



The Secretary of Energy
Washington, DC 20585
June 17, 1996

The Honorable John T. Conway
Chairman
Defense Nuclear Facilities Safety Board
625 Indiana Avenue, NW
Suite 700
Washington, DC 20004

Dear Mr. Chairman:

We have enclosed for your review a revised Implementation Plan for Recommendation 93-5. This revised Plan renews the Department of Energy's commitment to understanding and assessing risks, associated with the storage and **remediation** of Hanford tank wastes.

The Department's original Implementation Plan presented an approach that was strongly centered on sampling the tank waste. While sampling information is important to the resolution of tank safety, the experience gained to date indicates that other information is also required. Since Recommendation 93-5 is concerned with the resolution of safety issues, both near- and long-term, it is appropriate that the Implementation Plan be revised to cover the broader scope of characterization activities that the Department believes is necessary to resolve the issues. In revising the Implementation Plan, we have included a **milestone** for completing work, and documenting the results, needed to resolve the ferrocyanide safety issue covered by Recommendation 90-7. With the inclusion of this commitment in the revised Implementation Plan, the Department has transferred any open commitment under Recommendation 90-7, and I propose the closure of Recommendation 90-7 upon the Board's acceptance of this revised Plan.

Sampling and analysis remains an important component of our revised Plan, and we intend to sample all of the tanks, if necessary. Recent work performed by the Los Alamos National Laboratory and the Pacific Northwest National Laboratory is providing **new** insights and offers the promise of providing a more coherent picture of the situation **and** the actions necessary to resolve the outstanding safety issues. As this work matures, we anticipate that there will be

an opportunity to revise the Implementation Plan **further**. In the interim, as we complete the acquisition of **essential** data, we will remain vigilant regarding the known and latent risks associated with the tank farms.

As the Department **of Energy** implements this revised Plan, we look forward to the involvement of your staff **as a means of** keeping you **informed** of our progress.

Sincerely,

A handwritten signature in black ink, reading "Hazel R. O'Leary". The signature is written in a cursive style with a long, sweeping underline.

Hazel R. O'Leary

Enclosure

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EXECUTIVE SUMMARY

On July 19, 1993, the Defense Nuclear Facilities Safety Board transmitted Recommendation 93-5 on the Hanford Waste Tank Characterization Studies to the Department of Energy. The recommendation was accepted on September 9, 1993. Recommendation 93-5 noted that there was insufficient tank waste technical information to ensure that Hanford Site wastes could be safely stored, that associated operations could be conducted safely, and that future disposal data requirements could be met. As a result the Board recommended that the characterization effort be upgraded and expedited. The original Implementation Plan was accepted by the Board in March 1994. This Implementation Plan revision presents a modified approach to achieve the original Implementation Plan objectives. The approach concentrates on actions necessary to ensure that wastes can be safely stored, that operations can be safely conducted, and that timely characterization information for the tank waste Disposal Program can be obtained.

Since Recommendation 93-5 was issued, significant progress has been achieved in understanding tank safety-related phenomena, resolving tank safety issues, and enhancing the capability and efficiency of tank characterization. Reviewing this progress led to the realization that tank safety issues could not be resolved solely by accelerating sampling and analysis to improve the characterization of tank contents. The key to expediting resolution was to better understand safety-related phenomena that cause the safety issues.

A revised characterization and safety strategy evolved. The characterization and safety strategy presented in this Implementation Plan revision builds on the improved understanding and significant progress made to date. The revision is multifaceted and consists of the key elements listed below.

- Maintain tanks in an interim configuration using safety controls and, where necessary, mitigative actions.
- Upgrade and complete the Authorization Basis for the Tank Farms. This includes producing a Basis for Interim Operation, Final Safety Analysis Report, Technical Safety Requirements, Compliance Implementation Plan, and Safety Evaluation Report.
- Complete the ongoing programs to resolve the ferrocyanide, organic complexants, organic solvents, flammable gas, high heat, and criticality safety issues.
- Analyze core samples from key tanks (referred to as the High Priority Tanks) to understand phenomena and resolve issues associated with groups of tanks. These tanks were selected by integrating the information needs of the Safety and Disposal Programs. Appendix F provides a summary of the High Priority Tanks identified and the basis for information requested.
 - Sampling the High Priority Tanks will satisfy the highest priority core sampling.
 - Sampling and analysis of the High Priority Tanks is intended to provide scientific and technical data to confirm assumptions, calibrate models, and measure safety-related phenomenological characteristics of the waste. The most important of these are verification of ferrocyanide decomposition, refinement of gas retention and gas release models, verification of organic complexant decomposition and solubility, and verification of simulant studies on propagation. Verification of propagation phenomena by testing real waste should confirm the conclusions drawn from simulant studies (Fauske 1996). This sampling activity will also

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establish confidence intervals in historical data and meet initial Disposal Program needs.

- Continue to safety screen tanks using the Safety Screening Data Quality Objective. Sample all 177 tanks unless characterization by other methods can be technically justified.
- Qualify the Rotary Mode Core Sampling System for use in flammable gas atmospheres.
- Sample the headspace of all passively ventilated Single-Shell Tanks using combustible gas meters to determine steady-state flammable gas concentrations. This activity satisfies the highest priority safety information need.
- Sample the headspace of all tanks and screen for the presence of organic solvents.

When the sampling and analysis program associated with the High Priority Tanks (this list includes 22 of the 54 Watch List tanks) is completed, the safety issues may be resolved to the point that the subsequent characterization requirements can be significantly restructured.

The Characterization Project is working three shifts per day, five days per week, and some overtime on weekends to accelerate sampling. It is with this same sense of urgency that this strategy seeks to expedite the understanding of safety-related phenomena based on sampling the High Priority Tanks and on completing key safety assessments. This Implementation Plan will be reviewed at least annually and progress reports will be provided quarterly.

This 93-5 Implementation Plan revision meets the Department of Energy's understanding of the Board's fundamental concern that the Department of Energy provide sufficient and timely information to ensure that wastes can be safely stored and associated operations are conducted safely, and that future Disposal Program data requirements can be met. Completion of the milestones in this plan will close out the Department of Energy's actions associated with the Recommendation 93-5 .

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1 BACKGROUND

1.1 ACCEPTANCE OF THE ORIGINAL RECOMMENDATION

On July 19, 1993, the Defense Nuclear Facilities Safety Board (DNFSB or Board) transmitted Recommendation 93-5 (Conway 1993) on the Hanford Waste Tank Characterization Studies to the Department of Energy (DOE). The recommendation was accepted on September 9, 1993 (O'Leary 1993). The Recommendation 93-5 noted that insufficient tank waste technical information was available to ensure that Hanford Site wastes could be safely stored, that associated operations could be conducted safely, and that future Disposal Program data requirements could be met. As a result the Board recommended that the characterization effort be upgraded and expedited. The original Implementation Plan (DOE-RL 1994) was accepted by the Board in March 1994 (Conway 1994).

The original Implementation Plan committed to developing a technical basis for characterization (Technical Basis) and improving the sampling equipment. This was to be done in parallel with sampling and analyzing all Watch List tanks by October 1995 and the remaining tanks by October 1996. The Technical Basis was to define the programmatic information requirements and actions necessary to characterize the Hanford Site High-Level Waste (HLW) tanks. Data Quality Objectives (DQOs) that define the programmatic needs have been issued for all programs. The *Tank Waste Characterization Basis* (Brown et al. 1995) integrated programmatic DQO requirements into a prioritized tank sampling list. Sampling and analysis of all Watch List tanks was not completed by October 1995; sampling and analysis of the remaining tanks cannot be achieved by October 1996. Completing the Watch List tank commitment was prevented by fabrication difficulties and poor reliability associated with the Rotary Mode Core Sampling Systems.

1.2 RECOMMENDATION 93-5 ISSUES

Recommendation 93-5 identified two general safety issues:

- Insufficient tank waste technical information exists and the pace of acquiring additional information is too slow to ensure that wastes can be safely stored and that operations can be conducted safely, and
- Insufficient tank waste technical information exists and the pace of acquiring additional information is too slow to ensure that future Disposal Program data requirements can be met.

In Recommendation 93-5 the Board noted that safety analyses and confirmatory characterization must be expedited to understand tank safety issues. Section 5.1 of this document provides a discussion of the Board's recommendation and the Department's understanding of the Board's guidance regarding safety issues.

1.3 TANK SAFETY ISSUES WHEN RECOMMENDATION 93-5 WAS ISSUED

At the time Recommendation 93-5 was issued, significant gaps existed in the Safety Basis for the Hanford Site Tank Farms. Safety issues had been identified related to inadequate safety analyses and high levels of uncertainty regarding the risks to workers, the public, and the environment. Potential radioactive and toxic chemical releases due to propagating exothermic

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chemical reactions, criticalities, or high heat induced tank structural failures had not been adequately evaluated.

Several issues required attention.

- Tank SY-101 was episodically releasing large volumes of flammable gas and a deflagration risk existed.
- Many safety analyses were outdated or did not exist and the Authorization Basis was inadequate.
- Unreviewed Safety Questions (USQs) existed for criticality, ferrocyanide, flammable gas, and the organic solvent layer in tank C-103.
- Conditions necessary for propagating exothermic condensed-phase reactions were not understood.
- Effects of radiation and alkalinity on chemical reactivity had not been determined.
- Data generated by sampling was inconsistent.
- Sampling techniques and analytical methods were inadequate.

When Recommendation 93-5 was issued, controls were only placed on tanks suspected to involve safety issues. However, the existing characterization information was not adequate to identify tanks with safety issues.

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2 UNDERLYING CAUSES

The situation with the Hanford Site HLW storage tanks was characterized by numerous safety questions and significant uncertainty regarding the content of the tanks and associated phenomena. There has been significant difficulty in developing an understanding of the root cause of the tank safety issues and in developing and implementing practices to obtain tank waste samples and data. There are several underlying causes. The following is a short discussion of these causes.

2.1 HISTORICAL PERSPECTIVE

The initial Hanford Works were built under the duress of war on a crash schedule. Two processing plants (T-Plant and B-Plant) were built on a common schedule. Both were designed to use the same process. T-Plant initiated operations in the fall of 1944 and produced plutonium in late 1944. The fuel cycle planning at that time was that waste from the processes would be discharged into the tanks for long-term storage. A mind set evolved that disposing of the HLW in the tanks was safe and acceptable. Except for maintaining certain operational tank parameters to prevent release of radioactive materials, there was no comprehensive plan to understand the nature and composition of the tank waste.

The initial process (Bismuth Phosphate [BiPO₄]) to dissolve reactor fuel and recover plutonium was inefficient. It allowed valuable plutonium to be discharged in the waste; it did not recover a significant quantity of uranium in the process stream; and it produced large volumes of waste that presented a storage space problem. These factors drove the development of alternative processing methods. The BiPO₄ process was replaced by the Reduction/Oxidation process (REDOX) which was subsequently replaced by the Plutonium/Uranium Extraction process (PUREX). Each of these processes had different chemistries and waste products.

In the 1950s, uranium was not readily available and there was a need to recover it from the waste. The tanks became, in a sense, mineral resources, and the contents were mined and processed to recover the uranium. A uranium extraction process was placed in service; the associated waste streams and some new process chemicals were transferred to the tanks. Subsequently, ferrocyanide was added to the tanks to precipitate cesium (Cs) and calcium nitrate was added to precipitate strontium (Sr).

The decay heat from the Sr and Cs in the waste caused another waste storage problem. The waste was processed to recover the Sr and Cs. Unintentional discharges of strontium-containing material to tank C-106 resulted in the High Heat Safety Issue.

There have been five different major processing operations and a variety of minor processes that produced the waste in the tanks. These processes have resulted in a collage of tank materials in a variety of combinations and configurations. This material was regarded as waste and there was little perceived need to understand the details of the combinations and configurations. Until recently, around 1985, there was little consideration given to Single-Shell Tank (SST) waste recovery and processing to support disposal. In 1991, a commitment was made to remove all the waste from the tanks for processing and disposal. The commitment was made 45 years after the first transfer of the waste to the tanks, 19 years after 95% of the waste was transferred, and four years after material processing operations ceased. Thus, the need to understand the details of the tank waste composition and configuration was not realized until long after the waste transfers were initiated.

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2.2 CURRENT SITUATION

The tank wastes consist of approximately 240,000 metric tons and are distributed in 177 tanks. There is an incomplete picture of the status of the waste in the tanks. Process flowsheets and records of process chemicals purchased are indicators of the mass and chemical nature of materials that have been deposited in the tanks. Additional information is available in the records of material transfers in the separation processes. This information provides a general understanding of the masses and composition of materials transferred, and the sequences in which they were transferred to and deposited in the tanks. However, it is clear that these records are incomplete. There are analytical measurements that indicate the presence of materials in the tanks that did not come from known processing chemicals. The historical record, by itself, is not sufficiently accurate to authoritatively establish a basis for safety decisions. It does provide a reasonable framework to guide the sampling program and clarify the interpretation of results.

The diversity in the stored waste, coupled with an incomplete record of tank waste operations and transfers, creates a complex challenge for waste characterization. Access risers into the tanks are limited, which further restricts available sampling options. Historical sampling information is limited because the constituents of concern for continued safe storage and ultimate retrieval and disposal of the wastes differ from those collected for past waste management operation controls. The chemical and physical heterogeneity of the waste add further complexity to the problem. The relative fraction of material sampled from a tank (compared to the overall tank content) is quite small. This fraction may not be sufficient to authoritatively resolve each safety issue.

Recommendation 90-3 (Conway 1990a) was written to request that the resolution of the ferrocyanide issue be accelerated. This recommendation included a statement that tank sampling should be accelerated to provide information for this resolution. Recommendation 90-7 (Conway 1990b) was written to express a sense of urgency toward resolution of the ferrocyanide issue, and again recommended that the program of tank sampling should be accelerated. Recommendation 93-5 stated that progress in understanding the content of the Hanford Site HLW Tanks was too slow. The Board assigned one of its highest priorities to the assurance of tank safety.

