those produced by radiolysis and long-term exposure to a highly alkaline environment, must be studied to understand what effect the chemical nature of the cyanide may have on the explosive hazards associated with the presence of ferrocyanide in the SSTs.

Cyanide was added to the SSTs as sodium or potassium ferrocyanide along with an equimolar quantity of nickel sulfate to effect carrier precipitation of cesium as cesium nickel ferrocyanide $Cs_2NiFe(CN)_6$. The bulk of the cyanide could have been precipitated as sodium or potassium nickel ferrocyanide, $(Na,K)_2NiFe(CN)_6$, or possibly as dinickel ferrocyanide, $Ni_2Fe(CN)_6$. In addition to the unknown nature of the original precipitates, the effects on the ferrocyanide of extended storage at elevated temperatures in a high-radiation field and in a highly alkaline environment for 35 years is unknown.

Exposure to a radiation field in a highly alkaline environment for 35 years could have affected the chemical form of the cyanide in the SSTs. As noted by Burger (Burger 1984), the available literature suggests moderate instability of aqueous solutions of cyanide or ferrocyanide and identifies several different products. Very limited testing at PNL on the effect of radiation on solid ferrocyanide indicates that cesium nickel ferrocyanide is quite resistant to radiation damage. Radiolysis, because radiolytic systems tend to be oxidative, could also affect the possible conversion of ferrocyanide to ferricyanides; PNL's calculations predict that although ferrocyanides are normally more stable, the ferricyanide may form in oxidizing alkaline media and further decompose to ferric hydroxide and oxidized carbon-nitrogen species.

Little is known about the actual chemical nature of the cyanide in the SSTs, and studies to determine the behavior of each possible species are needed. Ferrocyanide precipitates will be prepared using the flowsheet conditions and compositions that were used in the scavenging process. The precipitates will be irradiated in a highly alkaline environment. These precipitates, their aging products, and pure compounds of nickel-, iron-, and mixed ferrocyanides, will be chemically characterized and species identified, and their solubilities, reactivities, sensitivities, and enthalpies of formation will be measured.

Reactivities and sensitivities with nitrates and nitrites will be measured using DSC, STG, TTX, impact, friction, and spark tests, accelerating rate calorimetry (ARC), and adiabatic scanning calorimetry (ASC). Reaction products will be determined when pertinent.

The work described here will be conducted using waste simulants. It is possible when actual samples of waste are obtained and analyzed using the same methods that analyses will show that different compounds (e.g., relative abundance of ferro- and ferricyanides) are present in the waste than was predicted from the synthetic waste studies. If this is found to be the case, the work with the synthetic wastes will be critically examined to determine why different results were obtained, and additional work to resolve the differences will be proposed.

4.3.2 Reaction Mechanisms and Kinetics

The way the oxidation reactions of cyanide-containing compounds proceed (mechanism) will determine the amount of energy released. The speed with which the oxidation proceeds at any temperature, coupled with the enthalpy of the reaction and the thermal conductivity and heat capacity of the system, will determine the maximum point temperature at which the material can be safely stored. It is therefore important for predictive purposes to determine the mechanism by which ferrocyanide and its aging products are oxidized by nitrates and nitrites and the kinetic parameters for the reaction or reactions.

In this subtask, reactions between ferrocyanide and its aging products with nitrates and/or nitrites and other waste constituents, such as water, will be studied to determine pathways and Arrhenius constants for significant steps in the oxidation. To investigate the mechanism, isothermal and nonisothermal tests will be performed using DSC, STG, ARC, and possibly other calorimetric methods to allow monitoring of various stages of the reactions. As reactions occur, gases and solid products will be collected and analyzed using such methods as gas chromatography (GC), infrared spectrometry (IR), mass spectroscopy (MS), x-ray diffraction spectroscopy (XRD), electron microprobe, electron spectroscopy for chemical analysis (ESCA), Mossbauer spectroscopy, nuclear magnetic resonance spectroscopy (NMR), high-pressure liquid chromatography (HPLC), and standard chemical analysis methods, such as inductively coupled argon plasma atomic emission spectroscopy (ICP), and ion chromatography (IC).

As in Section 4.3.1, the work will be conducted using waste simulants. If actual waste samples show the presence of different compounds, the work of this subtask will be refocused on determining the reaction mechanisms and kinetics of the compounds that are found in the actual waste.

4.3.3 Effects of Catalysts and Initiators

The SSTs contain a very broad range of materials that could act as catalysts or initiators for the ferrocyanide reaction with nitrates or nitrites. Studies by PNL to date have shown that potential waste constituents, such as 5 mol% EDTA and 5 mol% nickel hydroxide, can affect ferrocyanide oxidation by nitrate and nitrite. It is suspected, based on DSC and STG analyses, that metals are acting as catalysts, and the EDTA is acting as an initiator. Other potential catalysts that may exist in the SSTs include Cu, Pb, Mn, and Cl, and other organic solvating agents.

Investigations to determine the effect of potential catalysts and initiators will employ DSC, STG, TTX, and possibly other isothermal or nonisothermal methods such as ARC and ASC. Analyses of the product gases and solids will also be performed using some of the analytical methods mentioned earlier.

4.3.4 Effect of Solid Diluents

Ferrocyanides in the SSTs may be mixed intimately with other waste constituents that could serve as inert diluents and mitigate the effects of any ferrocyanide oxidation by nitrates and/or nitrites. Possible diluents include other waste constituents such as bismuth phosphate, sodium aluminate, and sodium carbonate. Solid diluents increase the mass that must be heated by the reaction before a temperature is reached that is sufficient to initiate a runaway reaction. This investigation on dilution effects should indicate, among other things, whether a remediation technique, such as mixing the ingredients in the tank, will render the wastes nonexplosive.

This activity will investigate the effect of solid diluents on the nitrate and nitrite oxidation of possible ferrocyanides and aging progeny using DSC, STG, TTX, ARC, ASC, and possibly impact, friction, and spark tests. Other tests and analytical methods may be used as appropriate. Gases and solid products will be analyzed as necessary.

4.3.5 Effect of Increasing Mass

The explosivity of a material is dependent on its mass, geometry, and confinement. The ability of a material to transfer reaction heat from the reaction zone to its outer boundaries will determine whether the reaction will reach the thermal runaway temperature. It is therefore important that tests be conducted using larger, kilogram quantities of material. If possible, geometries similar to those possible in the SSTs should be investigated.

The mixtures to be tested will be chosen based upon results obtained from other subtasks. These mixtures (ferrocyanides and/or aging products, nitrates, nitrites, catalysts, initiators, and diluents) will be prepared by PNL and/or WHC; testing may be conducted at the Hanford Containment Systems Test Facility or off-site, at locations such as LANL. Initially, 1- to 10-g samples of selected mixtures will be tested for thermal initiation. Depending on the information obtained, larger samples (kilogram quantities) may then be thermally tested. Using larger quantities of material would require that sensitivity testing indicate that the material can be handled safely.

4.3.6 Testing of Actual Ferrocyanide-Bearing SST Waste

Only when samples of ferrocyanide-bearing wastes are obtained (using a statistically-based sampling plan) and tested for reactivity and sensitivity by the methods described above can there be reasonable assurance that this category of SST waste will not react in an undesirable manner or that it can be treated and disposed of safely.

Once a method of safely obtaining a sample of ferrocyanide-bearing waste is identified, and a sample of waste obtained, the reactivity of actual ferrocyanide-bearing waste will be evaluated. This evaluation will begin with sensitivity and reaction studies using, at a minimum, DSC, ASC, STG, and TTX. Gas samples obtained from thermal tests would be analyzed. The reaction-product solids would be chemically characterized using methods that can be used for radioactive samples, including ICP and XRD.

4.4 EXPANDED TANK MONITORING AND MODELING

Task Leader - Carl P. Schroeder, WHC

This task includes developing thermal models and analyses for determining tank temperatures; upgrading tank monitoring systems; designing, fabricating, and procuring new instrument trees for the tanks; and developing alternative tank monitoring technologies.

4.4.1 Thermal Model Development and Analyses for Ferrocyanide Tank Temperatures

The decay of radioactive materials in the waste tanks generates heat. Undesirable chemical reactions could occur if the temperatures in a tank reach a value high enough to cause uncontrolled exothermic chemical excursions. Presently, the temperature data for each tank are taken from a string of thermocouples arranged vertically on a single holder, called a tree. There is one tree per tank, but the trees are not always at the same location for each SST. As a result, uneven heat generation resulting in hot spots could exist in these tanks and not be detected because of the sparse instrumentation. The purpose of this task is to analyze available temperature data and develop a computer model to determine the heat load and temperatures within the ferrocyanide waste storage tanks. Included in this task are sensitivity and parametric analyses to determine the magnitude and effects of the presence of hot spots within the waste and identification of the technical requirements for the instrumentation systems necessary to detect the hot spots.

The modeling will be performed with state-of-the art computer codes. Both the sludge thermal behavior and the airspace hydraulics (natural circulation) will be modeled. The models will be benchmarked with existing data. These models will then be used to perform the thermal and hydraulic analyses needed to support the new instrument tree design and to analyze the new temperature data collected. These same models will be useful in evaluating infrared mapping data and will support the evaluation of temperature-dependant chemical reaction rates.

4.4.2 Upgrade Existing Tank Monitoring Systems

This subtask will determine the accuracy of presently installed thermocouples on the ferrocyanide SSTs and the adequacy of instrumentation and tank monitoring program employed for tank farm operations. The prime objective is to eventually provide continuous temperature monitoring on all ferrocyanide tanks. Continuous monitoring will be installed in the near-term on a selected list of higher-risk ferrocyanide tanks, that is, those tanks containing significant quantities of ferrocyanide, which also have higher heat loadings.

Near-term activities include providing commercially available equipment and software to continuously monitor existing thermocouples in Tanks 104-BY, 105-BY, 108-BY, and 110-BY and designing and coordinating equipment and software installation. The equipment will include local data acquisition equipment as well as data display, storage, and alarming at the CASS Operator Station at Building 2750E, which is manned 24 hours a day.

4.4.3 New Multifunctional Instrument Trees

New instrument trees for ferrocyanide tank temperature profile measurement, gas sampling, and possibly gamma scan access (initially for tanks 104-BY, 105-BY, 108-BY, 110-BY, and 101-TY) are needed to replace existing obsolete thermocouple trees and expand the measurement capability. Design, procurement, and fabrication of the new instrument trees and associated commercial equipment, such as data acquisition instrumentation, are included in the subtask. Installation engineering support to tank farm operations is also included. Documentation similar to that listed in Section 4.4.2 will be included in the deliverables.

Mechanical design, temperature testing design, and prototypic testing for the instrument trees are also included in this subtask. Mechanical engineering design for field installation is included as well as control systems engineering design and equipment acquisition for the new instrument tree. Data acquisition equipment compatible with the new sensors and field installation engineering support will be provided.

Thermocouples - Specially designed thermocouple assemblies will be evaluated for the instrument trees because they can be assembled and deployed based on well developed and commercially available thermocouple technology. However, deploying the thermocouples within the tank contents to provide the needed temperature profiles could present a significant engineering problem within prevailing safety and other constraints. Calibration techniques will be developed to ensure needed system accuracy, and redundant thermocouple designs should be considered to provide system reliability. The baseline approach will be to design, fabricate, and install thermocouple bundles with approximately 20 thermocouples in each bundle. The thermocouples will be staggered in length to provide vertical temperature profiles. A number of design issues are yet to be resolved, such as a method for penetrating the solid waste to insert the new trees and measures to ensure corrosion control in the highly alkaline environment.

4.4.4 Alternative Tank Monitoring Technologies

Infrared Scanner - The feasibility and practicability of using an infrared scanning/imaging system for detecting hot spots on the solid (and liquid) surfaces of tank contents will be evaluated. A commercially available infrared imaging radiometer will be procured and modified for insertion into the tanks using the 12-in.-diameter photography riser on each tank. This modification would involve enclosing the radiometer in a protective case, providing for a liquid nitrogen coolant (if required), and providing for greater length between the head and electronic image processing units. Key issues for applying this technology include the following:

- Thermal mapping records the combined effect of temperature and emissivity variations over a surface.
- Data are presented as a temperature map, although it is known that the true temperature can only be determined if the emissivity is known for each part of the surface. Detecting differences in the temperature map as function of time is the most important element of temperature monitoring.
- Temperature changes from one day to the next can be determined with an accuracy (to be determined) for a given area. Measuring of temperature change would be relatively independent of emissivity.

Other capabilities for tank monitoring will be considered and studied, such as cover gas sampling, gamma scanning, and liquid-level monitoring combined with features of the instrument tree to the extent practical.