The original Recommendation 93-5 Implementation Plan committed to developing a Technical Basis and improving the sampling equipment. This was to be done in parallel with sampling and analyzing all Watch List tanks by October 1995 and the remaining tanks by October 1996. However, the *Tank Waste Characterization Basis* (Brown et al. 1995) was not developed until mid-1995. Watch List tank sampling and analysis was not completed on schedule and the remaining tanks cannot be sampled by October 1996. Fabrication of the Rotary Mode Core Sampling Systems was more difficult than expected. The fabrication time was extended by design modifications to correct field performance deficiencies. In addition, difficulties in using the Rotary Mode Core Sampling Systems delayed achieving the sampling rate per crew committed to in the Implementation Plan.

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3 BASELINE PLANNING ASSUMPTIONS

This section presents the key assumptions that are the foundation for planning actions necessary to resolve those safety issues that lead to Recommendation 93-5.

- 3.1 Some safety issues can be resolved on a global basis; however, others may have to be resolved on a tank-by-tank basis. Safety issues that must be handled on a tank-by-tank basis may require controls and/or mitigative actions to maintain safety until the waste is removed from the tank.
- 3.2 Experimental and analytical work necessary to understand the phenomena associated with conditions that can potentially lead to disruptive events will be completed.
- 3.3 Experiments with real wastes will be conducted to confirm the understanding of information gained from experiments using simulants .
- 3.4 The strategy for identifying tank sampling priorities is based on various DQOs for the Safety and Disposal Programs; this reflects the priorities of the Safety Program and the Watch List Tanks. The strategy is detailed in the *Tank Waste Characterization Basis* (Brown et al. 1995) and involves confirming safety analysis and modeling assumptions, establishing confidence in the historical models, and obtaining waste materials for disposal process development tests.
- 3.5 DOE plans to sample and analyze wastes from all 177 tanks unless characterization of the tank waste content important to resolving safety issues and disposal process development requirements can be met by other methods.
- 3.6 Vapor sampling can identify tanks containing organic solvents and thus can be used to identify any tanks that may have to be modified to provide an adequate vent path to improve safety margins.
- 3.7 Schedules for acquiring waste samples, completing chemical analyses, and other measurements are to be based on rates achieved during the last quarter of Fiscal Year (FY) 1995 and first quarter of FY 1996. Continued improvement in the efficiency of obtaining samples is expected.
- 3.8 The source terms for the Hazards Analyses for the Basis for Interim Operation (BIO) and Final Safety Analysis Report (FSAR) will be confirmed using results from sampling and analysis completed over the past year (FY 1995). Reactor operating data and a combination of historical tank contents estimates and currently available sample data will be used to validate the source terms. Using this approach, no additional sampling is required to determine bounding source terms for waste storage. However, sampling and analytical results will continue to be evaluated; any unexpected results will be addressed using the USQ process.
- 3.9 Schedules for approving safety assessments and subsequent incorporation into the Interim Safety Basis (ISB) are based on delegation of ISB approval authority to Department of Energy, Richland Operations Office (DOE-RL).

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4 SUMMARY OF COMPLETED AND NEAR-TERM ACTIONS

Appendix E references letters documenting action completion.

4.1 SUMMARY OF IMPLEMENTATION PLAN PROGRESS

The following table summarizes the status of the primary elements and sub-elements made in Recommendation 93-5 (Conway 1993). The text of the Recommendation is repeated in full in Section 5.1.

Table 1: Status of Recommendation 93-5

No.	Recommendation by Primary Elements and Sub-Elements	Status
1.	Undertake a comprehensive reexamination and restructuring of the characterization effort with the objectives of accelerating sampling schedules, strengthening technical management of the effort, and completing safety-related sampling and analysis of watch list tanks within a target period of two years, and the remainder of the tanks by a year later;	Open
1.a	In accordance with the above, give priority in the schedule of tanks to be sampled to the watch list tanks and others with identified safety problems, and priority to the chemical analyses providing information important to ensuring safety in the near term during the period of custodial management. Other analyses, required by statutes such as the Resource Conservation and Recovery Act prior to final disposition of the waste, should not be cause for delay of safety-related analyses. In most cases, analyses needed for long-term disposition may be postponed until more pressing safety-related analyses are completed.	Open
1.b	Reexamine protocols for gaining access to the tanks for sampling with the objective of simplifying documentation and approval requirements.	Complete
1.c	Increase the laboratory capacity and activities dedicated to tank sample analysis: <ul style="list-style-type: none"> (i) Expedite efforts to obtain and begin utilizing additional sampling and analytical equipment now being procured, and the training of personnel needed for an enlarged through-put capacity. (ii) Explore availability and utility of laboratory services on- and off-site, such as Hanford's Fuel Materials and Examination Facility and the INEL and LANL laboratories, for accelerating the waste characterization effort. 	Complete
2.	Integrate the characterization effort into the systems engineering effort for the Tank Waste Remediation System:	Open
2.a	Schedule tank sampling consistent with engineering and planning for removal, pre-treatment, and vitrification of the tank wastes.	Open
2.b	Critically examine the list of chemical analyses done on samples to establish the smallest set needed to satisfy safety requirements.	Complete

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Table 1: Status of Recommendation 93-5

No.	Recommendation by Primary Elements and Sub-Elements	Status
2.c	Strengthen the management and conduct of the sampling operations.	Complete

Appendix E documents those completed actions credited to each Recommendation 93-5 primary element and sub-element. Where the sub-element is noted to be closed, completion of the commitments listed in Appendix E is considered adequate to close that primary element. Where the primary element or sub-element is noted to be open, the completed commitments listed in Appendix E and the Milestones in Appendix D of this document are considered to be adequate to close Recommendation 93-5.

4.2 NEAR-TERM MILESTONES

The following is a summary of near-term milestones to be completed over the next six months.

- Complete a Comprehensive Source Terms Report by June 1996.
- Complete a report documenting analyses to determine if additional tanks have potential to exceed 25% of the Lower Flammability Limit (LFL) by June 1996.
- Complete lightning evaluations and if the probability exceeds 1×10^{-6} per year, evaluate potential mitigating options for lightning strikes by August 1996.
- Complete evaluation of gas monitoring instrumentation upgrade needs for additional tanks with the potential to exceed 25% of the LFL by August 1996.
- Approve the safety assessment for rotary mode core sampling in flammable gas tanks and document incorporation into the Authorization Basis by September 1996.
- Qualify Rotary Mode Core Sampling System for use in Flammable Gas Tanks by September 1996.
- Complete comparison between truck and cart vapor sampling systems by September 1996.
- Approve the safety assessment for saltwell pumping in flammable gas tanks and document incorporation into the Authorization Basis by October 1996.
- Complete tank C-106 supernatant and sludge sampling and analysis by October 1996.
- Complete the safety assessment covering pool and entrained organic solvent fires by October 1996.
- Complete the organic speciation of core samples for BY-108 and BY-110, and auger samples for C-102 by October 1996.

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5 SAFETY ISSUE RESOLUTION

5.1 RECOMMENDATION

Section 5.1.1 repeats the recommendation of the Board and Section 5.1.2 is a statement of the DOE's understanding of the recommendation's fundamental concern.

5.1.1 Recommendation 93-5

The entire text of Recommendation 93-5 (Conway 1993) follows:

"Hanford Waste Tanks Characterization Studies

Dated: July 19, 1993.

Since its beginning almost four years ago, the Board has assigned one of its highest priorities to assurance of safety at the high level nuclear waste storage tanks at the Hanford Site. The Board addressed two of its sets of recommendations (90-3 and 90-7) to potential hazards associated with tanks containing ferrocyanide compounds and pointed to the need for action in connection with tank 101-SY, which periodically vents flammable mixtures of nitrous oxide and hydrogen gas. In Recommendation 90-7, the Board emphasized the urgent need for more rapid and complete sampling and analysis of tank wastes. The wastes in the Hanford tanks differ markedly from tank to tank. Identification of what specifically is in each tank is essential and urgent. Without timely characterization of the wastes, the nature of the risks associated with the tanks cannot be fully assessed and, where necessary, mitigated. Further, until the characteristics of the wastes are known, final methods for tank waste monitoring, retrieval, transport, and treatment cannot be realistically established.

The Board has repeatedly expressed its dismay at the continued slow rate of conduct of this characterization program and has urged a greater rate of progress. At last count only 22 of the 177 tanks on the site have been sampled. Only four of those sampled were among the 54 tanks on the watch list of tanks that generate the greatest safety concerns. The number of samples per tank continues to be insufficient to provide adequate characterization of the full tank. While the published schedules for sampling and analysis promise improvement, they seem optimistic when viewed against the record to date. They appear to present wishes rather than anticipated activities.

Two sets of problems appear to be principal contributors to the slow pace of characterization of the contents of the tanks. The first is a complex of factors acting to impede access to the interiors of the tanks and extraction of samples of their contents. The second is the exhaustive set of measurements made on each sample, along with limitations on laboratory capability for completing these measurements. The Board notes that measurements made for safety purposes do not necessarily receive priority over those done for other reasons, such as satisfaction of formal EPA-related requirements for final waste disposition.

The Board believes that accelerating the pace of the program of characterizing the contents of Hanford's high level nuclear waste tanks is important to nuclear safety at this important defense site. This view is shared by other experts, including DOE's own "Red Team", which reviewed the waste characterization program for the Hanford Tank Farm (DOE-EM, July 1992, Independent Technical Review of Hanford Tank Farm Operations). Characterization is essential for ensuring

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safety in the near term during custodial management and remedial activities, and also in the long term for advancing the development of permanent solutions to the HLW problems at Hanford.

In addition to the matter of acceleration and reprioritization of the sampling schedules, the Board is also concerned about the sampling effort itself. The Board notes that a recently released DOE/RL audit (DOE-RL/OPA Audit 93-02, April 1993) of the sampling programs revealed significant weaknesses in the control, management, and technical implementation of core sampling, laboratory, and supporting activities.

Because the failure to vigorously pursue tank waste characterization raises important health and safety issues, DOE needs to take action to accelerate and strengthen the management of the characterization effort to ensure adequate protection of public health and safety.

Therefore, the Board recommends that DOE:

1. Undertake a comprehensive reexamination and restructuring of the characterization effort with the objectives of accelerating sampling schedules, strengthening technical management of the effort, and completing safety-related sampling and analysis of watch list tanks within a target period of two years, and the remainder of the tanks by a year later;
 - a. In accordance with the above, give priority in the schedule of tanks to be sampled to the watch list tanks and others with identified safety problems, and priority to the chemical analyses providing information important to ensuring safety in the near term during the period of custodial management. Other analyses, required by statutes such as the Resource Conservation and Recovery Act prior to final disposition of the waste, should not be cause for delay of safety-related analyses. In most cases, analyses needed for long-term disposition may be postponed until more pressing safety-related analyses are completed.
 - b. Reexamine protocols for gaining access to the tanks for sampling with the objective of simplifying documentation and approval requirements.
 - c. Increase the laboratory capacity and activities dedicated to tank sample analysis:
 - (i) Expedite efforts to obtain and begin utilizing additional sampling and analytical equipment now being procured, and the training of personnel needed for an enlarged through-put capacity.
 - (ii) Explore availability and utility of laboratory services on- and off-site, such as Hanford's Fuel Materials and Examination Facility and the INEL and LANL laboratories, for accelerating the waste characterization effort.
2. Integrate the characterization effort into the systems engineering effort for the Tank Waste Remediation System:
 - a. Schedule tank sampling consistent with engineering and planning for removal, pre-treatment, and vitrification of the tank wastes.
 - b. Critically examine the list of chemical analyses done on samples to establish the smallest set needed to satisfy safety requirements.
 - c. Strengthen the management and conduct of the sampling operations.”

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5.1.2 DOE Analysis of Recommendation 93-5

Two general safety issues were identified in Recommendation 93-5:

- Insufficient tank waste technical information exists and the pace of acquiring additional information is too slow to ensure that wastes can be safely stored and that operations can be conducted safely, and
- Insufficient tank waste technical information exists and the pace of acquiring additional information is too slow to ensure that future Disposal Program data requirements can be met.

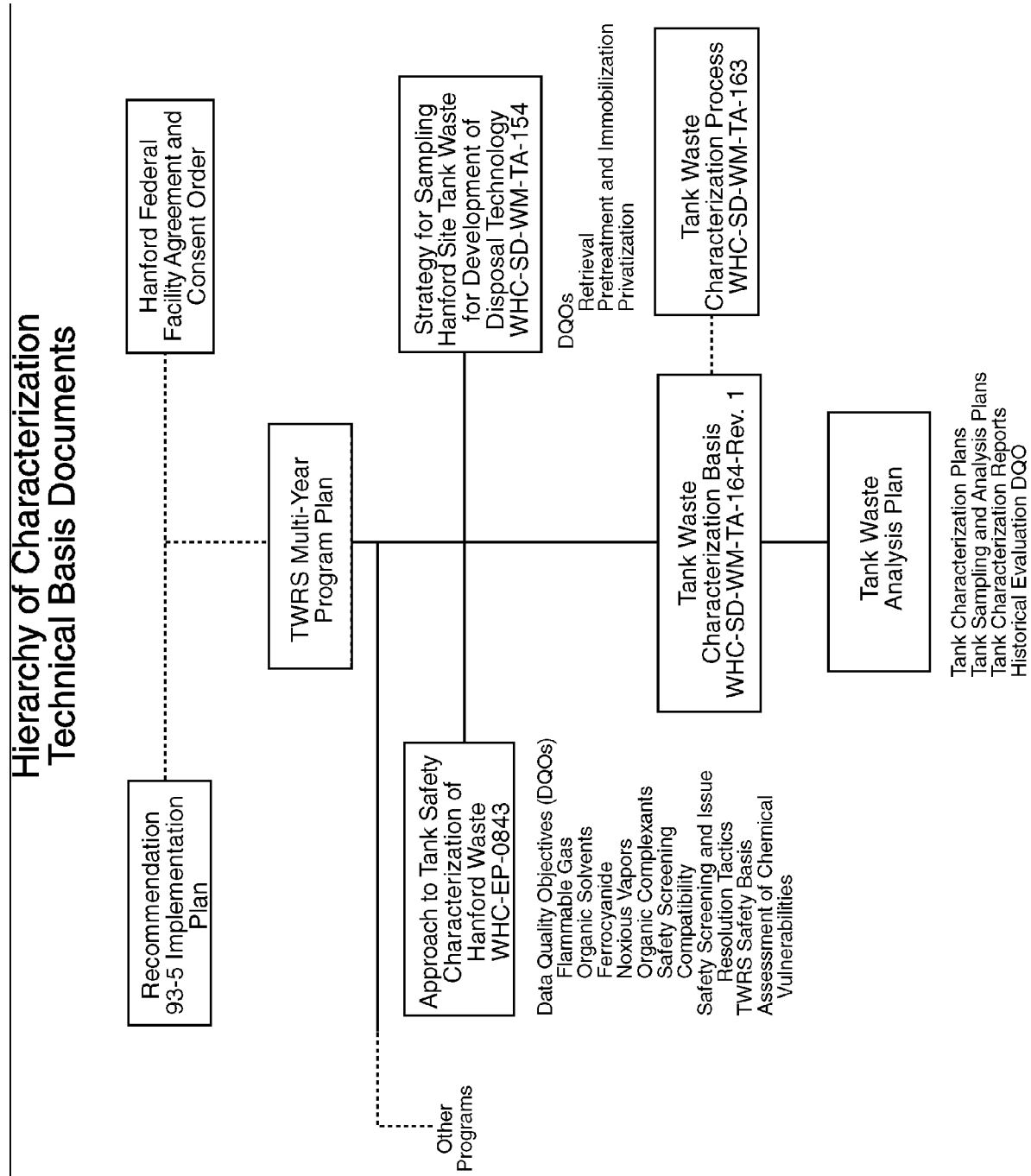
Recommendation 93-5 presented two primary elements and six sub-elements that would improve the safety status of the tanks and supporting infrastructure. The status of each element and sub-element of the recommendation is provided in Table 1, Status of Recommendation 93-5. The actions described in DOE's original Implementation Plan were intended to address and resolve the underlying safety issues through the implementation of the two primary elements and six sub-elements of the recommendation.

This Implementation Plan revision meets the intent of the overall recommendation by an alternate strategy to resolve the two general safety issues described above; however, this revision does not provide verbatim execution of each remaining element of Recommendation 93-5. This revised plan outlines a course of action that reflects the knowledge, understanding, and experience gained in the past three years in addressing the characterization of the waste, and resolves the Safety and Disposal programmatic issues that are the fundamental concern of the Board's recommendation. The approach to resolving the issues will be achieved through characterization of the tank waste contents, as well as characterization of the chemical and physical phenomena that are the underlying causes of the safety issues.

5.2 MAJOR ACCOMPLISHMENTS RELATED TO RECOMMENDATION 93-5

Execution of the original Implementation Plan has been mixed in terms of performance. Many tasks were far more difficult than initially perceived. Despite the inherent difficulties of operating experimental equipment in high radiation fields with significant contamination and conditions that could create gas release events, substantial progress has been achieved. These achievements have been related to tank safety, Disposal Program process development, and waste characterization. Since the issues are complex, not every attempt to find a solution has been successful or complete. Progress has been documented in numerous technical reports. Figure 1 provides a graphical representation of the hierarchy of these documents.

Figure 1: Hierarchy of Characterization Technical Basis Documents



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The following is a summary of the key achievements realized since Board Recommendation 93-5 was issued.

Tank Safety. The accomplishments listed below are related to understanding tank safety-related phenomena and resolving tank safety issues.

- The flammable gas condition in tank SY-101 was mitigated. Subsequent tests on real and simulated waste as well as analytical and empirical analyses have increased the understanding of phenomenological mechanisms of gas generation and retention.
- Three of the four USQs (ferrocyanide, criticality, and organic solvents in tank C-103) related to waste tank contents were closed. The remaining USQ involves flammable gases.
- Ferrocyanide waste decomposition of high-energy compounds into low-energy products (aging) was demonstrated in laboratory experiments and confirmed by waste sampling.
- A probabilistic safety assessment by Los Alamos National Laboratory (LANL) (MacFarlane et al. 1995) concluded that the health risks to co-located workers and the public from airborne and liquid pathway releases from the Hanford Site HLW Tanks are low.
- Studies have shown that spontaneous chemical runaway reactions due to self-heating are highly unlikely (Fauske 1996). The passive cooling rate exceeds both radionuclide decay and chemical heating rates in all SSTs, except for tank C-106. No credible mechanisms to increase tank temperatures to the thresholds for chemical runaway reactions were identified.
- Controls to protect workers and to prevent accidents leading to radioactive and chemical releases were placed on all tanks. These controls accommodate uncertainties and variations in tank waste conditions.
- An ISB document (Stahl 1993) was developed to provide an interim Authorization Basis for most Tank Farm activities.
- DQOs that identify the characterization information needs for the major tank safety issues were completed.

Waste Disposal. The accomplishments listed below are related to improving use of systems engineering and obtaining timely information to support Disposal Program needs.

- A Tank Waste Remediation System (TWRS) Systems Engineering Management Plan (Peck 1996), Baseline System Description (Johnson 1996), Mission Analysis (Knutson 1995), Functions and Requirements (WHC 1996), Risk Management List (Collard 1995), and Risk Management Plan (Seaver 1995) were issued.

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- A strategy for obtaining Disposal Program information requirements was developed (Kupfer et al. 1995) and the associated DQOs were issued.
- Disposal Program process development tests were performed on samples taken from approximately 22 different tanks that represent 50% of the sludge in SSTs. Tests show that the wastes can be treated with the planned processes.

Waste Characterization. The accomplishments listed below are related to enhancing the capability and efficiency of waste characterization.

- The management of the characterization program was strengthened. A Characterization Program Office was established in 1994 to centralize program planning, tracking, financial management, and reporting. In 1995, the Characterization Project was established to bring all the assets required to carry out tank characterization under one senior manager. This Project organization has effectively improved the efficiency of sampling and laboratory operations. To provide added emphasis to technical integration of the Characterization effort with other TWRS programmatic efforts, the Contractor has realigned the Technical Basis effort under the TWRS Vice President and Manager. The Project will continue to function as before; reaping the benefits of the Project concept, however, the Vice President's personal involvement will improve the technical integration of the Characterization effort within TWRS.
- The technical expertise of the Characterization Program was improved by using outside technical resources, including LANL, University of Washington, Oak Ridge National Laboratory (ORNL), Pacific Northwest National Laboratory (PNNL), ICF Kaiser Hanford Company, the Tank Characterization Advisory Panel, the Tank Sampling Advisory Panel, Management Systems Inc., Nuclear Utility Services, Sonalyst Corporation, and workshops for senior scientists in the relevant fields.
- Programmatic information requirements were defined using the DQO process and an integrated core sampling priority list was issued (*Tank Waste Characterization Basis* [Brown et al. 1995]).
- *Historical Tank Content Estimates* (Brevick et al. 1994a, 1994b, 1995a, 1995b) were completed and a *Tank Layering Model* (Agnew 1994a, 1994b) was developed.
- Tank access was simplified through acceptance of the ISB and approval of an environmental assessment for the TWRS Manage Tank Waste Function.
- Three Rotary Mode Core Sampling Systems were placed in service.
- Modifications were completed which improved rotary mode core sampling truck availability from 17% to more than 60%.
- Three new drilling crews were hired and all four drilling crews were trained and certified in accordance with DOE Order 5480.20A, *Personnel Selection, Qualification, and Training Requirements for DOE Nuclear Facilities* (DOE-HQ 1994a).

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- Push mode sample recovery was increased to more than 90%.
- An improved auger design that enhances near-surface sample recovery was placed in service.
- Three new instruments (viscometer, void fraction meter, and retained gas sampler) were developed to improve measurement of properties affecting gas retention in condensed-phase waste.
- X-ray units were added to the core sampling systems to provide real time determination of sample recovery.
- Analytical laboratory capacity was increased 42% and laboratory output was increased 400% since mid-1994.

5.3 OVERVIEW OF RECOMMENDATION RESOLUTION 93-5

This section provides an overview of the sampling plans, tank safety status, sampling rates, and revised strategy. Sections 5.4, 5.5, and 5.6 describe the approach to resolving Recommendation 93-5. The discussion in each section details current understanding of the status and activities necessary to accomplish milestones and resolve associated safety issues. Only those items detailed in Milestones sections are commitments to close Recommendation 93-5. The first Section, 5.4, Issue: Safe Storage of Tank Wastes and Safe Operation of Tank Farms, describes actions planned to obtain sufficient tank waste technical information to ensure that wastes can be safely stored and the waste operations can be conducted safely. The second Section, 5.5, Issue: Disposal Program Data Requirements, describes actions planned to obtain tank characterization information to meet future waste disposal process development requirements. The third Section, 5.6, Technical Basis for Characterization, describes how programmatic information needs have been integrated and prioritized. Sections 5.4 and 5.5 include information about the current status, resolution plans, uncertainties, characterization needs, and associated milestones.

5.3.1 Extent of Sampling and Analysis Program

The overall tank sampling strategy is multifaceted and involves a combination of condensed and vapor phase waste sampling to improve the understanding of phenomena associated with the wastes, to benchmark the phenomena in selected tanks, and to sample the remaining tanks.

Condensed-Phase Sampling. DOE plans to sample and analyze all 177 tanks to determine the tank waste content (composition, condition, and configuration) important to resolving safety issues and disposal process development requirements, unless it can be clearly shown that further sampling is not necessary. A combination of sampling, historical data, modeling, monitoring, and analyses will be used to characterize each tank. The information needs for each TWRS programmatic issue have been identified through the DQO process. Improved understanding of key phenomena associated with the wastes, coupled with recent tank data, and integration with programmatic needs, resulted in a

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revised characterization strategy to select the most beneficial tanks for core sampling. The resultant 28 tanks (called the High Priority Tanks) were selected by integrating the information needs of the Safety and Disposal Programs. Appendix F provides a summary of the High Priority Tanks identified and the basis for information requested. Additional information on the basis for the High Priority Tank selections is discussed in the *Tank Waste Characterization Basis* (Brown et al. 1995). Sampling and analysis of these tanks is intended to:

- Confirm assumptions and simulant testing results, calibrate models, and measure safety-related phenomenological characteristics of the waste
- Establish confidence intervals in historical data
- Meet initial Disposal Program information needs.

Following the sampling and analysis of these 28 tanks, DOE plans to continue to core sample the remaining tanks unless there is a definitive, technically justified basis that safety and other issues can be adequately addressed and resolved by other means. Analysis of samples from the 28 tanks are expected to provide the basis for subsequent sampling priorities. The tanks selected for sampling and analyses may change as DOE's understanding of the tank waste phenomenology improves. The plan to core sample all tanks is scheduled to be completed in 2002. This assumes that an average of three core samples are required from each tank, that the core sampling productivity rates remain the same as the current rates, and that no repeat sampling is required. Appendix I describes the derivation of the 2002 date in greater detail. If repeat sampling is required, all tanks should be completed in 2004.

Headspace Sampling. DOE plans to vapor sample tank headspaces to address five different topics, including: a) confirming steady-state flammable gas concentrations (all 133 passively ventilated SSTs), b) identifying tanks containing organic solvents (all tanks), c) confirming headspace homogeneity analyses (three SSTs), d) determining variations in headspace vapor concentrations in passively ventilated tanks with changing atmospheric temperatures (four SSTs), and e) satisfying the air permit requirements to operate the rotary mode core sampling exhauster (82 tanks to be rotary sampled). DOE is committed to accelerating completion of safety screening the headspaces of passively ventilated SSTs with combustible gas meters to determine steady-state flammable gas concentrations. This sampling will be completed by November 1996. DOE plans to continue vapor sampling to identify organic solvent tanks, but not on an accelerated schedule. Accelerating the vapor sampling would reduce the uncertainty with respect to the remaining tanks, but the overall consequence reduction of a disruptive event caused by organic solvents is not sufficient to justify the acceleration (Fritz 1996). The vapor sampling to identify organic solvent tanks is scheduled to be completed in December 2000. Vapor sampling to confirm headspace homogeneity and determine if headspace vapor concentrations of passively ventilated tanks vary significantly with changes in atmospheric temperature is scheduled to be completed in October 1997. Vapor sampling in support of the air permit for the rotary mode core sample exhauster will be completed on an as needed basis prior to exhauster operations. Appendix I describes the headspace sampling in greater detail.

5.3.2 Overview of Tank Safety Status

This section provides an overview of the key safety issues and associated controls necessary to confirm the safety of tank waste storage and operation. Tank safety can be assured based on a combination of credible safety analyses derived from an understanding of tank safety-related phenomena coupled with effective controls to ensure that the key assumptions in the safety analyses are valid.

A major effort was initiated in 1993 to develop a credible safety analysis for the Tank Farms. This effort included improving the near-term safety posture by combining the existing safety bases into an ISB document while working in parallel to develop an FSAR that meets the requirements of DOE Order 5480.23, *Nuclear Safety Analysis Reports* (DOE-HQ 1994c). The first step was to develop an ISB that defined a set of controls or limits to provide added assurance of safety in tank farm operations. The ISB was issued in mid-1993. At that time, several USQ's (ferrocyanide, C-103 organic layer, flammable gas, and criticality) existed with consequences that exceeded the risk acceptance criteria. By mid-1994, all of the USQs had been closed except flammable gas. A key shortcoming of the ISB was that controls were not applied to all tanks. They were selectively applied based on available characterization information. The validity of the available characterization information was questionable. This shortcoming was eliminated in late-1995 by placing controls on all tanks. Future sampling information should fine tune the controls, but is not expected to add more controls to ensure safe storage. Many of the controls will be required until the wastes are removed from the tanks. Another shortcoming of the ISB was that the adequacy of controls was not evaluated and that not all of the controls were implemented as Operations Safety Requirements (OSR). These shortcomings should be eliminated in late-1996 when the BIO is scheduled to be approved.

The major tank safety issues are associated with ferrocyanide, organic complexants, organic solvents, flammable gases, criticality, and high heat. The sections below briefly describe each issue and DOE's improving knowledge of conditions that affect safety. Detailed discussions of the approach and progress related to each safety issue are included in Section 5.4.