4.5 FERROCYANIDE WASTE CHARACTERIZATION

Task Leaders - George L. Borsheim and David B. Bechtold, WHC

This task will estimate and determine the inventory and concentrations of materials important to ferrocyanide oxidation reactions in the 23 ferrocyanide tanks. Characterizing the ferrocyanide tank contents is necessary to guide chemical reaction studies, allow application of the study results, and facilitate the estimation of the probability and consequences of an uncontrolled ferrocyanide reaction. Knowledge of the relative position of the materials within the tanks is also important to determine the proximity of potential reactants. Lacking such data, conservative bounding assumptions must be used.

The important reaction materials present in the SSTs are fuel (ferrocyanides and reduced carbon species, such as organic complexants), oxidants (nitrates and nitrites), and inerts such as phosphates, sulfates, carbonates, oxides, and hydroxides. Fission products, such as Cs-137 and Sr-90, are important because they act as heat sources which raise and maintain the temperature of the tank contents and because they are source terms in the event of a radiological release. The transuranic content of the waste is also radiologically significant in accident scenarios. The water content of the waste is very important because the high heat capacity and the heat of vaporized contained water makes it an effective inerting material and prevents sustained combustion. Other materials may be important as potential catalysts (for example, Ni, Cu, Pb, rare earths) or potential initiators (EDTA or other organic complexants).

Some characterization information can be obtained from existing ferrocyanide scavenging program records, tank farm operating records, sample analyses, and measurements of tank liquid levels. Further information may be inferred from laboratory-scale simulations of the original scavenging operation flowsheets and identification of the resulting products. These products can then be tested in laboratory adiabatic calorimetry tests to determine their reactive properties as input for the safety documentation required for intrusive core sampling of the tanks. More definitive data will be obtained from future sampling and in-tank measurements. The following sections describe work planned to characterize the ferrocyanide tank waste.

4.5.1 Characterization of Tank Waste from Existing Information

The focus of this subtask is to collect, review, and evaluate existing plant records and sample data to provide best estimates of the ferrocyanide tank contents. It may also be possible to secure limited additional information, such as surface samples for analysis and liquid level measurements, before new core samples are obtained for analyses.

The most comprehensive SST inventory information now available is the output from the Track Radioactive Constituents (TRAC) computer runs performed in 1985. This computer simulation used Hanford Site nuclear fuels production models and records, reprocessing and waste management flowsheets, and waste transfer records to model the flow of materials in waste tanks from 1944 through 1980. The program was originally developed to track radionuclides and expanded to provide estimated inventories for 65 radionuclides and 30 chemical constituents (including NO_3^-, NO_2^-, $Fe(CN)_6^{4-}$, EDTA, HEDTA, citrate, and hydroxyacetate). The estimated inventories are useful, but the program output has never been validated and has not been run since 1985. The present tank listings for the 23 tanks containing more than 1000 g-mol of ferrocyanide was compiled from both the ferrocyanide scavenging program records[a] (later used as input to TRAC) and the 1985 TRAC output inventories. Many of the tanks that received ferrocyanide scavenged waste were later used for storage and transfer of other tank farm waste, such as aluminum decladding wastes. The TRAC simulation included these waste transfers.

Ferrocyanide scavenging records are currently being analyzed in detail to re-estimate the inventories of ferrocyanide, Cs-137, and Sr-90 in the ferrocyanide tanks at the end of the scavenging program in 1957. These results will be compared to the TRAC output and available sample records. The data will be documented, evaluated, and used as best estimates for these constituents until new core sample results are available.

Some analyses of ferrocyanide tank solids are available, including partial analyses of tanks 104-BY (1976), 103-TY (1979), 101-TY (1986), and 103-TY (1986). The last 101-TY and 103-TY samples were later analyzed for total cyanide. These results are included in the ferrocyanide database.

The flowsheets that describe the original scavenging operations have been recovered. A first order estimate of the precipitated solids and decanted supernates from those operations will be made by performing laboratory-scale beaker tests of the process followed by appropriate chemical analyses. Additionally, an estimate of the stoichiometry of oxidants and fuel in the sludge will be made by compacting the wetted precipitates to a consistency approximating the sludges that were sampled from ferrocyanide tanks in the past. The two-phase mixture will be analyzed for nitrate, nitrite, and total cyanide. These tests, coupled with estimates of subsequent processing and/or degradation of the precipitates, will provide the best approximation for a surrogate tank waste. This surrogate waste will be used as a basis for safety documentation until better information is available from Task 4.3 and actual tank waste is recovered.

To provide the baseline for safety documentation required for core sampling, these surrogate wastes will be subjected to thermal analyses, including adiabatic calorimetry. Adiabatic calorimetry provides a measure of

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(a) Letter, K. S. Pickett to L. L. Burger, "Hexacyanoferrate (II) in Waste Tanks as a Result of Scavenging Operations," dated March 23, 1984.

the magnitude of an exothermic runaway reaction ("explosion") in terms of onset temperature, maximum temperature reached, and quantity of gas generated, all in detailed time-series data. Thus, the potential consequence of a coring operation may be evaluated as a function of important parameters such as bit temperature, moisture content, and percentage of inerts present. An adiabatic scanning calorimeter has been procured and will be delivered by December 1, 1990. A laboratory test plan will be drafted and approved to permit operation of the calorimeter on radioactive wastes in the 222-S Radioactive Laboratory at WHC. The plan will include a safety evaluation. Before calorimetry begins with radioactive wastes, however, the instrument will be used on best-estimate surrogate waste compositions to provide sampling safety evaluation data.

It may be possible to obtain new information from an archive core sample remaining from tank 101-TY. This tank's waste was cored in 1986, but the two cores were combined before performing chemical analyses. Data from the analyses have been documented, but the data are not sufficient to answer all questions regarding ferrocyanide safety issues. Approximately 3 grams of composite material remain that may yield additional information, despite the loss of detail that compositing caused. A suite of additional analyses on this remnant are being planned and prioritized to reflect the amount of material remaining. The plan includes XRD speciation of ferrocyanide, scanning electron microscopy, and DSC to complement the analyses performed previously.

Liquid-level measurements have been made in many of the ferrocyanide tanks in salt wells and/or liquid observation wells (LOWs). These data will be useful in determining the amount of moisture remaining in or on top of the tank solids. The ferrocyanide solids are believed to be in the bottom portion of the waste unless or until additional information indicates otherwise. The LOW data were obtained using both neutron and gamma monitoring probes. The gamma probe data will be examined to determine if the position of the Cs-137 can be determined in the tanks. The possibility of using a modified gamma probe to secure this information will also be examined. Another technique that will be evaluated for moisture determination is radar imaging. Ground penetrating radar has been used to map buried waste, and applying it here might also be useful to map the distribution of constituents in the sludge-type waste. Ground penetrating radar may be particularly sensitive to agglomerations of ferrocyanide because of its effect on the reflectivity of the radar signal. Thus, a three-dimensional map of the distribution of segregated solid tank contents might be possible by scanning the surface of the tank contents. Special robotics might be needed to negotiate in-tank obstacles. The radar signals will not penetrate liquid-phase waste because of its expected high electrical conductivity. This fact could be exploited to map solid/liquid interfaces.

Two additional techniques will be evaluated for their effectiveness in detecting and mapping of paramagnetic materials. The influence of ferrocyancide on the magnetic properties of the bulk waste will determine the efficacy of these methods. The techniques will be investigated, evaluated versus data requirements, and prioritized for further development based on cost/benefit issues. In all cases, the fact that the sensors must be intrinsically safe in an explosive environment will be addressed.

The use of sensors for determining the physical properties and structure (solid-liquid interfaces, for example) of the waste will also be evaluated. These properties may be determined by combining information from several techniques. Knowledge of these properties may be important for numerical modeling of gas generation and dynamics, heat transfer, etc. Knowing the macroscopic structure of the waste will be necessary to develop remediation strategies whether they be mechanical venting, chemical alteration, or others. The properties of primary interest may include thermal conductivity, electrical conductivity, magnetic permeability, pH, porosity, density, viscosity, and water content (bound and free). A number of methods might be applied to measure these properties. Methods will be developed if there is a specific need identified for the information that they provide.

Identifying specific chemical species and their locations in the tanks is also important. One potential method for obtaining these data is with remote chemical sensors. These sensors typically combine a selectively reactive coating (one that will interact with the desired chemical of interest) and a physical transducer that can measure the extent of that interaction. For example, PNL has developed chemical sensors using fiber optic probes and piezoelectric resonators to detect airborne chemical warfare agents and underground chemical contamination.

Initial efforts might focus on developing of sensors for nitrates, nitrites, and cyanides. Participation of off-site laboratories, such as the Center for Process Analytical Chemistry (CPAC) at the University of Washington, will be invited. If chemical coatings can be developed that are both sensitive and selective, this technology promises to be cost effective and responsive for providing critically needed information.

Sampling the vapor space of the ferrocyanide tanks will undoubtedly be a prerequisite for core sampling and other in-tank work. The sampling methods and analyses required must be developed. The lessons learned from gas sampling in DST 101-SY will be used to develop the sampling plan and prepare the necessary safety documentation.

4.5.2 Ferrocyanide Tank Core Samples

The waste characterization plan for the Hanford Site SSTs (Winters et al. 1990) calls for obtaining two core samples from each SST by 1998. The sampling pattern for the SSTs has previously been based on a rational, statistical experimental design tailored to the chemical characterization needs of the SST Characterization Program. The safety issues raised by the possible presence of ferrocyanides, other reduced carbon species, nitrates, and nitrites in close proximity require additional characterizations to be resolved. These additional characterizations in turn require increased sampling, but the decisions on how many cores to take from what locations in the tanks must be reevaluated. The WHC Statistics Group, which performed this task for the SST Characterization Program, are available to modify or replace the sampling plan with a new one reflecting these additional needs.

Originally, the ferrocyanide tanks were not a high priority for sampling because a layer of salt cake in several of these tanks is expected to make sampling difficult. The priority for sampling these tanks has now changed because of the need to determine reactive properties of the tank contents. The critical path will be the time required for preparation and approval of safety evaluations for core sampling these tanks. The safety evaluation for core sampling DST 101-SY will provide guidance for establishing safety parameters and procedures for core sampling and handling ferrocyanide tank sample cores.

A safety evaluation for laboratory handling and analysis of the cores will also be required; this evaluation will be coordinated with laboratory/safety staff.

4.5.3 Core Sample Analyses

The magnitude of the hazard associated with possible explosive mixtures in SSTs is extremely sensitive to the chemical details of the tank contents. The details of where the reduced carbon species are in relation to the nitrates, nitrites, catalysts, and inerts determines the size of the explosion; the details of where the radionuclides are in relation to the potentially explosive mixtures contributes significantly to the magnitude of the off-site population dose. Whether or not a mixture could possibly be made to explode will depend critically on moisture content.

Examining core samples calls for a detailed chemical analysis at a resolution not previously sought for characterization of SST sludges. As a consequence, the core sample analyses to be performed for this program will encompass all of those planned for the present SST characterization plan (Winters et al. 1990) (Appendices A through F), but in greater segment-by-segment detail. Additional speciation analyses will also be required, including analyses for ferrocyanide, ferricyanide, cyanate, formamide, and others. The planning of analyses and resources for this task will build on the planning for the SST Characterization Program and will precede the sampling plan to properly allow for increased sample volume requirements. Input from Task 4.3 is required for the success of this effort.

4.6 EMERGENCY PREPAREDNESS

Task Leader - David A. Marsh, WHC

This task involves reviewing safety evaluations and safety analysis reports to determine the impacts of potential accidents resulting from a ferrocyanide event in an underground storage tank. These reviews will result in comments and revisions to the emergency planning and response elements of the safety documents. The tasks associated with hydrogen generation in underground storage tanks and associated activities will also be reviewed for lessons learned and to correlate planning efforts.

Specific deliverables from this task will be to develop and implement of a series of procedures to respond to emergencies associated with the ferrocyanide tanks, including an event recognition and classification procedure and a notification procedure. Additional procedures will be developed and issued as required by the planning and assessment efforts. This activity is expected to require approximately 9 man-months of effort to complete and has a targeted completion date of May 15, 1991. The procedures will be used to recognize and classify an emergency event at any underground storage tank based on observable events and/or instrumentation. A training session will be conducted to implement the procedures after they are issued.

Developing and issuing the procedures will require coordination with state, county, and local agencies affected or potentially affected by the postulated accidents. Reviews of past emergency exercises will also be a part of the emergency plan assessments.

4.7 FERROCYANIDE TANK INTERIM STABILIZATION

Task Leader - C. William Dunbar, WHC

This task will define and develop interim stabilization options for the 23 ferrocyanide tanks so the tanks can be maintained in an environmentally safe condition. To understand what actions can be taken, it is necessary to have information about the chemical inventory (including homogeneity/distribution information) within each tank, as obtained from Task 4.5, and a thorough knowledge of the possible chemical reactivity of waste constituents, as determined in Task 4.3. Because the Hanford SSTs have exceeded their design life, the probability that a tank will leak (if it has not already leaked) will tend to approach unity as time passes. Therefore, this task must address the safety of continued salt-well pumping versus the apparent need to keep the tank waste moist to prevent possible hot spots or a more reactive condition that might exist if the ferrocyanide dries out. It is possible that the ferrocyanide-bearing waste, in its present form, is very stable. This task must address therefore the safety of continued interim storage of the ferrocyanide, as is, in the SSTs.