Ferrocyanide. Sufficient concentrations of ferrocyanide, in the presence of oxidizing material such as sodium nitrate, can react exothermically if heated to sufficiently high temperatures or subjected to a credible initiator of sufficient energy. Under certain conditions, reactions of this material can result in explosive energy releases. Analysis of twenty-six core samples from eight ferrocyanide tanks has demonstrated that ferrocyanide has decomposed to levels 10 to 40 times lower than concentrations required to sustain a propagating reaction. Additional analyses are in progress on samples from one tank. These analyses are expected to continue to confirm that the decomposition phenomenon is pervasive and consistent in all ferrocyanide tanks. Preliminary results indicate that there is no longer sufficient ferrocyanide in the tanks to cause a disruptive event. Once confirmed by the remaining analyses, the ferrocyanide issue will have been resolved. The associated controls could be removed and no additional sampling to resolve the ferrocyanide issue would be required.

Organic Complexants. Sufficient concentrations of organic compounds and their decomposition products have the potential to react exothermically when combined with

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nitrate/nitrite oxidizer. The key to assuring that organic complexants are safely stored is either to determine if there is sufficient material to support a propagating exothermic reaction, or to ensure that there are no credible initiators to raise tank waste temperatures to reaction thresholds. Analysis of the phenomena associated with propagating reactions indicate that a minimum energy content of approximately 1,200 Joules/gram (J/g) is required for the reaction to propagate. The Safety Screening DQO (Dukelow et al. 1995) has an energetics limit of 480 J/g. If this limit is exceeded, Total Organic Carbon (TOC) (3 weight percent [wt%] limit) and moisture (17 wt% limit) are measured. As of February 1996, waste samples from 102 tanks have been evaluated against the DQO criteria for energetics and moisture. Not all of these were full depth core samples; however, they do establish a trend. Only six percent (six tanks) exceeded both the energetics and the moisture DQO limits. None of the samples from these tanks reached energetics and moisture levels necessary to support a propagating reaction (greater than 1,200 J/g and associated moisture limit). Recent experimental work with simulants has indicated that the complexants are water soluble and therefore most are likely to be removed from the SSTs during interim stabilization. Seventy-six percent of the SSTs have been interim stabilized. Initiation of the reaction requires an ignition source of robust energy content. Potential igniters are limited to three known sources. These include lightning and the heat generated by gasoline fires or rotary mode core sampling upsets. Studies indicate the probability of lightning striking any Hanford Site HLW tank is on the order of 5×10^{-4} per year (MacFarlane 1994). Gasoline fires are prevented by controls on the sources. The Rotary Mode Core Sampling System contains a nitrogen purge to prevent the drill bit rotation from raising waste temperatures to organic complexant ignition thresholds.

Organic Solvents. Given a sufficient ignition source, there are two potential hazards associated with organic solvents: (1) an organic solvent pool fire; and (2) ignition of organic solvent that is entrained in waste solids (a wick fire). Organic solvents used in the nuclear material separation process are difficult to ignite. Sparks, impacts, shocks, and friction sources lack sufficient energy to ignite organic solvent pool fires. The credible ignition sources have been narrowed to robust and/or sustained energy sources such as lightning strikes or gasoline fires (resulting from vehicle gasoline tank ruptures). Controls have been implemented to prevent ignition of organic solvent fires. Therefore, wastes containing organic solvents can be stored safely using existing controls and lightning protection (if necessary).

Vapor sampling has proven to be an effective method for identifying organic solvent tanks. As of February 1996, 63 tanks have been vapor sampled for organic solvents. Although the data evaluation for these tanks is not complete, only 5% (three tanks) have been identified to contain a significant amount of organic solvent. It is not anticipated that the percentage of tanks identified will change significantly once the remaining tanks have been sampled. Once a tank is identified, the safety margins can be increased by verifying that the tank has an adequate vent path to minimize the pressure buildup in the tank if the solvent is ignited. An evaluation was completed to determine the benefit (in terms of reduced risk) of accelerating the schedule to identify organic solvent tanks (Fritz 1996). The conclusion of the evaluation was that cost increases to accelerate the vapor sampling schedule are not warranted based on the potential decrease in the incremental health effect to the public.

Flammable Gas. Radiolytic and chemical decomposition reactions occurring in tank waste produce flammable gases and oxidizers. Relatively low energy level ignition sources could

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lead to deflagration of these gases. The action limit for flammable gas is 25% of the LFL. Flammable gas releases to the tank headspaces are either episodic releases at relatively high rates or slow steady accumulations. To date, significant episodic releases have only been observed in tanks with supernatant. The supernatant has been removed from 114 SSTs by saltwell pumping. No significant gas release events have been observed in interim stabilized SSTs (based on surface level changes). After interim stabilization, SSTs still have sufficient interstitial liquid to generate and trap significant quantities of gas and small local releases are possible. However, unless the waste is disturbed by intrusive activities, it is unlikely to reach 25% of the LFL in the headspace. Steady-state combustible gas meter readings (to date) indicate no tanks with headspace concentrations approaching 25% of the LFL. While not all tanks have been sampled, the headspace is sampled for flammable gases every time work is conducted in a tank. Continuous hydrogen monitors were installed on all 25 Flammable Gas Watch List tanks in FY-1995. To date, only Double-Shell Tanks (DSTs) AW-101, AN-105, and SY-101 had measured episodic releases above 25% LFL, and only SY-101 exceeded the LFL. Nineteen of the monitored tanks are SSTs. To date, these SSTs have shown relatively constant gas concentrations that are significantly below 25% LFL.

As a precautionary measure, DOE placed controls on all tanks to minimize the potential to ignite flammable gases. Before tank intrusive activities, the tank headspace, risers, pits, and the vapor area of any other item associated with the activity that protrudes into the tank waste are sampled to verify that flammable gas concentrations are below 25% of the LFL. Before waste intrusive activities, tank level records are checked to ensure that the tank is not approaching an episodic gas release event. During waste intrusive activities, flammable gas concentrations are periodically monitored and activities are stopped before 25% of the LFL is exceeded. DOE is relying on administrative controls and where necessary, engineering changes or physical barriers to reduce the potential hazard or reduce the vulnerability to personnel errors. Tank SY-101 is an example of engineering changes. Periodic tank level and pressure changes led to the declaration of a USQ due to the potential for flammable gas deflagration. A mixer pump was designed and placed in service. The mixer pump operations cause periodic controlled small gas releases and thus have effectively prevented headspace flammable gas concentrations from exceeding 25% of the LFL. Removing the supernatant from the SSTs also appears to be an effective mitigation technique. However, the SY-101 mixer pump did not eliminate the need for controls. These controls are still required to conduct waste intrusive operations in the tank. These operations could reach a small rich pocket of flammable gas. This pocket may be too small to result in a headspace concern, but could have a local concentration in the waste that exceeds the LFL. The controls on waste intrusive activities are necessary to prevent ignition of the gases.

High Heat. This safety issue involves the need for periodic water additions to maintain temperatures in SSTs below concrete degradation limits and chemical reaction thresholds (e.g., thermal runaway reaction). Tank temperature measurements and thermal modeling were used to identify the ten SSTs with the highest heat loads. Only tank C-106 contains sufficient thermal energy to require periodic water additions to maintain tank temperatures below limits. None of the other SSTs require water additions to prevent tank temperatures exceeding limits. Administrative controls require periodic water additions to provide tank cooling and to ensure that tank temperatures remain well below these levels.

Criticality. The Criticality Safety Issue involves the lack of definitive knowledge of the tank waste fissile material and neutron absorber inventory and distribution. Several tanks contain sufficient fissile materials to support a criticality event, but other conditions, such as insufficient fissile material concentration and geometry, support the conclusion that criticality events are highly unlikely. A bounding safety assessment was used to support the conclusion that the tank wastes are substantially subcritical (Braun et al. 1994). This assessment was used for closure of the criticality USQ and provided resolution of the criticality safety issue for tank waste storage. When core samples are required for reasons other than criticality safety and if the screening limit for total alpha is exceeded, additional analyses are scheduled to improve the knowledge of fissile materials and primary neutron absorbers. These analyses should help improve the understanding of safety margins, but are not required to ensure safe storage.

Safety controls. The controls discussed in the previous sections are intended to maintain the integrity of assumptions used in the safety analyses and to prevent the initiation of disruptive events. Many of the existing controls are not OSRs. The BIO will upgrade the appropriate controls to OSRs. Personnel errors can compromise effectiveness of controls. These errors can be limited by disciplined operations with a combination of good procedures, meaningful training, clearly communicated management expectations, and periodic compliance inspections. Tank Farms has upgraded operating procedures and conducted thorough reviews to provide added assurance that the procedures implement all of the safety requirements. Personnel have been trained on the upgraded procedures. Rigorous qualification and certification programs were developed and implemented for all tank farms operators. Management expectations have been clearly communicated. Finally, a series of independent conduct of operations, maintenance, and engineering assessments have been completed to benchmark the Characterization Project status in each of these areas. After each assessment an improvement plan has been generated and implemented. Approximately every six months, the assessments are repeated to benchmark status and make adjustments for continuous improvement. In addition to the assessments, a comprehensive program of management field overviews and independent over checks have been implemented. These actions will not prevent personnel errors; however, they have been successful in substantially improving procedure compliance. Over the last six months, the conduct of operations index (a measure of personnel error caused occurrences) within Characterization Sampling Operations has decreased by 80%.

5.3.3 Revised Tank Characterization And Safety Strategy

Significant work has been completed concerning understanding the safety issues associated with the tank waste and the need for a disposal process development program.

Reviewing this progress led to the realization that tank safety issues could not be resolved solely by accelerating sampling and analyses to improve the characterization of tank contents. The key to expediting resolution was to better understand safety-related phenomena that are the basis for the safety issues. A revised characterization and safety strategy has evolved and is presented in this Implementation Plan. The revised safety-oriented strategy is multifaceted and consists of the key elements listed below.

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- **Maintain tanks in an interim configuration using safety controls and, where necessary, mitigative actions.**
- **Upgrade and complete the Authorization Basis for the Tank Farms. This includes producing a BIO, FSAR, Technical Safety Requirements (TSRs), Compliance Implementation Plan, and Safety Evaluation Report.**
- **Complete the ongoing programs to resolve the ferrocyanide, organic complexants, organic solvents, flammable gas, high heat, and criticality safety issues.**
- **Analyze core samples from the High Priority Tanks to understand phenomena and resolve issues associated with groups of tanks.**
 - **Sampling the High Priority Tanks will satisfy the highest priority core sampling.**
 - **Sampling and analysis of the High Priority Tanks is intended to provide scientific and technical data to confirm assumptions, calibrate models, and measure safety-related phenomenological characteristics of the waste. The most important of these are verification of ferrocyanide decomposition, refinement of gas retention and gas release models, verification of organic complexant decomposition and solubility, and verification of simulant studies on propagation. Verification of propagation phenomena by testing real waste should confirm the conclusions drawn from simulant studies (Fauske 1996). This sampling activity will also establish confidence intervals in historical data and meet initial Disposal Program needs.**
- **Continue to safety screen tanks using the Safety Screening DQO. Sample all 177 tanks unless characterization by other methods can be technically justified.**
- **Qualify the Rotary Mode Core Sampling System for use in flammable gas atmospheres.**
- **Sample the headspace of all passively ventilated SSTs using combustible gas meters to determine steady-state flammable gas concentrations. This activity satisfies the highest priority safety information need.**
- **Sample the headspace of all tanks and screen for the presence of organic solvents.**

When the sampling and analysis program associated with the High Priority Tanks (this list includes 22 of the 54 Watch List tanks) is completed, the safety issues may be resolved to the point that the subsequent characterization requirements can be significantly restructured.

The application of this strategy broadens the sense of urgency from characterizing the contents of all tanks to expediting the understanding of safety-related phenomena based on conducting experiments with waste samples for the High Priority Tanks and on completing key safety assessments.

5.3.4 Major Resolution Steps

Resolution of Recommendation 93-5 involves the major steps listed below.

- **Upgrade and complete the Authorization Basis for the TWRS Manage Tank Waste Function.**
- **Sample and analyze the High Priority Tanks. This includes, but is not limited to Watch List tanks. Technically justified substitute tanks may be used if tanks cannot be sampled due to equipment or physical constraints (Eberlein 1996).**
- **Adjust tank controls and sampling priorities as dictated by new information.**
- **Verify modeling assumptions and simulant-based testing using real waste.**
- **Adjust sampling to meet long-range Safety and Disposal Program needs.**
- **Sample and analyze all 177 tanks unless characterization by other methods can be technically justified.**
- **Vapor sample all tank headspaces for identification of tanks containing organic solvents.**
- **Screen passively ventilated SST headspaces with a combustible gas meter to determine steady-state flammable gas concentrations.**

Throughout the following three sections are discussions of the information needs and schedules for each program. These discussions review the status, issue resolution plans, and uncertainties. Milestones for all issues are summarized and a schedule is provided in Appendix D. A schedule for sampling the High Priority Tanks is provided in Appendix G.

5.4 ISSUE: SAFE STORAGE OF TANK WASTES AND SAFE OPERATION OF TANK FARMS

This section describes the approach for acquiring the information and understanding to resolve issues concerning safe storage of tank wastes and safe operation of Tank Farms.

5.4.1 Issue Description

Insufficient tank waste technical information exists and the pace of acquiring additional information is too slow to ensure that wastes can be safely stored and that operations can be conducted safely.

5.4.2 Resolution Approach

Since Recommendation 93-5 was issued, significant progress has been made in understanding tank safety-related phenomena and resolving safety issues. In addition, controls to protect workers and to prevent accidents leading to unacceptable releases were placed on all tanks. These controls accommodate uncertainties and variations in tank waste conditions. An ISB document has been developed to define the interim Authorization Basis for most tank farm activities. A defense-in-depth approach is being used to ensure tank safety. A major effort is underway to upgrade and complete the Authorization Basis for the TWRS Manage Tank Waste Function. A BIO is scheduled to be approved in December 1996 and an FSAR is scheduled to be approved in June 1997.

5.4.2.1 Major Safety Issues Related to Tank Contents

The major safety issues related to tank contents include ferrocyanide, organic complexants, organic solvents, flammable gases, high heat, and criticality. The following sections describe the current status, controls, and approach to issue resolution for the major safety issues.

5.4.2.1.1 Ferrocyanide Safety Issue

Ferrocyanide was used to scavenge Cs from tank waste liquids. Ferrocyanide, in the presence of oxidizing material such as sodium nitrate, can react exothermically if heated to sufficiently high temperatures or subjected to a credible initiator of sufficient energy. Under certain conditions, reactions of this material can result in explosive energy releases. Because the scavenging process precipitated ferrocyanide from solutions containing nitrate, an intimate mixture of ferrocyanide and nitrate may have been established in some regions of the ferrocyanide tanks.

Status. The initial efforts to resolve the ferrocyanide issue involved attempting to measure the amount of ferrocyanide (fuel) and oxidizers present in the tank wastes to determine if the concentrations were sufficient to support a propagating exothermic reaction. During the process of sampling the waste for ferrocyanide content; additional information from literature searches, experiments, and analysis improved the understanding of the ferrocyanide hazard. A literature search revealed work that indicated that sodium nickel ferrocyanide decomposed (aged) to lower energy compounds when exposed to a typical Hanford Site tank environment (Babad et al. 1993). Recent studies with waste simulants corroborate that ferrocyanide decomposes under waste tank conditions (Lilga et al. 1993, 1994, and 1995). Three parameters (temperature, exposure to high pH, and radiation dose) strongly affect the rate of decomposition. With the recognition that ferrocyanide decomposes to lower energy and less reactive compounds, tanks were selected for sampling and analysis to bound the conditions of ferrocyanide decomposition. If the decomposition phenomenon has occurred in these tanks, then it has occurred in all the ferrocyanide containing waste. The decomposition phenomenon can be confirmed by analyzing waste samples for ferrocyanide energy levels and nickel. If nickel is present and the energy levels are low, then the ferrocyanide has decomposed.

Nine tanks have been selected for sampling to confirm that ferrocyanide has decomposed to low levels. Waste sampling and analysis has been completed for eight of the nine tanks.

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Results confirm that ferrocyanide has decomposed to concentrations more than a factor of ten lower than the original concentrations. The ferrocyanide concentrations are 10 to 40 times lower than concentrations required to sustain a propagating reaction (Meacham et al. 1995a).

Controls. Controls were implemented to reduce potential ignition sources and to prevent waste transfers into the ferrocyanide tanks. Sampling and analysis results indicate insufficient ferrocyanide remains in the tanks to support a propagating reaction and that controls are no longer required. However, until acceptance of the final report, existing controls will conservatively remain in place.

Issue resolution. The resolution of the Ferrocyanide Safety Issue is tied to understanding of the sodium nickel ferrocyanide decomposition phenomenon in the waste tank environment. This phenomenon appears to be pervasive and consistent and can be confirmed by sampling tanks expected to have the highest concentrations of ferrocyanide and tank environment least conducive to decomposition.

a) **Sampling and analysis.** Sampling has been completed on all nine tanks selected to benchmark the ferrocyanide decomposition phenomenon. Analyses have been completed for eight of the tanks (BY-108, BY-110, C-108, C-109, C-111, C-112, T-107, and TY-104). Analytical results will be evaluated for the remaining ferrocyanide tank (BY-104) to confirm ferrocyanide decomposition. If the results for the remaining tank demonstrates that the ferrocyanide has not decomposed to a safe level, this Implementation Plan will be revised to define additional work to resolve the issue. A final topical report on the Ferrocyanide Safety Issue is scheduled to be issued by January 1997.

b) **Uncertainties.** The uncertainties pertain to sampling and analysis of the ferrocyanide tanks. Analyses of the tank samples have shown some variabilities in the remaining fuel concentration, ranging from 0.02 to 2.00 wt%. As discussed above, the measured ferrocyanide concentrations are a factor of ten less than original concentrations and are 10 to 40 times lower than concentrations required to sustain a propagating reaction.

c) **Characterization needs.** Condensed-phase samples have been taken from nine ferrocyanide tanks to benchmark the ferrocyanide decomposition phenomenon. Analyses have been completed for eight tanks and are pending for one tank (BY-104). If the ferrocyanide decomposition phenomenon is further confirmed in tank BY-104, no additional sampling and characterization are required to resolve the Ferrocyanide Safety Issue.

d) **Summary of approach.** Analysis of twenty-six core samples from eight ferrocyanide tanks has demonstrated that ferrocyanide has decomposed to low levels. Additional analyses are in progress on samples from the remaining tank. Those analyses are expected to continue to confirm that the decomposition phenomenon is pervasive and consistent in ferrocyanide tanks. If this phenomenon is consistent in tanks least conducive to ferrocyanide decomposition, the issue will have been resolved without characterizing the contents of each ferrocyanide tank. A final topical report is scheduled for completion in January 1997.

5.4.2.1.2 Organic Complexants Safety Issue

Organic complexants were sent to the HLW tanks during the defense mission at the Hanford Site. These compounds and their decomposition products have the potential to react exothermically when combined with nitrate/nitrite oxidizer. The organic complexant hazard is represented by two distinct types of reactions: (1) spontaneous chemical runaway (self-heating) reactions through the waste mass, and (2) propagating chemical reactions typified by a passing reaction front stimulated by a single point ignition.

Status. An improved understanding of the phenomena associated with organic complexants has been gained through analysis and experimentation. Analysis indicates that (with the exception of tank C-106 which requires cooling water additions) spontaneous conditions leading to a chemical runaway reaction throughout the waste mass are highly unlikely under current storage conditions (Fauske 1996). This conclusion is reached by evaluating the energy balance for storage tanks. For a spontaneous chemical runaway reaction to occur, the radionuclide and chemical heating rate must exceed the tank cooling rate (Gygax 1990). This condition can be evaluated by comparing the characteristic time of cooling (i.e., the time required to reach a new equilibrium temperature following an instantaneous change in the heating rate) with the waste storage time.

Based on methods derived from the energy balance, calculations (Fauske 1996) indicate that the characteristic time of cooling ranges from a few hours to 3.1 years. Some waste has been stored for more than 40 years, and there have been no transfers of waste into the SSTs for about 15 years. Several characteristic times of cooling have passed over the last 15 years of storage; consequently, bulk runaway reactions are highly unlikely to be a hazard under current storage conditions. In addition, no credible mechanisms to increase tank temperatures to chemical runaway reaction levels have been identified. Drying the wastes can decrease the thermal conductivity; however, this decrease would not be sufficient to lead to an adiabatic runaway reaction. Post interim stabilization waste temperatures (in all 114 interim stabilized tanks) have continued to decline consistent with radioactive decay rates. *Assessment of Chemical Vulnerabilities in the Hanford High Level Tank Wastes* (Fauske 1996) discusses this technical rationale in detail.

Since 1991, tank A-101 has shown a slight increase in the time averaged headspace and waste/dome interface temperatures on the order of 0.7 C/year. The tank cooling efficiency was reduced in 1991 when the A farm ventilation was turned off. The temperature increase was confined to the head space and the upper six feet of the waste. Tank A-101 contains ~ 8.7 meters (~ 28.5 feet) of waste and has a calculated heat load of about 5 kW. The relatively long-term small temperature increase in tank A-101 is not indicative of spontaneous chemical runaway reactions. The bulk of the solid waste time average temperatures in tank A-101 are decreasing consistent with the decrease in decay heating rate. The thermal behavior of A-101 is discussed in greater detail in Ogden et al. (1996). Small fluctuations in temperatures within the Hanford tank waste are not unexpected as a result of salt precipitation, changes in cooling efficiency, and slow chemical degradation reactions within the waste.

Propagating reactions require an ignition source, and sufficient fuel and oxidizer to support the reaction. Tube propagation tests with waste surrogates, coupled with theoretical analyses, have shown that ignition sources greater than 1 Joule (at least 1,000 times more

than that required for gas phase ignition sources) are required to initiate organic complexant reactions (Fauske 1996). Sparks, impacts, and shocks lack sufficient energy to initiate organic complexant propagating reactions. Credible ignition sources for organic complexant reactions have been narrowed to energy sources such as lightning strikes, gasoline fires (resulting from vehicle gasoline tank ruptures), or rotary mode core sampling upsets (e.g., loss of nitrogen purge). Controls have been implemented to prevent initiation of propagating organic complexant reactions. Therefore, wastes containing organic complexants can be safely stored using existing controls and lightning protection (if needed).

The risk posed by lightning strikes is being evaluated to determine the need for lightning protection. The theoretical probability of lightning striking any Hanford Site HLW tank is 5×10^{-4} per year. This probability was calculated assuming one strike per square kilometer per year and ten thunderstorm days per year. Magnetic detection finder data over the last ten years indicates that the actual number of lightning strikes per square kilometer ranges from < 0.02 to 0.05 per year with an average of ten thunderstorm days per year. The work listed below supports completion of the milestone on lightning evaluations and protection.

- Check above ground tank penetrations resistance to ground in accordance with Institute of Electrical and Electronics Engineers Standard 142-82, *Recommended Practice for Grounding of Industrial and Commercial Power Systems* (IEEE 1991).
- Complete a conceptual design on lightning protection.
- Evaluate the probability of lightning striking a tank concurrent with a flammable gas release that exceeds the LFL in the tank headspace.

Safe storage criteria (Webb et al. 1995) have been established through theoretical analysis and tests on waste surrogates. The minimum fuel concentration required to support a propagating reaction has been determined using a contact-temperature ignition model (Fauske et al. 1995). A necessary (but not sufficient) condition for a propagating reaction is that the fuel concentration be greater than 1,200 J/g (4.5 wt% TOC), on an energy equivalent basis (Fauske et al. 1995). Sampling the High Priority Tanks should confirm the criteria using actual waste samples. Until the criterion is confirmed, the current 480 J/g (3 wt% TOC) fuel criterion will continue to be used. For fuel concentrations between 1,200 and 2,100 J/g, the waste moisture (free water) content required to prevent a propagating reaction varies linearly from 0 to 20 wt%. Above 20 wt%, the fuel-moisture linear relationship no longer holds because the mixture becomes liquid continuous and a stoichiometric fuel-oxidizer mixture reaction will not propagate (Fauske et al. 1995).

Simulant studies indicate that fuel concentrations in the tanks have been decreased by saltwell pumping and waste aging (i.e., decomposition of the high energy waste into low energy products). Experiments show that the more reactive organic complexant salts (e.g., nitrilotriacetic acid [NTA], iminodiacetic acid [IDA], and ethylenediaminetetraacetic acid [EDTA]) remain soluble in the tank solutions (Barney 1994), and are removed by saltwell pumping. Experiments indicate that organic compounds decompose to less energetic products (e.g., oxalate) (Camaioni et al. 1995). During decomposition, some of intermediate products can be more energetic. However, the net effect of decomposition decreases the potential chemical energy of the waste. Data from organic speciation of the

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liquid and solid wastes from tanks SY-101 and SY-103 are consistent with predictions based on the solubility and aging models. The organic material in the liquid waste (convective layer) was comprised of EDTA, NTA, and IDA, while the organic in the solid waste (non-convective layer) was comprised of mostly oxalate. Tube propagation tests have shown that these organic salts will not support propagating reactions (Fauske et al. 1995).

Controls. Controls have been implemented to reduce potential ignition sources. These controls are designed to prevent vehicle gasoline spills and to prevent the Rotary Mode Core Sampling System from raising waste temperatures to levels required to ignite organic complexants. Lightning is being assessed as a potential external initiator, for purposes of defining hazards and accidents. The probability of a lightning strike on any Hanford Site HLW tank is low (the estimated frequency is 5×10^{-4} per year) (MacFarlane 1994). Weather conditions are continually monitored by on-site meteorological stations and tank intrusive activities are not allowed if lightning storms approach within a 50-mile radius. The risk posed by lightning strikes is being evaluated further to better understand the need for action, if any. Even if lightning strikes a tank, a reaction will not propagate unless the waste is dry and has sufficient fuel content. To date no tanks have been identified that are both dry and contain sufficient fuel (i.e., greater than 1,200 J/g) to support a propagating reaction (Webb et al. 1995).

Issue resolution. The organic complexant hazard will continue to exist until the organic material is no longer capable of sustaining a propagating reaction. However, the Organic Complexants Safety Issue will be resolved if it can be shown that tank conditions will not support propagating reactions. An improved understanding of key parameters affecting propagating organic complexant reactions (i.e., fuel, moisture, and ignition sources) is necessary to resolve the Organic Complexants Safety Issue or reduce the controls. Analyses and tests will be conducted on selected waste samples to: a) confirm the safe storage criteria; b) quantify the initiator source requirement; c) determine the effects of organic solubility and aging on tank fuel content; and d) assess tank waste against safe storage criteria. A supporting technical document on Organic Complexant Safety Issue is scheduled to be issued in December 1996. This topical report will describe the current understanding of the issue and future work for resolution. Sections a) through d) are parallel paths for resolving the Organic Complexants Safety Issue. Sections e) through g) discuss uncertainties, characterization needs, and a summary of the approach.

a) **Confirm safe storage criteria.** The safe storage criteria were developed by conducting laboratory tube propagation tests using waste surrogates (Fauske et al. 1995). These criteria will be confirmed using waste samples from the High Priority Tanks (Meacham 1995).

b) **Quantify initiator source requirement.** It may be possible to show that no credible initiators exist. As previously indicated, credible initiators for organic complexant reactions have been narrowed to only robust and/or sustained energy sources. Laboratory tests using waste simulants are being conducted to determine the minimum waste moisture concentrations required to preclude initiation of propagating reactions.

Tests will be conducted on selected waste samples to determine the minimum moisture content of Hanford Site tank waste under equilibrium storage conditions. Test results will

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determine a lower bound on the level of tank waste moisture that may be sufficient to inhibit organic complexant reactions.

c) Determine the effect of organic solubility and decomposition on tank fuel content. It may be possible to show that the fuel content is too low to support a propagating reaction. Organic speciation analyses of actual waste will be conducted to confirm organic compound decomposition and solubility models. The aging model indicates that organic complexants decompose over time to less energetic species, providing additional confidence regarding the stability of stored waste. The solubility model indicates that energetic organic species are present principally as solutes in tank liquids. Therefore, saltwell pumping of SSTs should reduce the organic complexant fuel content.

d) Assess tank waste against safe storage criteria. It may be possible to show that tank waste contents meet the confirmed safe storage criteria. If solubility and aging models are confirmed, the associated information from selected tanks will be used to assess the potential fuel and moisture concentrations in the tanks.

e) Uncertainties. Results from sampling and analysis indicate that some wastes are quite heterogeneous. To bound potential fuel and moisture uncertainties, an analysis of variance technique is being used to estimate the characteristics of the most reactive 5% of the waste (that 5% of the waste that would have the highest fuel and lowest moisture concentrations).