If the ferrocyanide waste is to remain in the tanks until final remediation of the tanks, then the structural characteristics of the tanks must be assessed to ensure continued tank integrity. This assessment should include evaluating the seismic capabilities of the tanks under a design basis earthquake and determining that the tank contents will remain critically safe.

This task will evaluate various treatment options and their safety implications to provide a data base for comparison with the risks of leaving the waste in the tanks. Options to be studied will include in situ methods that would result in accelerated hydrolysis of the ferrocyanide to convert ferrocyanide complexes to inert materials. Processes to be studied will include the addition of hydrogen peroxide, ozone treatment, hypochlorite additions, and the addition of other chemicals that would react in a controllable fashion with ferrocyanide without producing excessive heat or reactive products. Options will also be evaluated that might require removing the waste from the tanks before final remediation or disposal.

Results of these studies will be coordinated with the Environmental Restoration and Remedial Action (ERRA) Program, which is responsible for ultimate remediation of the SSTs, including the 23 tanks containing ferrocyanide. The ultimate goal of this work will be to provide the technical basis for ERRA decision-making on the ferrocyanide tanks.

5.0 TASK MILESTONES

A draft Level 1 schedule through FY 1994 follows. Those milestones to be provided through the end of FY 1991 are shown in Level 2 schedules presented in Appendix E. Milestones are based upon the availability of adequate funding for the work described. Milestones for subsequent years will be identified at a later date.

6.0 ESTIMATED COSTS

The estimated FY-1991 costs for the activities described in this program plan are shown below by task. Program costs for the out years are in the process of being developed as Activities Data Sheets (ADSs).

6.1 EXPENSE

TASK	DESCRIPTION	FY 1991 BUDGET Expense $ (000)	
4.1	Program Management	850 280	WHC PNL
4.2	Ferrocyanide Accident Modeling, Risk Analysis, and Safety Evaluations	1,800	WHC
4.3	Chemical Reaction Studies	2,840 350	PNL LANL
4.4	Expanded Tank Monitoring and Sampling	1,000	WHC
4.5	Ferrocyanide Waste Characterization	950	WHC
4.6	Emergency Preparedness	100	WHC
4.7	Ferrocyanide Tank Interim Stabilization	150	WHC
	TOTAL:	$ 8,320	

6.2 CAPITAL EQUIPMENT

Capital equipment requirements are shown below. This equipment is needed to provide capabilities that are essential to the project but that are not currently available at Hanford, to allow real-time analyses of reaction products (such analyses will be necessary for reaction mechanism determinations), to provide essential upgrades of existing equipment, and to provide equipment for in-tank testing of potential tank monitoring technologies.

TASK	ITEM DESCRIPTION	ESTIMATED COST, $K	
Task 4.1 -		Program	
Management	- WHC (Reserve Account)		200
Task 4.2 -	Ferrocyanide Accident Modeling, Risk Analysis, and Safety Evaluations - WHC		
	High-speed Data Acquisition System	75	
	Adiabatic Calorimeter and Instrumentation	75	
	Miscellaneous Sensors and Instrumentation	15	
	High-speed Camera and Video Recording Equip	35	
	Subtotal:		200
Task 4.3 -	Chemical Reaction Studies - PNL		
	Impact Test Apparatus	100	
	Facility Upgrade for Impact Test Apparatus	250	
	Spark Test Apparatus	100	
	Friction Test Apparatus	20	
	Fourier Transform Infrared Spectrometer (FTIR)	110	
	Gas Chromatograph (GC)	25	
	Quadrapole Mass Spectrometer (MS)	50	
	Upgrade of Co-60 Irradiator	30	
	Accelerating Rate Calorimeter	100	
	Subtotal:		785
Task 4.4 -	Expanded Tank Monitoring and Modeling - WHC		
	Instrument Tree Equipment/Electrical Design	134	
	Instrument Tree Engineering Testing	40	
	Instrument Tree Control System Engineering	100	
	Instrumentation for Tank Continuous Monitoring	184	
	Infrared Scanning Equipment	42	
	Subtotal:		500
	Total:		1,685

7.0 QUALITY ASSURANCE

The activities described in the integrated plan shall be conducted in accordance with the requirements dictated by impact levels assigned to the various tasks in accordance the WHC Quality Assurance Manual, WHC-CM-4-2 or PNL's Quality Assurance Program. It is expected that all activities associated with sampling and analysis of the ferrocyanide tanks as well as equipment to be installed in the tanks will be WHC Impact Level II (or the PNL equivalent). Other activities may be assigned a WHC Impact Level III (or the PNL equivalent).

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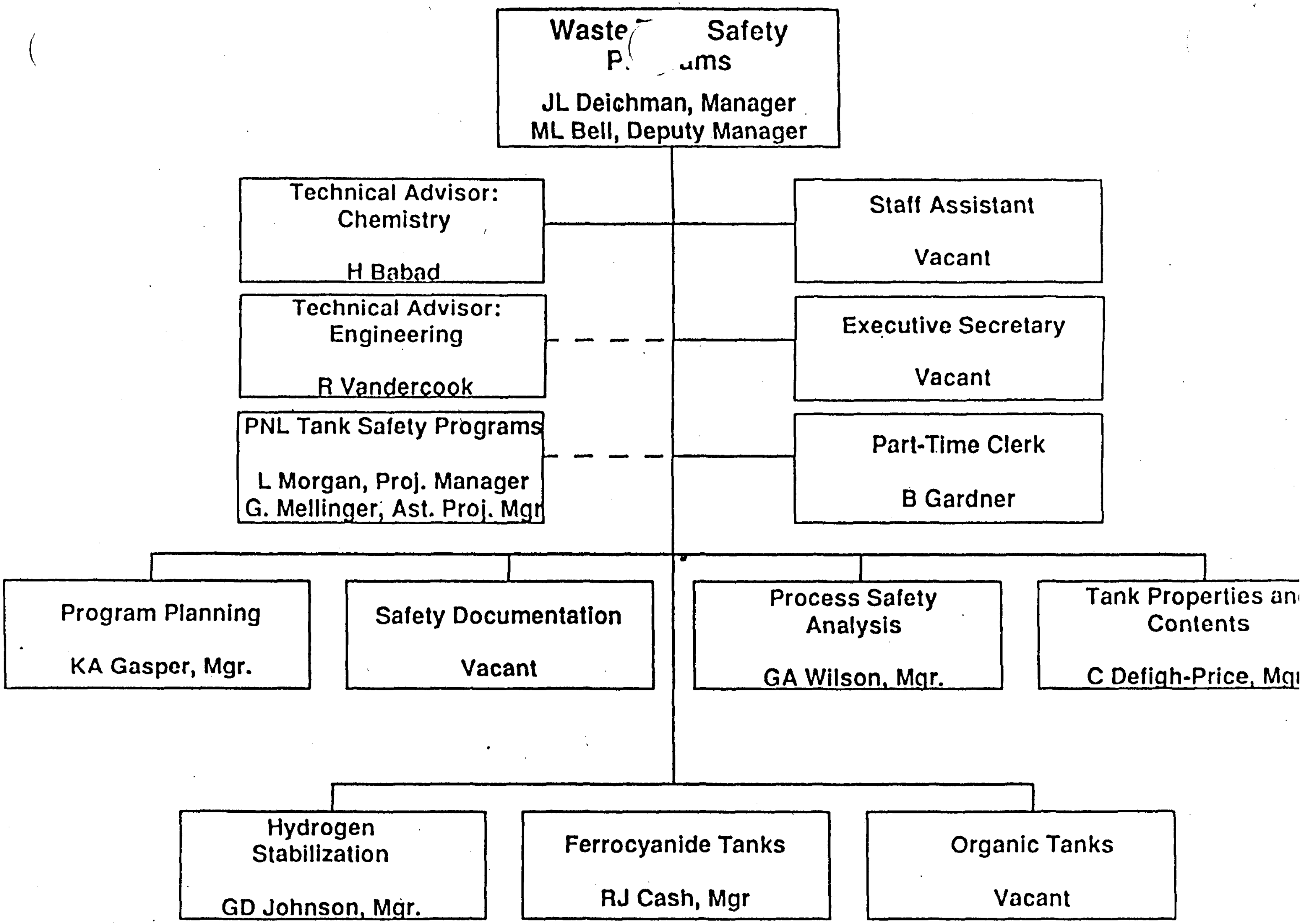
APPENDIX A

WESTINGHOUSE HANFORD COMPANY
WASTE TANK SAFETY PROGRAM ORGANIZATION

Predecisional Draft, 1/10/91


Waste [illegible] Safety
P[illegible]ams
JL Deichman, Manager
ML Bell, Deputy Manager
Technical Advisor: Chemistry
H Babad
Staff Assistant
Vacant
Technical Advisor: Engineering
R Vandercook
Executive Secretary
Vacant
PNL Tank Safety Programs
L Morgan, Proj. Manager
G. Mellinger, Ast. Proj. Mgr
Part-Time Clerk
B Gardner
Program Planning
KA Gasper, Mgr.
Safety Documentation
Vacant
Process Safety Analysis
GA Wilson, Mgr.
Tank Properties an
Contents
C Defigh-Price, Mg
Hydrogen Stabilization
GD Johnson, Mgr.
Ferrocyanide Tanks
RJ Cash, Mgr
Organic Tanks
Vacant

APPENDIX B

HANFORD FERROCYANIDE TASK TEAM MEMBERS

WESTINGHOUSE HANFORD COMPANY and PACIFIC NORTHWEST LABORATORY

FERROCYANIDE TASK TEAM MEMBERS

Robert J. (Bob) Cash, Chairman	Waste Tank Safety Program
Daniel D. Stepnewski	Safety Analysis and Regulation
David B. Bechtold	Operations Laboratories & Technology
Carl P. Schroeder	Advanced Systems Engineering
George L. Borsheim	Waste Management Technology
David A. Marsh	Emergency Preparedness
Harry Babad	Waste Tank Safety Program
Edgar G. Hess	Nuclear Safety
H. K. (Yogi) Ananda	Quality Assurance
Randall D. Scheele, PNL	Materials and Chemical Applications
George B. Mellinger, PNL	Materials and Chemical Applications
TBD	Offsite Explosives Consultant
TBD	Offsite FeCN Chemistry Consultant

APPENDIX C

DATA ON 23 FERROCYANIDE TANKS AT HANFORD

Predecisional Draft, 1/10/91

SIGNIFICANT DATA ON FERROCYANIDE TANKS

TANK	FeCN (1000 G-Moles)	HEAT LOAD (BTU/Hr)	MAX. TEMP °F (Oct 90)	ASSUMED LEAKER	INTERIM STABILIZED
102-BX	0 - 3	10,000	70	1971	11/78
106-BX	0 - 1	10,000	70	No	N/A
110-BX	0 - 1	10,000	69	1976	8/85
111-BX	0 - 1	10,000	71	1984	N/A
101-BY	0 - 1	8,200	74	No	5/84
103-BY	0 - 1	8,600	73*	1973	N/A
104-BY	100 - 200	17,000	130	No	1/85
105-BY	70 - 100	37,700	114	1978	12/84
106-BY	30	12,200	130	1984	N/A
107-BY	30 - 80	14,500	85	1984	7/79
108-BY	30 - 70	23,000	101	1972	2/85
110-BY	50 - 90	25,200	122	No	1/85
111-BY	0 - 3	34,200	79*	No	1/85
112-BY	2 - 3	<10,000	75*	No	5/85
108-C	9 - 20	10,000	81	No	3/84
109-C	30 - 50	10,000	84	No	11/83
111-C	10 - 30	<10,000	81	1968	3/84
112-C	50 - 70	<10,000	86	No	9/90
101-T	0 - 10	<10,000	62	No	N/A
118-TX	0 - 3	4,900	79	No	4/83
101-TY	0 - 30	<10,000	70	1973	8/83
103-TY	0 - 30	<10,000	73*	1973	2/83
104-TY	0 - 20	<10,000	81(7/88)	No	N/A