There are also some uncertainties within the criteria determined for fuel and moisture concentrations. However, tests with ferrocyanide and organic complexant simulant mixtures indicate that the dry fuel criterion are about 30% lower (more conservative) than what was necessary to support a propagating reaction (Fauske et al. 1995). Additional testing of actual waste samples will be conducted to verify simulant testing (Meacham 1995).

f) Characterization needs. Characterization is focused on understanding the phenomena associated with organic complexants and on determining actual waste characteristics.

Sampling and testing using actual wastes from selected tanks is planned to better understand organic complexant waste phenomena. This testing is designed to confirm safe storage criteria, determine the minimum fuel concentration required to support propagation, and confirm organic aging/solubility models (Meacham 1995).

Sampling and analysis is also planned in selected tanks (see High Priority Tank list [Brown et al. 1995]) to provide additional information on waste characteristics (energetics and moisture data). Safety Screening sampling and analysis is also planned for all tanks.

g) Summary of approach. The Organic Complexants Safety Issue should be resolved using the parallel paths discussed above. These paths should lead to an improved understanding of the fuel-moisture relationship.

5.4.2.1.3 Organic Solvents Safety Issue

Various separation processes involving organic solvents were used at the Hanford Site. Some of these solvents were sent to the storage tanks (Sederburg and Reddick 1994). Given a sufficient ignition source, there are two potential hazards associated with organic solvent: (1) an organic solvent pool fire; and (2) ignition of organic solvent entrained in waste solids (a wick fire).

Status. Experiments and analyses have improved the understanding of the phenomena associated with potential organic solvent fires in Hanford Site tanks. The results of these experiments indicate that the organic solvents used in the nuclear material separation processes are difficult to ignite (Meacham et al. 1995b, Fauske 1996). Sparks, impacts, shocks, and friction sources lack sufficient energy to ignite organic solvent pool fires. Credible ignition sources have been narrowed to robust and/or sustained energy sources such as lightning strikes or gasoline fires (resulting from vehicle gasoline tank ruptures). Therefore, wastes containing organic solvents can be stored safely using existing controls and lightning protection (if necessary).

Even if a pool fire could be ignited, radiological consequences from such a fire would be within risk acceptance guidelines if an adequate vent path exists. The vent requirements are determined by comparing calculated headspace pressure increases to tank design pressure. A pool fire would heat tank headspace gases and pressurize the tank. The fire would burn until the oxygen was depleted. The pressurization from a postulated pool fire would increase with the fire spread rate. If an adequate vent path was available, the tank dome would not collapse and the radiological consequences would be within risk acceptance guidelines. Calculations indicate that the pool area would have to be larger than two square meters to create enough pressure to collapse the tank dome.

Entrained organic solvent is also difficult to ignite (Fauske 1996). Hot steel spheres (up to 270 Joules) and an electronic match (about 138 Joules) failed to ignite entrained organic solvent (dodecane) during ignition experiments. Sparks, impacts, shocks, and friction sources could not ignite entrained organic solvent. Robust and/or sustained energy sources are required to ignite entrained organic solvent. Sampling and analysis of the organic solvent in tank C-103 confirms that the organic solvent has a high flash point (120 C) and thus would be difficult to ignite (Meacham et al. 1995b).

The consequences from an entrained organic solvent fire are less than an organic pool fire. Open literature (Akita 1973, Glassman and Dryer 1980, 1981) and preliminary calculations indicate that the spread rate for an entrained solvent fire is an order of magnitude lower than that for a pool fire and would not generate enough heat and combustion gases to result in a release hazard. Therefore, the Safety Issue is bounded by the organic solvent pool fire hazard. A safety assessment covering pool and entrained organic solvent fire scenarios for all Hanford HLW Tanks will be issued in October 1996.

Characterization results to date indicate that only a small percentage of Hanford HLW Tanks contain significant amounts of organic solvent. Of the 63 tanks sampled and analyzed for organic vapor, only one has a floating organic solvent pool [(tank C-103 and adequate venting is available in this tank (Meacham et al. 1995b)]. Two other tanks (BY-108

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and C-102) are suspected of containing organic solvent pools larger than two square meters. All three of these tanks have adequate vent paths.

Controls. Controls to prevent vehicle gasoline spills have been implemented. The need for lightning controls is being evaluated and will be included in the August 1996 report on lightning evaluations.

Issue resolution. Resolution of the Organic Solvents Safety Issue requires two steps: a) identification of tanks containing significant quantities of organic solvent (i.e., greater than a two square meter puddle) by vapor sampling and analyses; and b) ensuring an adequate vent path in those tanks that contain significant organic solvent. A supporting technical document on Organic Solvent Safety Issue is scheduled to be issued in December 1996. This topical report will describe the current understanding of the issue and future work for resolution.

a) **Identification of tanks.** Tanks containing surface organic solvent will be identified by vapor sampling the tank headspaces. There is a relationship between liquid organic solvent in a tank and the organic solvent vapors found in the headspace. The mass transfer of a semi-volatile species in an organic liquid (e.g., dodecane, tridecane, or tributyl phosphate) to the headspace vapor is determined by several parameters, including the mass transfer coefficient, gas-liquid contact area, ventilation flow rate, and solvent volatility. Criteria for organic solvent headspace concentrations have been developed using theoretical analyses and organic solvent sample data from tank C-103. All tanks will be vapor sampled (86 SSTs and all DSTs remain to be sampled and analyzed) and screened against the criteria to identify potential organic solvent tanks. An evaluation was completed to determine the benefit (in terms of reduced risk) of accelerating the schedule to identify organic solvent tanks (Fritz 1996). The conclusion of the evaluation was that cost increases to accelerate the vapor sampling schedule are not warranted based on the potential decrease in the incremental health effect to the public.

DST tank design will accommodate a substantially larger pressure transient than SSTs. Therefore, an organic pool fire could not build enough pressure to collapse the DST tank dome, and radiological consequences would be within risk acceptance guidelines. However, on-site toxicological consequences exceed guidelines. Appropriate resolution will be addressed in the BIO.

b) **Ensuring adequate vent path.** If a tank contains significant organic solvent, the tank configuration will be examined to ensure that an adequate vent path area is available. For those tanks with insufficient vent path area, controls will not be removed. The tank must be reconfigured or mitigated before the controls are removed.

c) **Uncertainties.** Most of the uncertainties are associated with vapor sampling and detection of organic solvent in the tank headspaces. Uncertainties include solvent volatility, ventilation rates, mass transfer coefficients, and headspace homogeneity. Criteria for screening tanks for organic solvents have factored in these uncertainties. The criteria are conservative by an overall factor of about two. This conservatism guards against not identifying tanks that do contain significant organic solvent (false negatives). Speciation of the organic solvents in waste samples should help refine the screening criteria, reducing the number of false positives.

d) **Characterization needs.** Characterization is focused on understanding the phenomena associated with organic solvent reactions, headspace vapor mixing, and variations in vapor concentrations due to tank breathing; and on determining actual waste characteristics.

Condensed-phase samples have been taken from three tanks suspected of containing entrained organic solvent (BY-108, BY-110, and C-102). These samples will be speciated to better understand the phenomena associated with organic solvents. Analyses have been completed on auger samples from tank C-102 and are in progress on core samples from tanks BY-108 and BY-110. Understanding the possible range of solvent compositions should help refine screening criteria for organic solvents. A total of eighteen vapor samples will be analyzed from three different tanks to confirm the headspace vapor mixing phenomenon. In addition, twenty vapor samples will be analyzed from four additional tanks to improve the understanding of phenomenon associated with headspace vapor content variations due to tank breathing (passive ventilation) . Six of the twenty vapor samples have been completed.

All SSTs will be vapor sampled for the presence of organic solvent by the December . DSTs will be vapor sampled by December 2000. Results from headspace sampling will be used to determine which tanks contain a significant amount of organic solvent.

e) **Summary of approach.** Headspace sampling is planned to identify tanks that contain significant (greater than a two square meter puddle) organic solvent. Tank configurations will be examined to confirm that adequate vent path area is available. For tanks with an insufficient vent path, controls to prevent ignition sources will remain until the tanks are modified or mitigated.

5.4.2.1.4 Flammable Gas Safety Issue

Radiolytic and chemical decomposition reactions occurring in tank waste produce flammable gases (principally hydrogen and ammonia) and an oxidizer (nitrous oxide). The hazard is related to two phenomena: (1) slow, steady accumulation of flammable gases in the tank headspace, and (2) episodic releases of flammable gases at comparatively high rates and concentrations.

Status. Flammable gas tanks were identified based on monitoring for fluctuations in waste level attributable to either episodic gas releases or atmospheric pressure variations, or by long-term waste level increase due to slurry growth. Gas retention models have been developed to better understand the phenomena of the flammable gas safety issue.

For steady accumulation of flammable gases, modeling indicates that retention in the tank headspace is not likely for most tanks. All DSTs are actively ventilated and air exchange is rapid enough to keep steady-state hydrogen concentrations in the tank headspaces well below 25% of the LFL (Graves 1994, Hodgson 1996). Previously, concern existed that flow through DST AP-102 may be too low to assure the headspace remains below 25% of the LFL (Barton 1996); subsequent vapor sampling demonstrated that the steady-state flammable gas concentration was only 0.12% of the LFL (Hodgson 1996).

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Sampling results consistently show that steady-state flammable gas concentrations in tank headspaces are low. Most SSTs are passively ventilated and analysis of the tanks sampled thus far (43 SSTs) show flammable gas concentrations an order of magnitude below 25% of the LFL (Huckaby et al. 1995).

During episodic releases, headspace flammable gas concentrations can exceed 25% of the LFL for brief periods. Episodic releases can be periodic or triggered by tank intrusive activities. Tanks subject to episodic releases were identified by monitoring for fluctuations in waste level (from potential gas release events). To date, significant episodic releases have only been observed in tanks with supernatant. The supernatant has been removed from 114 SSTs by interim stabilization. No significant gas release events have been observed in interim stabilized SSTs (based on surface level changes). After interim stabilization, SSTs still have sufficient interstitial liquid to generate and trap significant quantities of gas and small local releases are possible. However, unless the waste is disturbed by intrusive activities, it is unlikely to reach 25% of the LFL in the headspace.

An evaluation of tank level fluctuations was completed in 1995. The evaluation demonstrated a correlation between atmospheric pressure variations and tank waste level (Whitney 1995). Gas retained in the waste compresses with increased barometric pressure, leading to tank level fluctuations. A detailed evaluation of 59 tanks that exhibited this correlation led to the addition of 25 tanks to the Flammable Gas USQ (McClusky 1996). Localized releases may be possible in saltcake and sludges (Allemann 1995). Consequently, a decision was made to assess all 177 tanks to determine their potential to generate and release flammable gas and in the interim flammable gas controls were placed on all tanks. A summary of the assessment results will be issued in June 1996. An evaluation to determine instrumentation upgrade requirements for any additional flammable gas tanks will be completed in August 1996.

Continuous hydrogen monitors were installed on all 25 Flammable Gas Watch List tanks in FY-1995. To date, only DSTs AW-101, AN-105, and SY-101 have had measured episodic releases above 25% LFL, and only SY-101 exceeded the LFL. Nineteen of the monitored tanks are SSTs. To date, these SSTs have shown relatively constant gas concentrations that are significantly below 25% LFL.

Mitigative actions can be used to prevent elevated flammable gas releases or to minimize the risk associated with episodic releases. A mixer pump was installed in tank SY-101 to prevent flammable gas concentrations from exceeding the LFL. Periodic mixer pump operation induces small gas releases (much less than 25% of the LFL) and prevents the buildup of large quantities of flammable gas in the waste. Monitoring has shown hydrogen concentrations remain well below 25% of the LFL. Removing the supernatant from the SSTs also appears to be an effective mitigation technique. The remaining SSTs are scheduled to be interim stabilized by the year 2000. Supernatant (including organics) that will be added to the DSTs during interim stabilization may increase the potential for gas generation and release in the DSTs. However, overall safety risk will be reduced by completing the interim stabilization of the SSTs because the DSTs are within design lifetimes and are actively ventilated. The ventilation system in AW Tank Farm was upgraded with inlet dampers and flow controllers to minimize the time the flammable gas concentration is above 25% of the LFL. Similar upgrades will be completed on the AN Tank Farm ventilation system later this year.

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Controls. Controls were implemented on all tanks in November 1995 because of the uncertainty regarding flammable gas behavior in both the headspace and in the condensed-phase waste.

These controls reduce potential ignition sources from equipment, waste intrusive activities, and other operations involving access to the tank. Spark resistant tools are used and physical restraints are in place to prevent dropping objects into the tanks. Electrically conductive objects inserted into or connected to objects in the tank or headspace are electrically grounded in accordance with National Fire Protection Association guidelines (ANSI/NFPA 1993) for static grounding. The Rotary Mode Core Sampling System is being redesigned for operation in flammable gas environments. This design will meet National Fire Protection Association requirements (ANSI/NFPA 1989).

Before tank intrusive activities, the tank headspace, risers, pits, and the vapor area of any other item associated with the activity that protrudes into the tank waste are sampled to verify that flammable gas concentrations are below 25% of the LFL. Before waste intrusive activities, tank level records are checked to ensure that the tank is not approaching an episodic gas release event. During waste intrusive activities, flammable gas concentrations are periodically monitored and activities are stopped before 25% of the LFL is exceeded.

In addition to application of controls, an assessment of installed equipment in all tanks was completed to determine if any unacceptable potential accident initiator exist (Scaief 1995). Potential initiators inside the tanks were deenergized or removed. Potential external spark sources identified will be managed by appropriate controls or equipment modifications.

Analyses and experiments show that ignition sources for flammable gas deflagrations can be small, less than 0.1 milliJoule. Although controls are in place to reduce potential ignition sources, such small sources are difficult to eliminate completely. Corrective actions will be evaluated for any tanks with measured headspace flammable gas concentrations greater than 25% of the LFL.

Lightning is being assessed as a potential external initiator, for purposes of defining hazards and accidents. The associated report will be issued in August 1996. The probability of a lightning strike on any Hanford Site HLW tank is low (the estimated frequency is 5×10^{-4} per year) (MacFarlane 1994). Weather conditions are continually monitored by on-site meteorological stations and intrusive activities are not allowed if lightning storms approach within a 50-mile radius.

Continuous gas monitors only measure hydrogen. Therefore, a monitoring control limit has been established at 0.625 volume percent hydrogen (equivalent to 25% of the LFL for a bounding mixture of flammable gases). This limit was determined from an analysis assuming a burn of the most energetic gas composition; the limit takes into account the presence of other gases such as ammonia, methane, and nitrous oxide. Data from continuous gas monitors are routinely monitored and evaluated and corrective actions are taken as necessary.

Issue resolution. The flammable gas hazard will continue to exist until the wastes are retrieved from the tanks. However, DOE plans to resolve the Flammable Gas Safety Issue

on a tank-by-tank basis when the following steps are completed: a) determination of the amount and composition of gas retained in the wastes; b) establishment of an adequate understanding of the mechanisms for gas generation, retention, and release; and c) updating of the Authorization Basis for the Manage Tank Waste Function. A supporting technical document on Flammable Gas Safety Issue is scheduled to be issued in December 1996. This topical report will describe the current understanding of the issue and future work for resolution.

a) Amount and composition of gas retained in the wastes. Resolution of the Flammable Gas USQ and Safety Issue requires an understanding of the phenomenology with regard to the nature and amount of the stored gas mixture for each tank. Once the information has been obtained, an evaluation is conducted to ascertain if the existing Authorization Basis bounds the noted condition. If conditions are not bounded, the USQ will remain open until additional analyses are completed. The safety analyses used a bounding gas volume calculated with the gas retention model. Actual measurements from tank SY-101 gas releases indicate that the gas retention model conservatively overestimated gas volumes (Brewster et al. 1995).

Gas composition and the energy it can release has a direct influence on the consequences from a deflagration. As with the gas volume, a bounding approach has been used. The approach postulates a gas composition that results in the most energetic burn. As data are obtained on the gas composition for each tank, the analyses can be refined, possibly reducing consequences for the events analyzed in the safety assessment.

Resolution of the Flammable Gas Safety Issue requires verification that the gas retention model bounds the amount of stored gas within the waste. Gas measurement devices include the voidmeter and retained gas sampler. The voidmeter measures the non-dissolved gas content. The retained gas sampler will provide data on the amount and composition of stored gas, including dissolved gas, such as ammonia. Although the voidmeter has been used in selected DSTs, it may not be able to penetrate saltcake or sludge in some SSTs. The retained gas sampler may be the only device capable of measuring retained gas volume and composition in these tanks. This device will be tested in DSTs AW-101, AN-103, AN-104, AN-105, and in SST U-103 (e.g., Hey 1996, Bates 1995). The DSTs were selected because they have the most significant episodic releases and U-103 was selected to evaluate the retained gas sampler in an SST. If the retained gas sampler performance is satisfactory, a future deployment schedule will be developed .

b) Understanding the mechanisms for gas generation, retention and release. A gas generation model has been developed (Hopkins 1994). Current efforts are focused on conducting tests on selected tank waste samples to provide data on rates of generation and types of gases produced. Data from tank sample analyses and laboratory experiments will be used to refine the gas generation model and should help to set limits on evaporator slurry output to avoid creating future flammable gas tanks and better understand if interim stabilization can resolve the gas problem in selected SSTs.

The physics of gas retention and release for SST waste is not well understood. Modeling efforts indicate that the maximum void volume for SST wastes could range from 14 to 40% of the total waste volume and the releasible fraction of the retained gas could range from zero to 47%. Laboratory tests are in progress to gain more insight into these phenomena.

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Additional equipment has been developed to measure waste density and viscosity. Measurements have been conducted on three DSTs (SY-101, SY-103, and AW-101). Data obtained on density, viscosity, and void fraction should help provide an understanding of the SST waste gas retention phenomenon.

c) Updating the Authorization Basis for the Manage Tank Waste Function. Results from the evaluations described above will be used to confirm that tank conditions are bounded by the safety analyses. The Flammable Gas USQ will remain open until bounded by safety analyses. Safety assessments are in progress for saltwell pumping (interim stabilization) and rotary mode core sampling in flammable gas tanks. These assessments are scheduled to be approved and incorporated into the Authorization Basis in Calendar Year 1996

d) Uncertainties. Estimates of the retained gas have had fairly large uncertainties, because of inadequate knowledge about the waste physical properties and axial distribution of gas within the waste. However, the estimates are sufficiently conservative to bound anticipated occurrences.

Core sampling and subsequent analyses introduce uncertainties because the waste is altered. Measurements made in the laboratory hot cells do not truly reflect actual gaseous content of the waste. For example, the samples cool down to hot cell temperatures, resulting in changes in the amount and volume of solids. This affects both the density and physical property evaluations. Handling the sample (core sampling, extrusion, sub-sample preparation, and loading of a sample into test equipment) also has an influence on the measured viscosity and shear strength of the waste. To reduce this source of uncertainty, density and viscosity are being measured in-situ and the retained gas sampler was developed.

For the tests conducted to date, the uncertainty of the stored gas volume based on the voidmeter data is approximately $\pm 25\%$. As the actual data are obtained, this uncertainty should be reduced.

The gas monitoring instrumentation for hydrogen has a detection limit an order of magnitude below the control limit. Therefore, the sensitivity of the gas monitoring equipment is adequate to detect gas releases well below the control limit.

e) Characterization needs. Characterization is focused on understanding the phenomena associated with flammable gas generation/retention, headspace vapor mixing, and variations in vapor concentrations due to tank breathing; and on determining tank headspace flammable gas concentrations.

Retained gas sampling is planned for DSTs AW-101, AN-103, AN-104, AN-105, and in SST U-103. This sample data will be used to demonstrate satisfactory performance of the retained gas sampler. After the device has been shown to provide the requisite information, a schedule will be prepared for its use in selected SSTs. Data from the retained gas sampler will be used to refine gas generation and retention models and should help close the Flammable Gas USQ. Data from these samples should improve the understanding of the gas generation and retention phenomena. Voidmeter and viscometer tests will be conducted in selected DSTs to provide basic parameters for calculating the

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amount of stored gas. A total of eighteen vapor samples will be analyzed from three tanks to confirm the headspace vapor mixing phenomenon. In addition, twenty vapor samples will be analyzed from four additional tanks to improve the understanding of phenomenon associated with headspace vapor content variations due to tank breathing (passive ventilation) . Six of the twenty vapor samples have been completed.

Sampling the headspaces of passively ventilated SSTs for steady-state flammable gas concentrations [via the Safety Screening DQO (Dukelow et al. 1995)] needs to be completed. The results can then be compared with calculations for steady-state flammable gas concentrations in the headspace.

f) Summary of approach. The Flammable Gas Safety Issue will be resolved on a tank-by-tank basis. All passively ventilated SST headspaces will be sampled to determine steady-state flammable gas concentrations. Measurements of waste density, viscosity, void fraction, gas retention, and composition in selected tanks should allow refinement of gas generation and retention models. Refinement of these models should reduce the need for large conservatism and should allow resolution of the Safety Issue for many flammable gas tanks. Although understanding the flammable gas hazard phenomena may be possible, resolving the Flammable Gas Safety Issue on a global basis may not be possible due to the inability to prevent flammable gas generation. Consequently, the Flammable Gas Safety Issue may remain open until the waste is removed from the tank and processed.

5.4.2.1.5 High Heat Safety Issue

Several SSTs received high concentrations of Sr and Cs. High heating rates in the SSTs could lead to accelerated degradation of the tanks and result in release of radioactive materials to the environment. Tank temperature measurements and thermal modeling were used to identify tanks that may have high heat loads.

Status. Only tank C-106 is on the Watch List because it has a calculated heat generation rate of approximately 32 kilowatts and requires periodic additions of water. Extensive thermal modeling of tank C-106 shows that if active cooling were lost for an extended period, maximum waste temperatures would exceed 260 °C (Bander 1993). The tank must be maintained on active cooling with water additions and active ventilation. Liquid level monitoring has been upgraded on this tank.

Controls. Controls are in place for tank C-106 to maintain an adequate cooling water level. The temperature and water level in tank C-106 will be monitored and controlled until the waste is retrieved.

Issue resolution. The SSTs are beyond their design life and the probability of tank leakage increases with time. Therefore, resolution of the High Heat Safety Issue requires retrieval and transfer of the waste in tank C-106. A final topical report documenting resolution of the High Heat Safety Issue is scheduled to be issued in May 1998.

a) Retrieval and transfer. Resolution of this Safety Issue requires that most of the heat-producing waste be retrieved and transferred to DSTs. Tank C-106 contains a relatively hard bottom layer. This layer was deposited in the tank before the strontium and cesium campaigns. Most of the heat producing isotopes are thought to be contained in the

supernatant and sludge above the bottom layer. These upper layers should be readily removed during retrieval. However, a thermal analysis was completed to determine the post retrieval impact on tank cooling assuming that most of the heat producing isotopes are in the bottom layer and are not removed by sluicing. The results of the analysis indicate that the tank would be adequately cooled after retrieval of the supernatant and sludge with no water additions or active ventilation (Ogden et al. 1996). A safety assessment will be completed prior to retrieval and transfer. Retrieval and transfer are scheduled to begin in.

b) **Uncertainties.** The uncertainties related to tank C-106 retrieval are distribution of the heat-producing radioisotopes and whether the tank contents are compatible with the receiving DST. These potential uncertainties should be resolved by additional sampling and analytical modeling.

c) **Characterization needs.** Supernatant and sludge grab samples have been obtained from tank C-106. The grab samples will be analyzed for radionuclides and compatibility with the waste in the receiving DST. Analyses of the grab samples are required in October 1996 to factor results into the revised safety assessment for waste retrieval.

d) **Summary of approach.** Resolution of the High Heat Safety Issue requires retrieval and transfer of the waste in tank C-106. Data from grab sampling will be used to complete the retrieval safety assessment and to determine waste compatibility with the receiver tank.

5.4.2.1.6 Criticality Safety Issue

The Criticality Safety Issue involves the lack of definitive knowledge of the tank waste fissile material and neutron absorber inventory and distribution.

Status. A bounding safety assessment was used to support the conclusion that the tank wastes are substantially subcritical (Braun 1994). This assessment was used for closure of the criticality USQ. In addition, a new Criticality Safety Evaluation Report (CSER) was written, Criticality Prevention Specifications (CPS) were developed, operating procedures were revised to reflect the CPS limits, and operating personnel received appropriate training.

Controls. The Tank Farms controls ensure that the form and distribution of fissile material remain unchanged from the conditions of the evaluation and that incoming waste streams meet CPS limits. The pH of the waste is maintained alkaline to ensure that the fissile materials remain in the solids strata of the waste.

Issue resolution. To further improve the safety margins, potential physical and chemical concentration mechanisms are being evaluated. Associated tasks include historical data review, waste partitioning (chemistry), and waste distribution/modeling. A topical report to resolve the Criticality Safety Issue will be completed in December 1996. Documentation of these evaluations regarding criticality safety will be included in the FSAR.

a) **Analyses for fissile material.** Additional safety evaluations regarding the behavior of fissile and absorber material and criticality consequence evaluations are in progress. A separate safety assessment is required before retrieval or in-tank pretreatment activities

are conducted. The Criticality Safety Issue can be closed with the information currently available, but confidence in the accuracy of conclusions will increase as more data are obtained.

b) **Uncertainties.** The safety assessment (Braun 1994) used to close the Criticality USQ concluded that the tank wastes were subcritical by a large margin. This conclusion was reached after reviewing characterization data from input streams to the tanks and available waste tank sample data. However, not all tanks have been sampled. All existing data were used to calculate the infinite critical multiplication factor (k_{∞}). Using the highest concentrations of fissile material found and the lowest concentrations of neutron absorbers, the maximum k_{∞} was determined to be less than 0.02. This is considerably less than the administrative limit of 0.95. The highest concentration of plutonium was 0.35 grams per liter. This concentration is considerably less than the minimum critical mass concentration (independent of waste form) of 2.6 grams per liter.

c) **Characterization needs.** The Criticality Safety Program will rely on opportunistic sampling and analysis. This characterization data should provide added confidence that safety margins are maintained. These opportunistic analyses are requirements in the Safety Screening DQO (Dukelow et al. 1995). Each additional sample provides confidence in the conclusions established in the safety assessment and the CSER. The plutonium inventory tracking system will be adjusted if necessary as the characterization information is provided.

d) **Summary of approach.** Sufficient information is currently available to resolve the Criticality Safety Issue. When core samples are required for reasons other than criticality safety and if the screening limit for total alpha is exceeded, additional analyses should be completed to improve the knowledge of fissile materials and primary neutron absorbers. The criticality prevention controls and safe designs will continue to be required for all TWRS functions.

5.4.2.2 Additional Actions to Upgrade and Complete the Authorization Basis for Tank Waste Storage

Not all tank waste safety issues will be resolved with finality. Some may persist in individual tanks until the waste is removed and processed. The specific emphasis on the safety controls will be continued. A systematic effort will be continued to define and properly implement the safety controls. This effort includes updates to the ISB, the application of a defense-in-depth strategy, the preparation and implementation of a BIO and FSAR, and the definition of the appropriate source terms for evaluating the tank risks. The following is a discussion of these topics.

5.4.2.2.1 Interim Safety Basis

An ISB document has been developed and accepted by DOE as the interim Authorization Basis for the TWRS Level 3 Manage Tank Waste Function. New activities conducted in the Tank Farms will continue to be evaluated using the USQ screening process to ensure that they are within the Authorization Basis. Sampling and laboratory analyses intended to confirm assumptions that support safety analyses and models will be completed over the next three years. Any data concerns will be subjected to the USQ process.