23 Tanks

*Temperature data from Liquid Observation Well

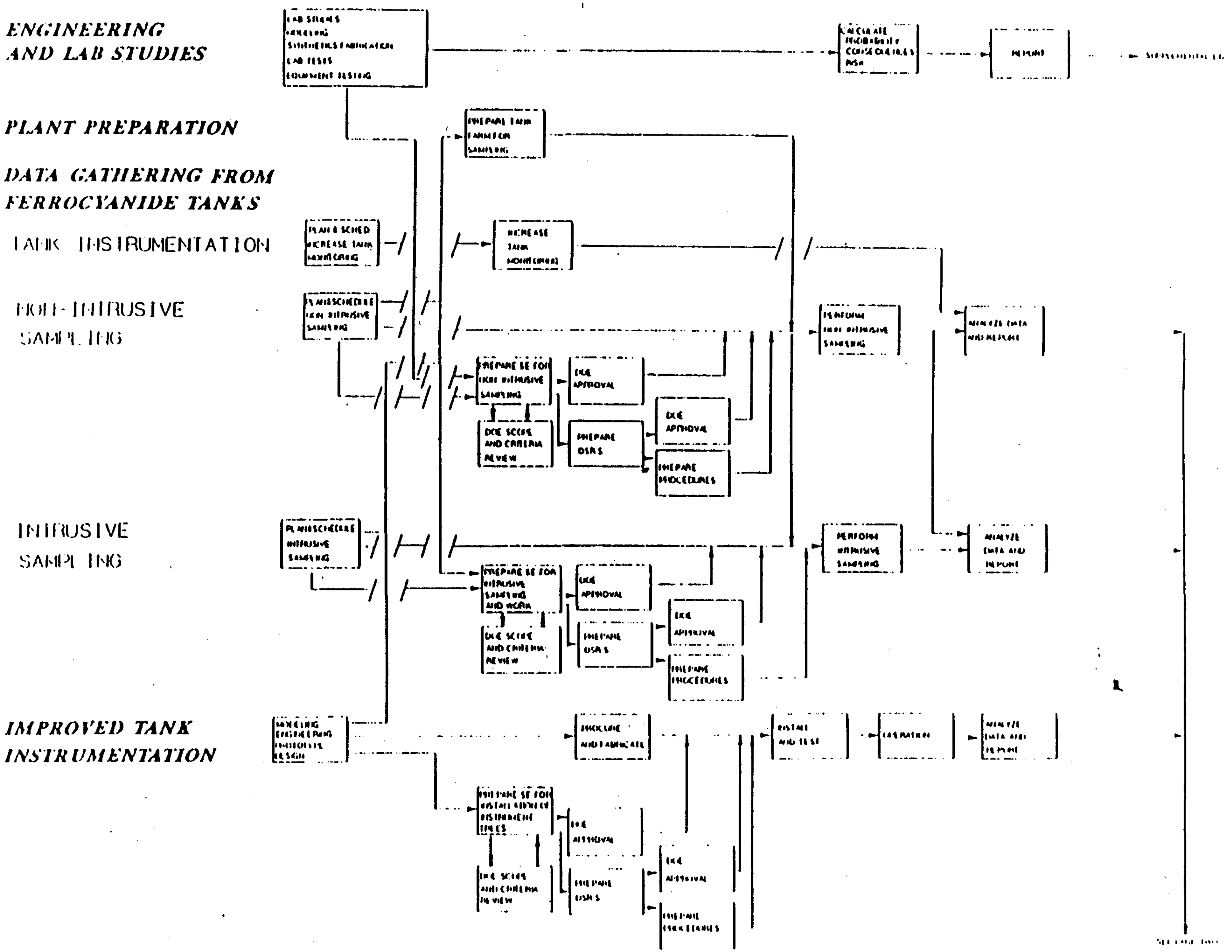
Predecisional Draft, 1/10/91

APPENDIX D

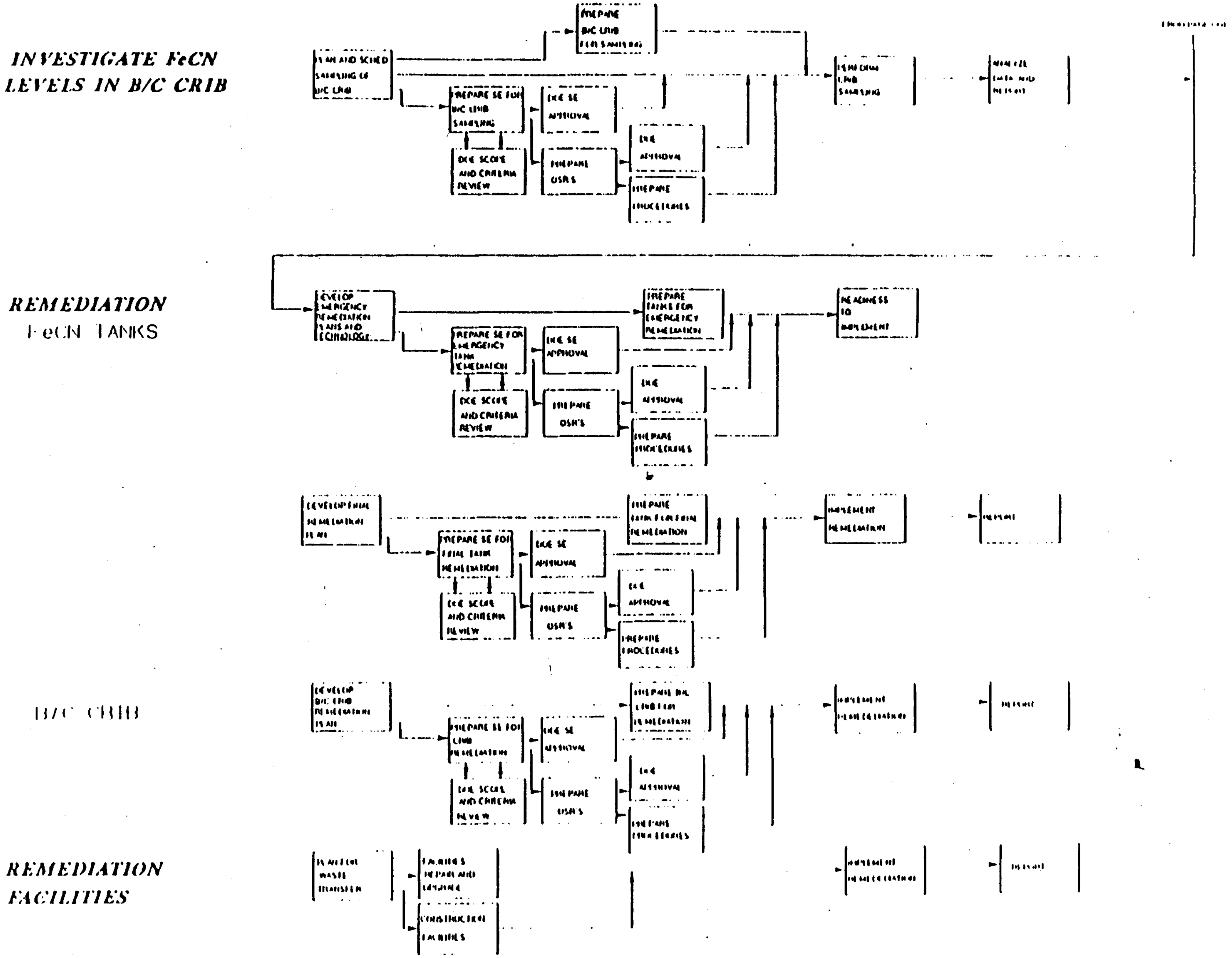
LEVEL "O" FERROCYANIDE TANKS LOGIC FLOW

Predecisional Draft, 1/10/91

LEVEL "0" FERROCYANIDE TANKS AND CRIBS LOGIC FLOW



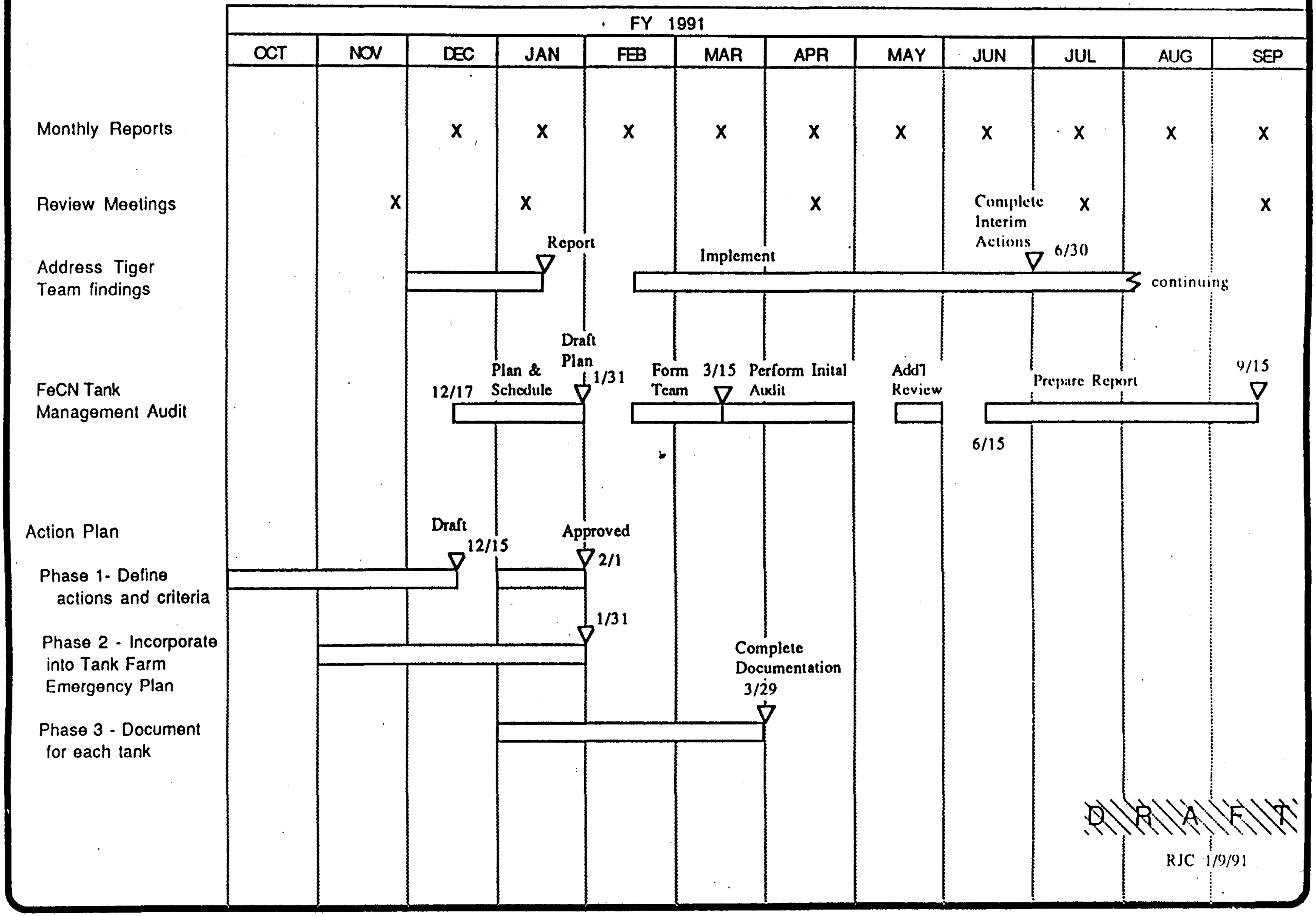
LEVEL "0" FERROCYANIDE TANKS AND CRIBS LOGIC FLOW



APPENDIX E

LEVEL 2 SCHEDULES FOR FERROCYANIDE TASK ACTIVITIES

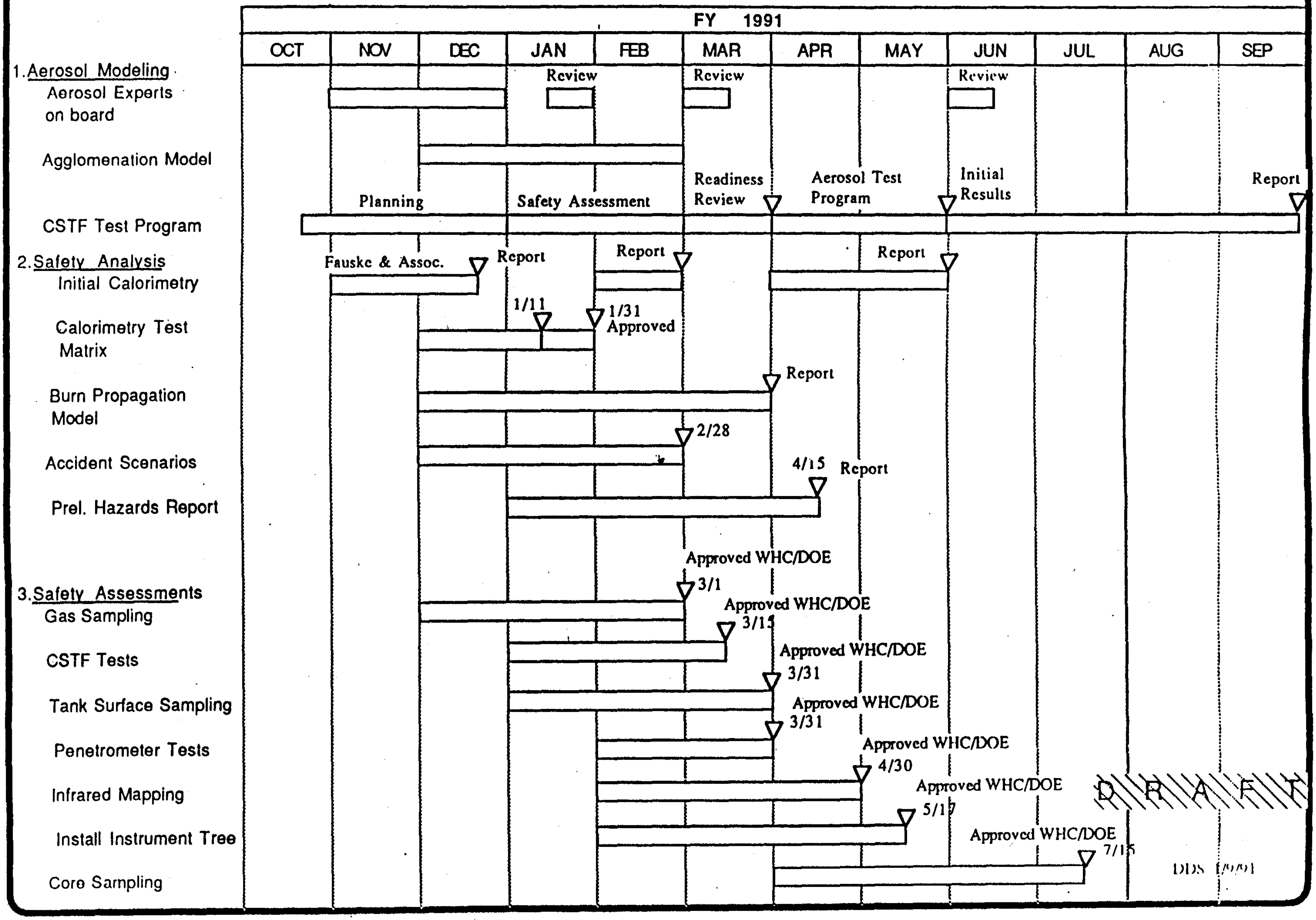
4.1 PROG ... MANAGEMENT



DRAFT

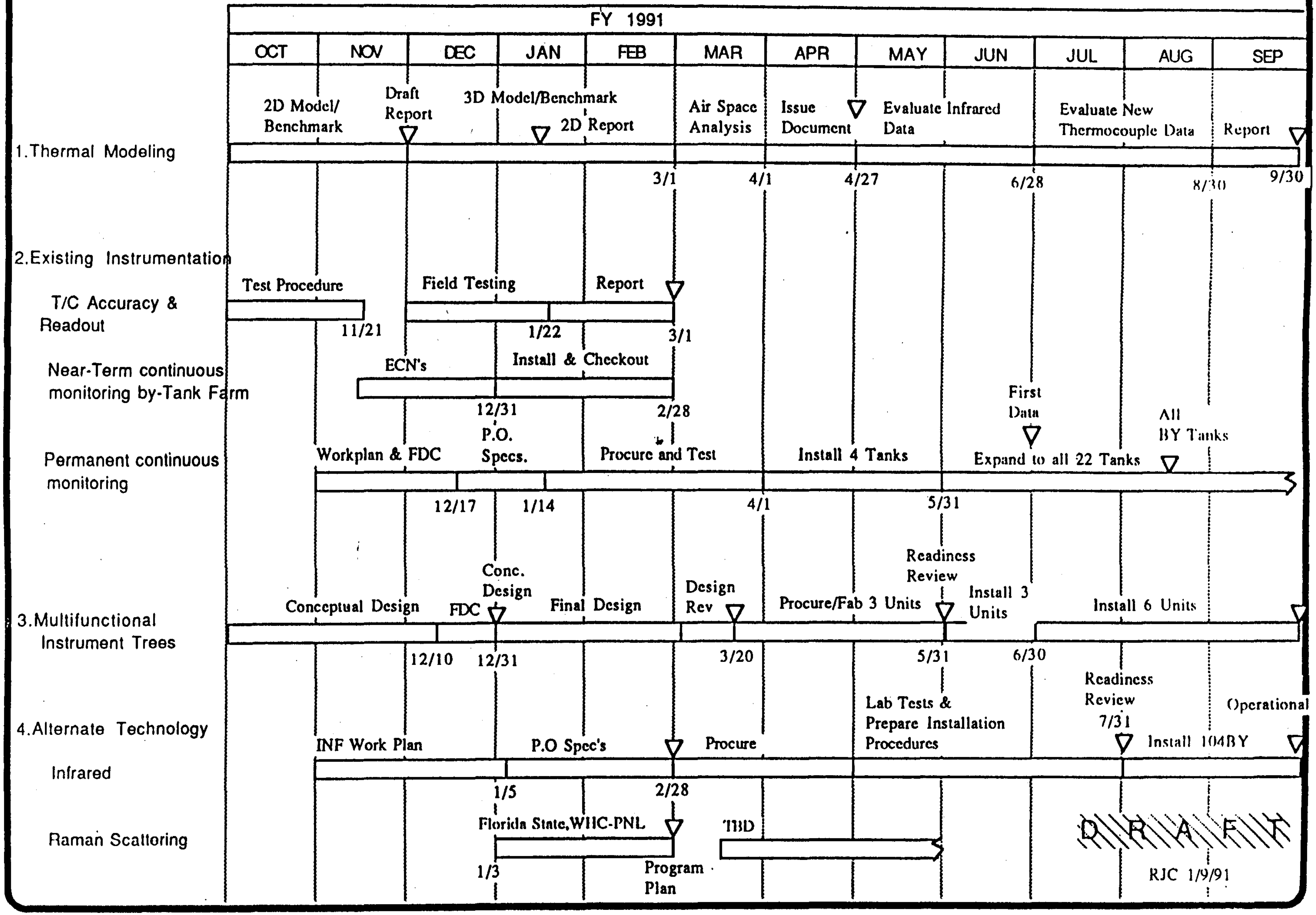
RJC 1/9/91

4.2 FeCN ACCIDENT LING, RISK ASSESSMENT,SAFETY ASSESSMENTS

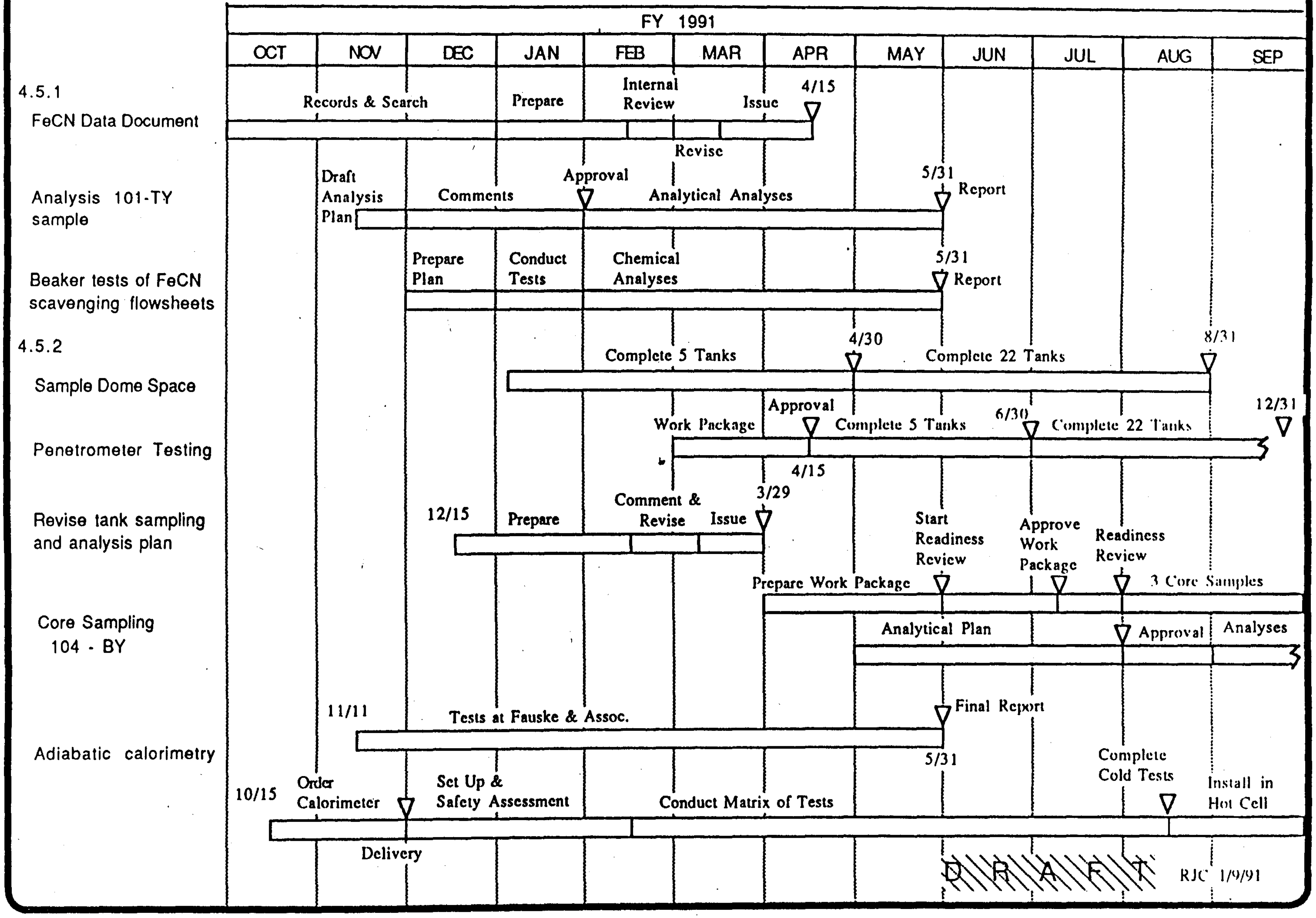


DDS 1/9/91

4.4 EXPANDED TANK MONITORING AND MODELING



4.5 FERROC\ – WASTE CHARACTERIZATION



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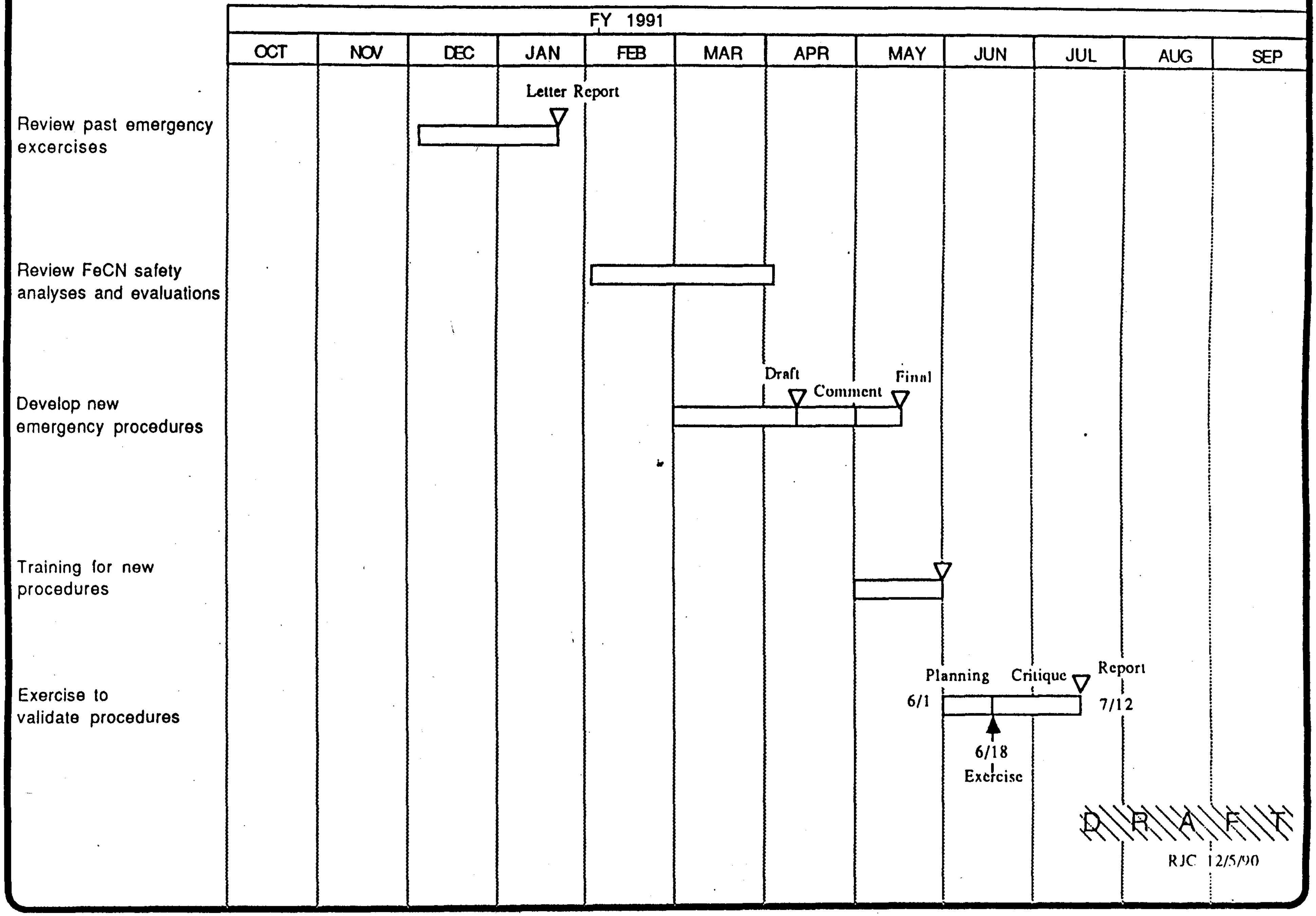

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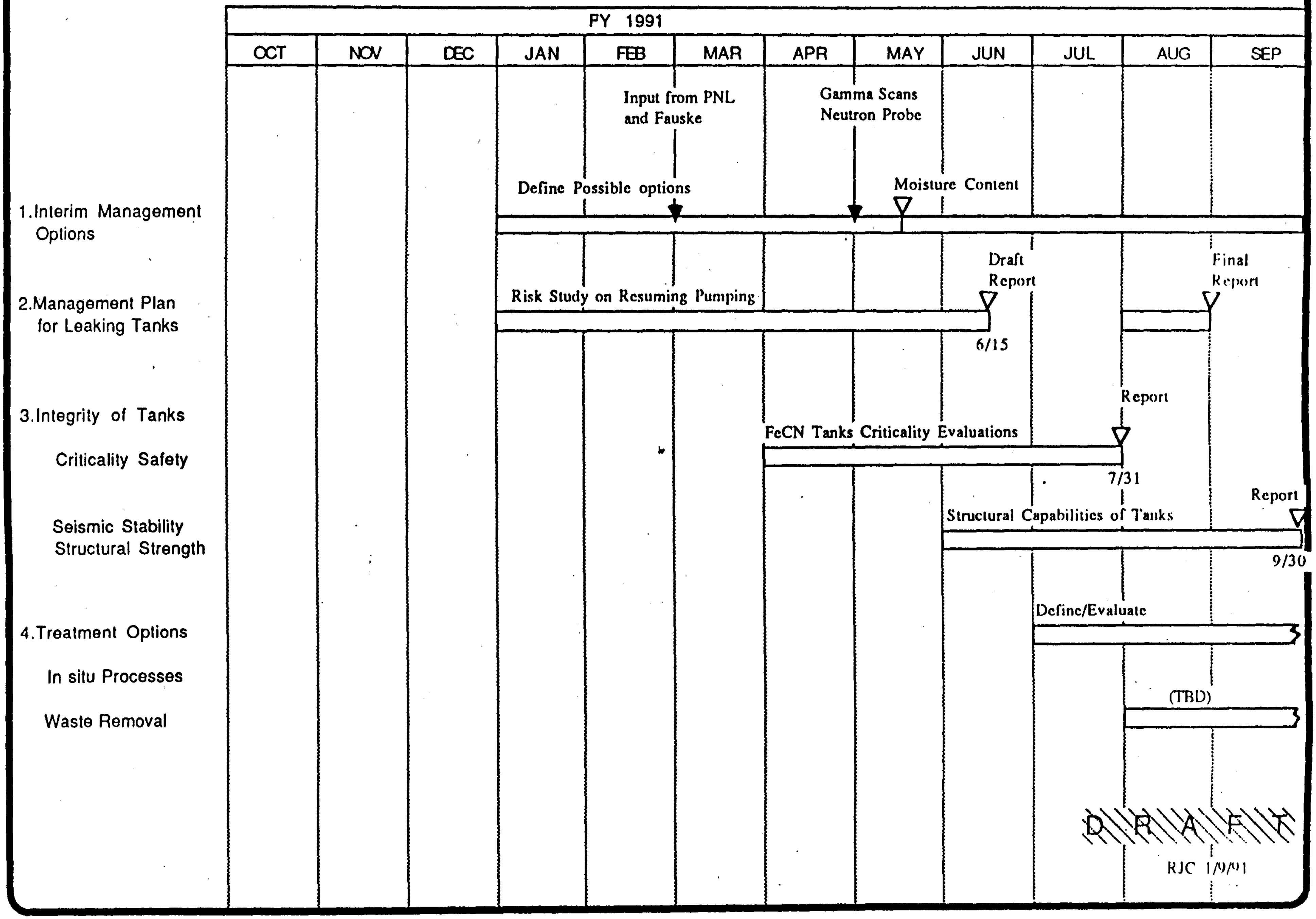
RJC 12/5/90

4.7 FERROCYANIDE TANK INTERIM MANAGEMENT



DRAFT

RJC 1/9/91

ENCLOSURE 5

91:633

PROGRAM PLAN FOR EVALUATION AND REMEDIATION OF THE GENERATION AND RELEASE OF FLAMMABLE GASES IN HANFORD WASTE TANKS

INTRODUCTION

In June 1990, a Safety Improvement Plan for Hydrogen in Waste Tanks was issued and it was revised in September 1990 (Safety Improvement Plan Hydrogen in Waste Tanks, WHC-EP-0377, Rev. 1). This plan provided a program that addressed the problem with respect to three main areas: Safety Analysis, Chemistry and Tank Characterization, and Engineered Remedies. Although there are 23 tanks on the Watch List, the major efforts are being directed to waste tank 241-SY-101. There is a near term focus to provide upgrades to the tank for improved monitoring and safety of operations. In particular, dome-space gas monitors are being prepared for the detection of various gases at different elevations with the tank dome space. Also, an engineering study is being performed for methods to increase the ventilation capacity of the tank.

The program plan for the resolution of the safety problem with the flammable gases is utilizing the resources and talents of not only the Hanford contractors, but also those of other DOE sites, universities, and private companies. Some aspects of this program are still being developed, so additional information will be coming for some of the activities.

A brief summary of the scope for the major program activities will be provided in this plan. Future updates will include detailed plans and schedules for each task.

1.0 PROGRAM MANAGEMENT

All activities will be coordinated through the program manager. This activity will provide for the planning, scheduling, and financial tracking of the program. It will also provide the focal point for the integration of the activities of this program with those of the facility operations and other site programs (TPA, ERRA, etc). Numerous reviews by DOE, SEAC, safety, as well as readiness reviews will be coordinated through this function.

2.0 TANK UPGRADES

A major effort is being conducted for upgrading the instrumentation and the ventilation system for 101-SY.

2.1 Gas Monitoring System

A gas monitoring system is being developed for the characterization of the 241-SY-101 tank vapor space. It will perform two primary functions on gas sample streams from three locations within the tank vapor space and a fourth location in the exhaust header. These functions are:

- Real time monitoring of hydrogen
- Real time characterization of gas constituents

Each vapor space location consists of a sample probe assembly installed in a four inch tank riser. Each assembly will have three individual probes of different lengths; one probe near the top of the vapor space, one near the crust and one in between. Only one probe on each assembly will be in use at a time; it will be remotely selected. The sample locations within the tank will help to characterize the gases during an event as well as during normal operations.

The gas monitor system includes H_2 specific monitors, gas spectrum analyzers, grab sample stations, data acquisition systems, and all supporting instrumentation and hardware.

The percentage of H_2 in each gas sample will be monitored continuously, with an operating range of 0 to 100% H_2 by volume, a resolution of 0.2% H_2 by volume and a repeatability of 0.1%. The maximum response time between when the gas enters the end of a sample probe until the instrumentation shows its H_2 concentration will be 120 seconds. There will be an adjustable alarm with a set point between of 0.1% and 4.0%.

The gas spectrum analyzer will have a resolution of 2 to 100 AMU (atomic mass units), scanning speed variable from 10 ms to 10 seconds per AMU, with a minimum detectable partial pressure of 5×10^{-12} torr. It is assumed that gases will be detectable to 200 ppm. The stability will be ±0.1 AMU for mass and ±2% peak height after a 30 minute warmup. The data interface to the data logger will be RS-232.

The grab sample station will consist of four 75 cc sampling cylinders connected in series in a sample line.

The differential pressure between the tank/ventilation header and atmosphere will be measured and logged for each of the four sample systems. The range of the differential pressure transmitters will be -5" to +20" water gauge. The header location is also instrumented to measure temperature, humidity and gas flow rate as described in Section 2.3.

Information from all of the instrumentation will be captured digitally on a data logger system. Data can be removed from the logger and taken elsewhere for off-line analysis. The data logger and mass spectrometers will be housed in an instrument trailer which will be located close to the tank.

Design requirements have been established and the design has progressed to approximately the 70% stage as of December 20, 1990. Installation procedures and safety documentation are being prepared for the installation of the in-tank equipment.

2.2 Tank Ventilation

A study is being conducted to evaluate various means for upgrading the tank ventilation system. The current system was designed to provide for radiological control and tank cooling only. The study is investigating ventilation flow rates achievable with the current hardware, with minor modifications, and with a new design. Operating conditions for purging and inerting this tank are also being reviewed. It appears that tank core sampling would not realize significant risk reduction with enhanced ventilation, purging or inerting, while there would be a quantifiable risk reduction for ongoing tank operations with an upgraded ventilation system to dilute the flammable gases during a release event.

A waste tank ventilation system upgrade plan has been prepared and internally reviewed and approved at WHC. A modular design concept has been proposed and design criteria are being developed. An analytical flow model is being utilized to develop the required system flow rate as a function of average hydrogen concentration limits during a release event. Two governing factors being analyzed are the maximum expected hydrogen release volumes based on past experience and the maximum hydrogen burn value tolerable for a worst case ignition. These analyses will result in a flow rate design value to proceed with design upon system concept approval.

2.3 Tank Process Instrumentation and Other Measurements

Upgrades are being made to the instrumentation used to monitor the operation of tank 241-SY-101. These upgrades include the replacement and addition of instruments to the tank.

- Instrumentation upgrades for the 241-SY-101 waste tank exhaust header include temperature, pressure, flow and humidity.

  The exhaust gas temperature is normally in the range of 90 to 130°F. The temperature monitoring will cover the range of 32 to 200°F to insure data capture during the tank venting process.

  The velocity measurement system, located in the 12 inch schedule 40 steel exhaust duct, will monitor flow in the range from 509 to 5093 ft./min. (i.e., this equates to a normal flow range of 400 to 4000 CFM for gases in a 12 inch pipe when combined temperature and pressure data). This flow range extends below the normal exhaust duct flow of nominally 828 ft./min. (650 CFM) and above the highest postulated flow to date, which ranged between 2546 and 3820 ft./min. (2000 and 3000 CFM). The range of the current flow monitoring system will also be widened to encompass the required flow range.

  The pressure measurement is used to calculate the actual exhaust duct volumetric flow as well as provide valuable data concerning the venting process. The pressure instruments will provide for monitoring in the range from -5 to +20 inches H_2O. This range extends below the normal tank pressure of nominally -2 inches H_2O and above the highest evaluated pressure, to date.

The humidity measurement is used to determine the heat carrying capacity and the relative flammability of the exhaust duct gases. It is also used to determine the evaporation rate of the tank contents. The humidity monitor will provide temperature compensated relative humidity measurements in the range of 10 to 90%.

- A new instrument tree is being designed for installation in 101-SY; it will accommodate a variety of measurement sensors. The objective of this activity is to design an instrument tree based on sensor technology which can be implemented in the near term. The instrument tree will consist of a group of tubes fitted to a riser adapter flange. Both open and closed-end tubes will be included to accommodate the measurements of temperature (thermocouples) below the top of the tank residuals, gas sampling in the vapor space and vapor space gas pressure. A second phase will design an instrument tree with enhanced measurement capabilities. The instrument tree will be connected to the data acquisition system of the gas monitoring system.

- Testing is being done to determine the feasibility of alternative methods of measuring the surface level of the waste crust. The currently installed equipment requires physical contact with the crust and also requires that the contacted crust be electrically conductive. A new surface measuring device which operates on radar technology has been procured and is being tested. Test completion and recommendations for implementation is planned for March 1991.

- Gamma scans are being conducted in five separate tank risers in the annulus of tank 101-SY using existing equipment routinely used to determine the interstitial liquid level in other tanks. Three scans have been taken as of December 20, 1990 and a schedule for periodic repeats has been established. Gamma spectroscopy at 17 vertical points in two riser locations in the annulus is also planned using a Cadmium-Telluride detector in the actual tank environment.

- The periodic hydrogen venting in tank 101-SY can be correlated with variations in surface level. It is likely that audible noise will be produced during (and possibly before) these crust level changes. Three audio range microphones will be inserted into the annulus space (a temporary change to the operating procedure). The initial objective is to determine if useful acoustic information can be detected; results will be recorded on a strip chart recorder. The first application is for late January 1991.

- The accuracy and integrity of the thermocouples presently installed in tanks 101-SY, 102-SY, and 103-SY are to be evaluated. The procedure will use electronic instruments to measure the loop resistance of various thermocouple configurations of installed and new comparison thermocouples and will record the data on the appropriate data sheets provided. In addition, the tests measure the output of installed and new comparison thermocouples using an electronic thermometer and a record the temperature readings on appropriate data sheets.

3.0 WASTE SAMPLING

The reference method for obtaining samples from the waste tanks is by drilling a core from top to bottom of the tank contents. The basic operation of this approach was discussed in the Safety Improvement Plan and in the tank 101-SY Core Drilling Safety Evaluation Report (WHC-SD-WM-TI-431). Recent tests with the drill rig on simulated hard waste forms using the drill in its normal rotational mode, led to unacceptable temperatures in the drill bit. Efforts are underway to redesign the drill bit to eliminate this problem, and also to utilize the drill in a simple "push mode" for soft material. Meanwhile, other efforts have been initiated to retrieve samples from the tank.

3.1 Retrieval of Samples from Tank Instruments

In an attempt to gain insight on the chemical nature of the crust, an effort was initiated to retrieve the FIC probe, the manual tape probe, and the sludge weight from 101-SY. Photos from the tank indicate that crust material is adhering to these devices. A readiness review for the retrieval of the items has been completed and an analytical plan has been prepared. Expected results from these analyses will be: an estimation of the potential for secondary reactions in the crust, a better approximation of the crust analogues for drilling tests and for synthetic studies, preliminary information on crust surface radionuclide source terms, initial guidance on crust solubility, and input for design and use of a grab sampler and penetrometer.

3.2 Crust Surface Sampler

A design effort is underway to provide a simple, intrinsically safe, method for obtaining a sample of the crust. It is intended that this approach could be used to sample the tank at various locations. This would provide sufficient material to permit a definitive answer to the issue of potential secondary reactions in the crust. It is anticipated that this method will be available for use in the first half of 1991.

3.3 Other Methods

In addition to the methods described in 3.1 and 3.2, evaluations are being conducted to determine the feasibility of other means to obtain samples from the tank. One method under consideration, is to pull samples from the inside or outside of the lances that are in the tank. There are many obstacles to this method, but they are being studied. One device that will provide information on the properties of the crust is a penetrometer. This tool is being modified for use in the tank. Data from this instrument will be of benefit to the work on the drill bit and to those analyses that require an estimate of the crust strength.

4.0 WASTE SAMPLE ANALYSIS

Analyses to be performed on all waste samples retrieved from the tank have been described in the Analytical Chemistry Plan (WHC-SD-WM-TP-090, Rev. 0). In addition, this document provided the priority for the analyses, in the event that insufficient material is obtained from any of the layers in the tank. There have been some minor revisions to the priorities, and they have been transmitted to DOE. In order to provide the requisite data for safety analyses, modeling, and remedial studies, a number of tests need to be developed. They are discussed below.

4.1 Development of Physical Property Tests

The following tests are being developed for use in the Hanford hot cell facilities: adiabatic calorimetry, surface tension, thermal expansion, crust strength, porosity, thermal conductivity, and explosivity. All other required physical property tests are in place and were described in the Analytical Chemistry Plan.

4.2 Development of Methods of Analysis of Organics

The Tank Waste Science Panel has provided the recommendation that one of the key items towards the understanding of the mechanism for hydrogen generation is the analysis of the various organics that are present in the waste. These organics include the chelators (EDTA and HEDTA), glycolic acid and various solvents. The organics have undergone reactions to form a variety of decomposition products. In order to provide for the analysis of the various organics, a number of techniques are being developed. They include functional group analysis by GC/FTIR, total chelation, chelator analysis by derivatization-GC/MS, chelator analysis by LC/MS, chelator analysis by capillary electrophoresis-electrospray, chelator and organometallics by LC/ICP/MS, chelator analysis by HPLC-UV, and chelators by HPLC. Although not part of the organic methods development, efforts are underway to provide methods for peroxide analysis.

5.0 DEVELOPMENT OF ADDITIONAL APPROACHES IN CHARACTERIZING HYDROGEN TANKS

The primary means for characterization of tank waste is through analyses of samples obtained from the core drilling rig. As indicated in Section 3.0, additional work is required to get the drill system ready for use in tank 101-SY. Additional technologies are being examined for application to tank 101-SY and other Watch List tanks so that information can be obtained on the chemical and physical nature of the waste.

A wide variety of technologies exist for the physical and chemical characterization of materials. A number of meetings at Hanford have been conducted to determine which methods warrant investigation. The methods were categorized as: evaluation of the physical condition of the tank and the contents, physical properties of the waste forms, and chemical information for the waste. Methods being examined include:

- The physics of acoustically detecting bubbles in liquids is well understood and has been considered by both PNL and by LANL. Additionally, there is the possibility to use acoustics to stimulate the release of small bubbles as they form. Ultrasound can access the tank volume from the annulus area, minimizing the risks associated with the vapor space. The issues of bubble detection, characterization, and remediation are the subject of a PNL phase 2 proposal (re: PNL's technical study above), a proposal from LANL (result of the DOEHQ directed technology team meeting - SNL, LLNL, LASL), and an emerging team effort which includes WHC, PNL and LANL.

- Infrared thermographic scanning of the surface of the waste tank's contents is being investigated to verify the analytical model. Activities supporting procurement of a commercial system have been initiated.

- The feasibility of using an acoustic temperature probe, torsional waveguide viscosity probe, and eddy current interface detection probe are being evaluated on a low priority basis.

- Fiber Optic (FO) instrumentation, specifically FO chemical sensors, are of some interest for 101-SY due to their being intrinsically safe. A task team has been evaluating the maturity of the technology and surveying the available resources and methods. National Labs (LLNL, LASL, SNL, and PNL) are being consulted. A private consultant has been contacted in the area of FO sensors in hostile environments. Several not for profit organizations and federal agencies have been contacted relative to their capabilities. The Westinghouse Science and Technology Center, has also been engaged to provide assistance in this area.

- Support is being obtained from Westinghouse Science and Technology Center. A specific scope of work, addressing near term needs, was mutually agreed to between W-STC and WHC during a two day work shop at Hanford. An IWR is being placed for approximately $90K over a few months. This IWR will get the joint effort initiated while a three-year $3,000,000 IWR shell is prepared and approved.

- Support is being obtained from the U.S. Bureau of Mines in Pittsburgh. Discussions have been held relative to explosivity classification and testing, intrinsic safety, instrumented drill string instrumentation, and fiber optic gas sensors. A scope of work was prepared which includes key U.S. Bureau of Mines resources to Hanford for several days of technical assistance.

The various methods listed here is not meant to be complete, but illustrates the methods being considered.

6.0 TANK MODELING

The reduction and eventual mitigation of the flammable gas accumulation and release requires an understanding of the mechanisms involved in each step of the process.

6.1 Thermo-Physical Model

It is necessary to understand the physical mechanisms occurring in the slurry and sludge that result in the release of large volumes of gas. The model must incorporate all physical parameters (heat capacity, conductivity, density, latent heat, viscosity, etc.) and processes (bubble formation, gas accumulation, density instabilities, interaction with suspended solids, etc.) together with the tank physical parameters (size, materials, etc). A thermal -physical code with multi-phase and multi-dimensional features will be employed in this effort. Bench scale studies in the laboratory may be needed to test the model. Input to the modeling effort will come from the analyses of the waste and from laboratory studies of synthetic waste. It will also be necessary to develop an understanding of the role of the crust in the whole process. Postulated roles for the crust range from no effect on the release of gases to that of acting as a valve to control the rate of gas release.

6.2 Gas Flow Model

A modeling effort has been initiated to describe the transport and distribution of the vented gases. This thermal-hydraulic modeling of tank 101-SY gas space and its associated vent system is being performed with a finite-difference code for solving the mass and energy equations. It features a flexible noding scheme that allows it to be run in a lumped parameter mode or in a one, two, or three-dimensional mode. Both lumped parameter and three-dimensional analyses are planned, as described below. An initial model has been developed using the lumped parameter modeling option (i.e., each waste tank is modeled as a single, perfectly mixed volume). Tanks 102-SY and 103-SY are included in the model since they connect to the same vent system as tank 101-SY. This model is being utilized to estimate the total volume and injection rate of gas required to produce the observed pressure pulse in the tank. The analysis also provides a calculated hydrogen concentration as a function of time in the tank as well as points downstream in the vent system (based on the perfectly mixed tank assumption). This model is being used as an integral part of the ventilation system studies (2.2). Good agreement has been obtained between the last three gas releases and the model. Sensitivity studies are now being conducted.

7.0 TANK INTEGRITY ASSESSMENTS

This work will evaluate the structural integrity of both the double- and single-shell tanks, including those that contain potentially hazardous hydrogen buildup. Tanks on the Watch List will be given priority in specific evaluations. State-of-the-art analytical methods will be used. Specific activities planned or underway include:

- Input into formal Watch List criteria relative to structural "fitness" criteria (e.g., define what critical structural information must be monitored and what the critical limits are to assure continued safe storage).
- Tank 101-SY (double-shell tank) hydrogen explosion analysis.
- Evaluate impacts of waste hydrogen explosion on two types of single-shell tanks (500,000 gal. and 1,000,000 gal. capacity tanks).
- Provide a structural accident assessment for all SSTs and DSTs on the Watch List.
- Prepare preliminary seismic assessment to respond to questions raised by the DNFSB.
- Evaluate all tanks, on a tank-by-tank basis, considering thermal cycling, material aging effects, corrosion, etc.
- Determine and implement program for monitoring tank structural properties, such as concrete strength, liner corrosion rates, etc.

8.0 SAFETY ANALYSES

This activity will provide for the preparation of safety analyses for all planned actions for tank 101-SY. These analyses will build on, where possible, the existing approved safety documents. The safety analyses for the core drilling will be updated, reflecting in the knowledge gained from the sampling and laboratory activities. Similarly, as additional data are obtained, an update of the analysis on the response of the tank to a postulated hydrogen burn will be conducted. Tests will be conducted to establish explosivity limits and burn rates for various mixtures of H_2, H_2O, and air.

All safety analyses will be reviewed by the independent groups discussed in Section 3.2 of the Safety Improvement Plan (WHC-EP-0377, Rev. 1).

9.0 SYNTHETIC WASTE STUDIES

An initial approach for conducting tests on synthetic wastes was given in the Safety Improvement Plan. Since the Plan was issued, the Tank Waste Science

Panel has provided some recommendations on an expanded program. Detailed task statements have been prepared for review by the various participating organizations. A summary of the program will be given below.

The synthetic waste studies provide a key element in the approach for understanding the mechanisms for gas generation and accumulation. In addition, these studies will provide valuable information for safety analyses and the studies being conducted for remedial actions.

9.1 Development of Methods for Producing Synthetic Wastes

The synthetic waste compositions tested will be based on an understanding of the wastes added to these tanks as well as the results from the chemical analyses of actual waste from tanks (101-SY, 103-SY, 103-AN, 107-AN). Based on these analyses and on the process operations, recipes and methods for producing simulated waste will be developed. To determine a reference waste composition, Hanford-site personnel responsible for mechanical analyses and preparation of synthetic wastes representative of slurry growth tanks will be contacted to obtain copies of pertinent reports and recipes. The recipes will be updated as information is obtained from tank sampling.

9.2 Crust Formation and Behavior

In tank 101-SY, crust formation and behavior may play an important part in the mechanism for retention and release of the generated hydrogen (H_2) and nitrous oxide (N_2O). Uncertainties in the composition of the crust have caused unreconcilable safety issues for obtaining a sample of the crust and of the underlying liquid waste. These safety issues center mainly on the possibility that the crust could contain reactive mixtures of organics and oxidants such as nitrate. Knowledge about the composition, physical properties, physical behavior, and reactivity of the crust is important in making decisions with respect to sampling and potential remediation and disposal operations. Using various synthetic wastes, the formation of the crust and selected physical and chemical properties will be determined.

9.3 Gas Generation

A lack of knowledge about the mechanism by which gases are generated in tank 101-SY has weakened the basis upon which the safety analyses are placed. Therefore, understanding the mechanisms by which gases are generated in tank 101-SY will lead to stronger safety analyses that will be needed to core sample and remediate tank 101-SY. The needed chemistry will include the mechanisms for the generation H_2 and N_2O.

Experiments will be conducted in which the gas production rate and composition will be determined as a function of organic functional groups and geometry, radiation and catalysts. Measurement of the production rate and composition as the organic is varied will provide insight of the role of the possible functional groups in the reaction mechanism(s). A key part of these tests is to employ isotopic labeling to help identify the source of the hydrogen, nitrogen, nitrous oxide, carbon dioxide, etc. One approach that can help focus this work is to explore the use of a statistically designed screening study to identify the factors that influence the gas producing reactions.

9.4 Chemical Reactions

The focus of this activity is to determine the stoichiometry, mechanism(s) and kinetics of the gas producing reaction(s). Tasks include:

- The stoichiometry of the reaction(s) will be determined by using simple systems of critical reactants; e.g., $NaNO_2$ and HEDTA. The goal will be to identify and determine the amount of gaseous, solid, and soluble organic and inorganic products produced per mole of reactant(s).

- Laboratory tests will be conducted to measure the rate of gas evolution as a function of the concentration of reactants and as a function of the temperature of the solution. Kinetic rate expressions will be developed from the results of these tests. Tests will be conducted to identify the composition of the gas and how the composition varies with time, and kinetic expressions will be developed for each gaseous species.

- Laboratory experiments will be conducted to attempt to identify the mechanistic origin of CO_2, H_2, N_2O, and NH_3. The work should involve the use of labeled compounds (^{15}N, ^{13}C, ^{2}H) as a means to isolate the source of C, N, and H for the formation of the various gases. A key portion of this work is to evaluate the role of HEDTA in the formation of the gases.

- It is important to determine if the generation of gas is affected by the formation of intermediate species. Tests will be conducted to provide data on the complexation with NO_3, NO_2, or the various complexing carboxylate anions. Isotopic labeling coupled with Nuclear Magnetic Resonance will aid in the identification of key intermediates.

9.5 Effects of Radiation

The wastes in 101-SY are highly alkaline and have been in the double shell tanks for approximately 15 years (and thus exposed to a radiation field). In that environment, many reactions can occur which will change the chemical nature of the constituents in the waste. It is, therefore, important to determine the effect of long-term exposure of the wastes to radiation. Tasks included in this activity are:

- Conducting a literature survey and documenting the rates of gas generation produced by radiolysis of water or organics. Results of work conducted on aqueous solutions of $NaNO_3$, $NaNO_2$, NaOH, Na_2CO_3, $NaAlO_2$, and a variety of organic molecules will be summarized for their relevance to the wastes in tank 241-SY-101. Results of the literature survey will be used to calculate overall yields for radiolysis products based on known rate parameters for potential reaction.

- Bulk irradiation tests will be conducted on solutions of synthetic waste to measure gas generation rates and products. Tests will be conducted to identify whether the hydrogen is a primary product and/or the result of secondary reactions. Data from these experiments will provide G values (molecules/100 eV) for specific reactions. The experiments will require tests on a variety of solutions as well as control tests conducted without radiation. These experiments should also determine which reactions are strongly dependent on temperature.
- Tests will be conducted to establish rate parameters for specific reactions. Pulse radiolysis tests can be conducted with the use of an accelerator facility. A principal objective of this task is to determine the rate of generation of primary radicals, identify subsequent reaction pathways, and to assess the viability of radical scavengers as a means to suppress hydrogen generation from radiolysis.

9.6 Synthesis of Results

A working group of the participants for items 9.1-9.5 will hold regular meetings to review the status of work and to ensure a close interaction of each organization. Status reports will be issued on these tasks and will provide up-to-date answers on the issues of gas generation.

10.0 EVALUATION OF WASTE TANK WATCH LIST

Twenty-three tanks (5 double shell, 18 single shell) were declared to be a Unreviewed Safety Question (USQ) because of their potential for generating hydrogen which, in turn, may lead to a potential release of waste due to uncontrolled increases in tank temperature or pressure. These tanks were also given interim Operational Safety Requirements.

The objective of this activity is to develop and implement a technical evaluation process whereby the tanks on the hydrogen generation Watch List (other than 101-SY) can be dispositioned. The evaluation process will identify those tanks that can be assigned to a lower category to remove operating restrictions on a near-term basis. For the remaining tanks on the Watch List, recommendations will be made for long-term surveillance expected to result in removal from the Watch List.

A task team will be formed to evaluate historical data from Watch List tanks and to recommend acquisition of new data, the associated measurement requirements and acceptance levels for category changes. This team will be comprised of representatives from Stabilization and Retrieval Engineering, Characterization and Waste Prevention, Safety Analysis and Regulation, Waste Tank Safety, Operations and Remediation, and Pacific Northwest Laboratory. This team will develop the technical justification for any changes in tank category.

One of the first activities will be to collect and review existing documents relating to the development of the Watch List and tank ranking evaluations. Historical data judged to be relevant to hydrogen generation and release will be collected and documented in a single report.

Next, the reason or cause for a given tank to be on the Watch List will be reviewed. Also, current tank data will be reviewed to determine if the original reason is still valid. If the original reason for including the tank on the Watch List is no longer valid, a report will be prepared documenting the information and recommending a change in category for the tank. If the results of the data reviews indicate that a tank should at least temporarily stay on the Watch List, then the engineering evaluation will include a recommendation as to what additional information/surveillance data collection is appropriate. After data are collected, another evaluation will be conducted. If justified, a recommendation for a category change will be made and documented as above. If a category change is not justified, long-term surveillance will be recommended and/or remedial action will be developed under other programs.

11.0 TANK DATA BASE

The entire Waste Tank Safety Program requires real time access to quality controlled, traceable data. These data include operational information (temperatures, liquid levels, etc.), waste inventory data (based on both historical records and laboratory analyses), and historical information, such as structural and construction information, operating records, safety evaluations, engineering evaluations, nonconformance reports, engineering change notices, laboratory studies, and all company correspondence related to tanks, etc.

In order to respond to the widely varying requests for information from different internal and external groups, a tank history organization has been established, in the Waste Management Technology organization, to network the existing computerized data bases and to compile the critical historical information into a centralized spot. This group will assure that adequate quality control is maintained over the data. This group is funded through W1W5, to assure that all critical tank safety data, including that related to flammable gas generation, are adequately controlled and accessible. A centralized "library" of information has been established in the 2750E Building of the 200 East Area to serve as a collection and resource center of information for individuals analyzing the tanks to use. This organization will also become the centralized group to respond to requests for existing information on tanks.

12.0 REMEDIAL ACTIONS

The Safety Improvement Plan discussed both near term and long term remedies. The basic approach has not changed, only the schedule for implementation. Implementation of any remedial action must await the results of tank sampling activities and of some of the laboratory tests. It is necessary to ensure that any remedial actions do not create a safety problem or enhance the generation, accumulation, and release of gases. In order to provide the best approach, studies of potential remedial actions are continuing.

Remedial actions being considered are:

- Dilution of tank contents
- Circulation of tank contents
    - Mechanical
    - Ultrasonic
- Transfer of tank contents
- Chemical treatment of tank contents

These studies will evaluate the safety issues associated with the treatment of high level wastes.

13.0 NEPA REQUIREMENTS

This task will recommend and prepare the appropriate documentation to comply with the National Environmental Policy Act (NEPA) and any other applicable environmental requirements for the county, state, and government.

14.0 QUALITY ASSURANCE

This section is being prepared.

ENCLOSURE 6

(10-89)

nited States Government **Department of Energy**

91:633

memorandum

ES - ________

ate. FEB 15 1991 **SECRETARIAL ACTION REQUESTED BY:**

rig Office: EM-35 (J. Tseng, 353-7170)

ransmittal: ACTION: Sample Collection from Hanford Tank 101-SY

o: The Secretary

hrough: Under Secretary J. C. Tuck

ssue: Authorization to collect crust samples from and install sampling/monitoring probes in Tank 101-SY.

iscussion: Potential flammable gas combustion and the potential for nitrate and organic reactions in the crust of Tank 101-SY have been identified as an unreviewed safety question.

Tank 101-SY vented most recently on October 24, 1990. Following the venting, three level detectors were retrieved from Tank 241-SY-101 and analyses were performed on waste materials encrusted on the detectors. Even though these limited samples may not provide representative information about the composition of the crust, they provided preliminary indications that: (1) there might be considerable moisture in the crust just beneath the surface that would act to significantly retard secondary reaction; (2) total organic content of the crust might be too low to support secondary reactions; and (3) synthetic crust materials are reasonably representative of the crust that was sampled. Based on these preliminary indications and the laboratory studies performed with synthetic waste, it appears that the possibility of a secondary crust reaction is low. This is a subjective conclusion, and the tank contents require much more sampling to support a quantitative risk assessment.

The next venting of Tank 101-SY could occur at any time. My staff proposes to collect crust samples through five tank risers, possibly using two different sampling devices, and install sampling/monitoring probes to obtain additional information following the venting concerning the crust characteristics and dome space conditions in Tank 101-SY. The Westinghouse Hanford Company (WHC) has determined that there is a 20-day window after the next venting for collecting crust samples and a 30-day window for work in the dome space.

The additional crust samples will increase the statistical confidence in the crust composition, thus providing a better understanding of the likelihood for crust reactions. Dome space sampling/monitoring will provide data for modeling studies and to evaluate the effectiveness of the ventilation system. The proposed activities are less intrusive than core sampling and will provide data to assist in preparing for future core sampling of Tank 101-SY. Core sampling will ultimately be necessary for DOE to understand the chemistry and physics of the hydrogen accumulation phenomenon. Questions regarding crust burn and ventilation, however, preclude obtaining a core sample by drilling through the crust. We plan to conduct core sampling in the May timeframe using data from the February sample.

EM approved a Safety Assessment and an Environmental Assessment (EA) and submitted them to the Offices of Nuclear Safety (NS) and Environment, Safety and Health (EH) for concurrence.

NS and EH both believe that the planned actions can be conducted safely, but the Safety Assessment will need to be revised. The EA and Finding of No Significant Impact (FONSI) have been approved by EH. The State of Washington concurred on this EA.

My staff is working also with the Richland Operations Office to ensure that procedures are adequate and available, and that operators are trained and ready to employ these procedures. Both DOE and WHC are conducting operational readiness reviews as part of the approval process before conducting these planned sampling activities.

EM conducted a review of Hanford laboratory readiness to perform the needed analyses. I believe Hanford laboratories are ready to analyze planned crust samples. Improvements will be required prior to readiness to analyze core samples planned to be collected in the May timeframe. This review was observed by NS staff.

Recommendation: That you authorize the proposed sample collection activities for Hanford Tank 101-SY, subject to satisfactory completion of Operational Readiness Reviews by both WHC and DOE, and final approval of the Safety Assessment by EH and NS. The Assistant Secretary for Environment, Safety and Health and the Director of Nuclear Safety concur in these planned efforts.

Leo P. Duffy
Director
Office of Environmental Restoration
and Waste Management

[✓ Approved:] ____________
Disapproved: ____________
Date: 2/15/91

Concurrence: EH Ziemer 2/[illegible]/91 NS Blush 2/[illegible]/91
Attached

United States Government Department of Energy

Memorandum

[illegible]

EM-35 (J. Tseng, FTS 233-7170)

SUBJECT: Sampling of Tank 101-SY

TO: Manager, Richland Operations Office

The attached Action Memorandum authorizes collection of crust samples from and installation of sampling/monitoring probes in the dome space of Tank 101-SY. Approval to proceed with these activities is subject to (1) revision to the Safety Assessment for EH and NS approval, (2) isolation of the ventilation system for Tank 101-SY from the other two tanks in the SY tank farm, and (3) satisfactory completion of the operational readiness reviews being conducted by the Department of Energy and by Westinghouse Hanford Company (WHC).

As discussed with your staff, sample collection needs to be conducted with high assurance of ventilation flow in Tank 101-SY. To that end, the emergency diesel generator should be operating and ready to support the back-up exhauster, if needed.

The most significant hazard associated with these sample collection efforts is the radiation exposure to the workers. Please ensure that necessary precautions are taken to keep radiation exposures to as low as reasonably achievable level and to minimize potential for spread of contamination.

Upgrading of Tank 101-SY instrumentation and data recording systems should continue as rapidly as possible. For example, given the trouble we have had with the level detection and the fact that the crust level is a primary indicator of upcoming venting, I would like you to expedite procurement and installation of a radar level detector for better crust level detection during this window. My staff will work with your staff to determine the necessary safety and environmental documentation required to support these activities.

Please continue to keep John Tseng of my staff informed of the status of activities associated with Tank 101-SY sample collections.

Leo P. Duffy
Director
Office of Environmental Restoration
and Waste Management

Attachment

cc w/attachment:
P. Ziemer, EH-1
S. Blush, NS-1
J. Ahearne, AC-21
J. Conway, DNFSB