5.4.2.2.2 Defense-in-Depth

Defense-in-depth is a fundamental approach to hazard control that relies on multiple layers of protection, including facility design features, location, operations, and management systems. An important aspect of the Tank Farms hazard analysis will be a description of the facility's defense-in-depth features. The hazard analysis will be included in both the BIO and the FSAR. This defense-in-depth approach will be consistent with the guidance of DOE Standard DOE-STD-3009-94, *Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Safety Analysis Reports* (DOE-HQ 1994b). For non-reactor nuclear facilities, like the Tank Farms, DOE-STD-3009 prescribes a graded approach, that considers the magnitude or severity of the facility hazard, the facility complexity, and the stage of the facility life cycle.

While a defense-in-depth approach is not formally developed and documented in the ISB, significant features of a defense-in-depth approach are in place as illustrated below. These features provide a degree of assurance to protect against an uncontrolled release of hazardous material from the waste tanks.

- Tank design features enhance protection of the public, on-site workers, and the environment.
 - The underground placement of the waste tanks provides inherent protection from most types of external initiators, mitigation of some types of releases, and protection of workers from high radiation exposures.
 - The DSTs have a second steel liner as added assurance against leakage into the soil.
- The remote location of the tanks on an isolated site that is more than 30 kilometers from major population centers minimizes potential exposure of the public even for postulated design basis events.
- The tanks are monitored for detection of significant changes in waste surface level or temperature.
- Interim Operational Safety Requirements are in place to ensure that safety-significant conditions are maintained within approved limits.
- Administrative controls and specifications govern operations.
 - Operators are trained and qualified.
 - Work controls and radiological controls are in place to prevent errors and to minimize personnel exposure to radiation and hazardous materials.
 - Tank Farm access controls prevent unauthorized access.
 - Controls are in place for all tank intrusive activities.

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- For added protection against leakage, 114 of 149 SSTs have been interim stabilized by transfer of pumpable liquids to DSTs. The remaining SSTs are scheduled to be interim stabilized by the year 2000.
- Where necessary, mitigative actions (such as installation of and periodic operation of the mixer pump in SY-101) have been completed to minimize risk.
- Emergency preparedness procedures are in place and practiced.

The adequacy of the defense-in-depth for Tank Farms will be verified by completion of the Safety Basis as documented in the FSAR and TSRs. This will include the safety classification of the waste tank structures, systems and components to verify conformance with the corresponding graded requirements.

5.4.2.2.3 Basis for Interim Operation

A BIO will be developed in accordance with DOE Standard DOE-STD-3011-94, *Guidance for the Preparation of DOE 5480.22 (TSR) and DOE 5480.23 (SAR) Implementation Plans* (DOE-HQ 1994d). The BIO and associated Interim Operations Safety Requirements will be based on the Hazards Analysis performed in support of the FSAR project. Approval and implementation of the BIO will be a significant improvement to the current TWRS Authorization Basis by providing a strong link between the hazards identified and the controls established to manage the hazards at acceptable levels. The BIO is a key transitional step from the ISB to the FSAR. It will establish an interim safety baseline in compliance with DOE Order 5480.23 and will serve as the TWRS Authorization Basis while the FSAR is undergoing DOE review and approval. The BIO is scheduled to be approved in December 1996.

5.4.2.2.4 Final Safety Analysis Report

A major effort is in progress to upgrade and complete the Authorization Basis for the Manage Tank Waste Function. This effort will include upgrading the storage Authorization Basis (initially with ISB upgrades and a BIO and ultimately with the production of the FSAR). The FSAR will meet the requirements of DOE Order 5480.23, *Nuclear Safety Analysis Reports* (DOE-HQ 1994c) and Standard DOE-STD-3009-94, *Preparation Guide for U.S. Department of Energy Nonreactor Nuclear Facility Safety Analysis Reports* (DOE-HQ 1994b), and the associated TSRs will comply with DOE Order 5480.22, *Technical Safety Requirements* (DOE-HQ 1992). The FSAR will include three of the four Level 4 Functions (Store Manage Tank Waste, Characterize Waste, and Transfer Manage Tank Waste Functions). The FSAR for the fourth Level 4 function (Concentrate Waste) was approved in November 1993. Technical documents that summarize the understanding of key safety topics are planned to support the FSAR. These summary documents include Source Terms, miscellaneous facilities, criticality, structural/seismic, flammable gas, and organics. DOE approval of the FSAR will be documented in a Safety Evaluation Report scheduled for June 1997. The FSAR, TSRs, Compliance Implementation Plan, and the Safety Evaluation Report will ultimately comprise the Authorization Basis for the Manage Tank Waste Function. Annual FSAR updates are required for future facility upgrades.

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Source Terms. The radiological source terms being developed for the Manage Tank Waste Function FSAR radiological hazard and accident analysis will be based primarily on historical reactor and processing facility records and on sample data. Six different radiological source terms are used to account for variation in waste types and different processing operations. These source terms are for SST Liquids, SST Solids, DST Liquids, DST Solids, Aging Waste Facility liquids, and Aging Waste Facility solids. Each source term is a composite of the highest concentration found (based on reactor and processing facility records) in that waste type for each of the key radionuclides. These radionuclides comprise 98% of the potential dose to receptors. The 11 radionuclides used in the source terms are comprised of a group of nine radionuclides that contribute 98% of the total inhalation dose and two additional nuclides that are large contributors to direct radiation. These radionuclides were selected based on computer models, *ORIGEN2 - A Revised and Updated Version of the Oak Ridge Isotope Generation and Depletion Code*, ORNL-5621, (Croff 1980) that calculate both the total curie output of the Hanford Site production reactors and the amounts of each radionuclide. After selection of these radionuclides, a panel of knowledgeable engineers and chemists reviewed all the historical sample data (more than 11,000 analyses) to provide added assurance that the highest concentration for each radionuclide was selected.

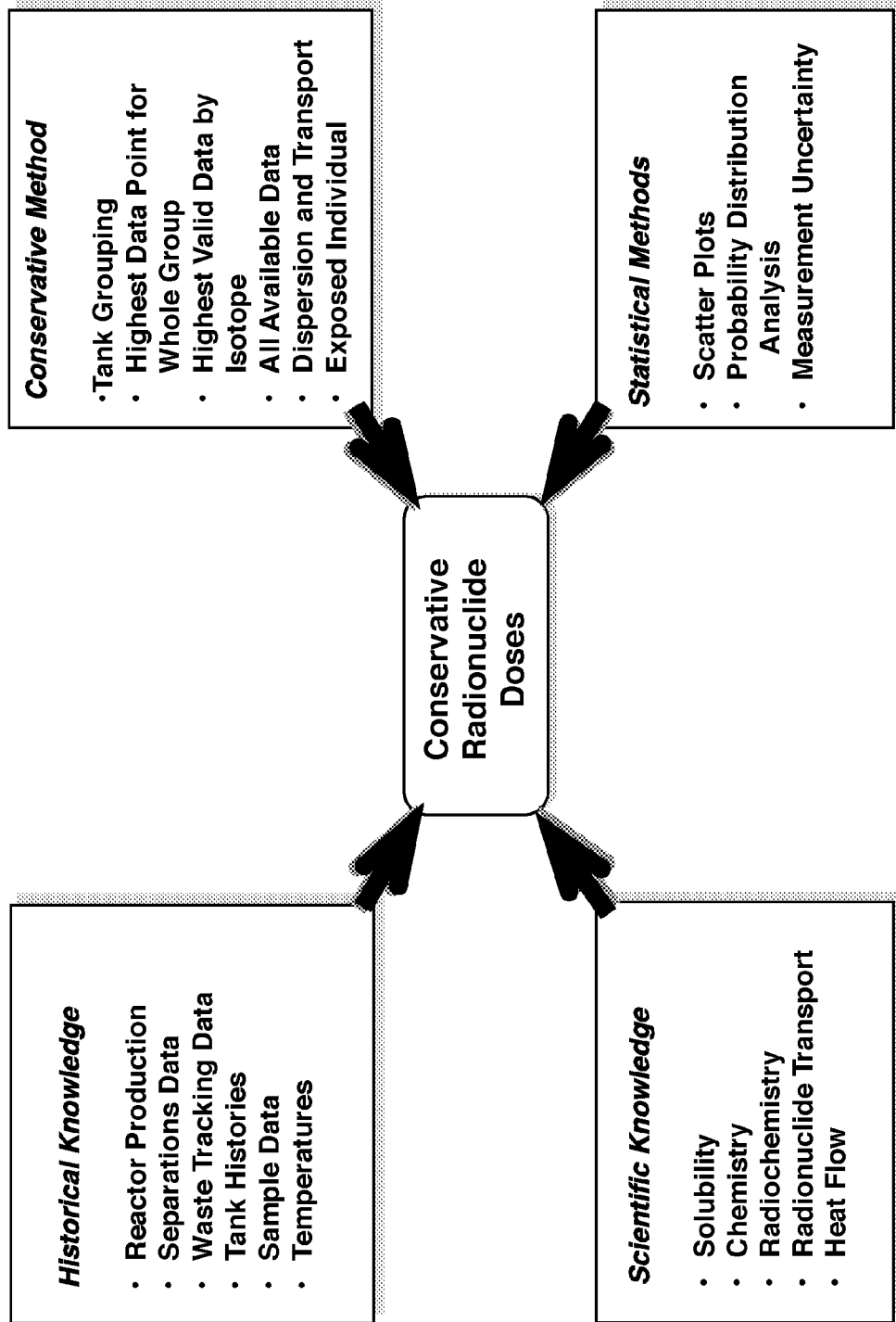
Figure 2 depicts the approaches used to demonstrate conservatism in the selected radionuclide concentrations. Inhalation doses based on the highest concentration are approximately 60 times larger than the inhalation doses calculated based on total Hanford Site production estimates (Croff 1980). The conservatism of the SST radiological source terms has also been checked by a calculation using tank temperatures, rather than sample data, as a starting point. The average heat load in the SSTs is approximately a factor of 100 lower than the heat load that would result from the concentrations of radionuclides used in the SST radiological source terms.

In addition to the conservatism built into the process of selecting the highest activity concentrations, additional conservatism is introduced in the process of calculating doses to the public. Factors such as quantities of material released in accident scenarios, assuming that the exposed person is standing on the site boundary, and using extreme weather conditions that maximize exposure all contribute to the overall conservatism of dose consequences.

The source terms prepared for recent analyses (e.g., Accelerated Safety Analyses) will be refined for the Hazards Analyses for the BIO and the FSAR by adjusting the assumptions, examining and revising the derived concentration methodologies, and updating the sample data base to include the results from the last twelve months of waste tank sampling. *Early peer review and acceptance of this revised source term will be obtained to support planned upgrades to the Authorization Basis. Refinement of the source terms for relaxing conservatism or future activities specific to a few tanks may require additional characterization. A comprehensive source terms document is scheduled to be completed in June 1996 to support the BIO and the FSAR.*

Figure 2: Radiological Source Term Inputs

Radiological Source Term Inputs



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5.4.3 Milestones

Completion of the milestones listed below will close out DOE actions associated with the 93-5 sub-elements on assuring tank safety.

5.4.3.1 TWRS Manage Tank Waste Function Authorization Basis

Statement: Upgrade the Authorization Basis for the TWRS Manage Tank Waste Function

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. *Letter reporting completion of Comprehensive Source Terms Report.
Due Date: June 1996*
- b. *Report on lightning evaluation, and if the probability exceeds 1×10^{-6} per year, evaluate potential mitigating options for lightning strikes.
Due Date: August 1996*
- c. *Approved BIO.
Due Date: December 1996*
- d. *Approved FSAR.
Due Date: June 1997*

5.4.3.2 Ferrocyanide

Statement: Analyze selected samples to reduce data uncertainties and issue final report.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. *Topical report on resolution of Ferrocyanide Safety Issue. This report will include the evaluation of sample analyses confirming ferrocyanide aging (If the results do not confirm that any remaining ferrocyanide is bounded by least favorable decomposition conditions, this Implementation Plan will be revised).
Due Date: January 1997*

5.4.3.3 Organic Complexants

Statement: Complete testing and evaluation confirming simulant results with real waste.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. *Letter reporting completion of supporting technical document on Organic Complexant Safety Issue. (This topical report will describe the current understanding of the issue and future work for resolution).
Due Date: December 1996*
- b. *Letter reporting results of testing completion (using real waste samples) to confirm safe storage criteria, and organic solubility and aging effects on fuel content. If models are confirmed, an assessment of tank wastes compared to safe storage criteria will be scheduled.
Due Date: November 1998*

5.4.3.4 Organic Solvents

Statement: Use vapor samples to identify organic solvent tanks.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Letter reporting completion of safety assessment covering pool and entrained organic solvent fires.
Due Date: October 1996
- b. Letter reporting completion of organic speciation of core samples for BY-108 and BY-110, and auger samples for C-102.
Due Date: October 1996
- c. Letter reporting completion of supporting technical document for Organic Solvent Safety Issue. (This topical report will describe the current understanding of the issue and future work for resolution).
Due Date: December 1996
- d. Letter reporting completion of vapor sampling of all SSTs.
Due Date: December 1999
- e. Letter reporting adequate vent path in all SSTs suspected of containing organic solvents.
Due Date: April 2000
- f. Letter reporting completion of vapor sampling of all DSTs.
Due Date: December 2000

5.4.3.5 Flammable Gas

Statement: Complete analytical evaluations and steady-state vapor samples to determine which flammable gas tanks require mitigative actions. Qualify saltwell pumping and rotary-mode core sampling for flammable gas environments.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Report documenting analyses to determine if additional tanks have potential to exceed 25% of the LFL.
Due Date: June 1996
- b. Letter reporting evaluation of gas monitoring instrumentation upgrade needs for additional tanks with the potential to exceed 25% of the LFL.
Due Date: August 1996
- c. Letter reporting approval of safety assessment for rotary mode core sampling in flammable gas tanks and documenting incorporation into the Authorization Basis.
Due Date: September 1996
- d. Letter reporting qualification of Rotary Mode Core Sampling System for use in Flammable Gas Tanks.
Due Date: September 1996
- e. Letter reporting approval of safety assessment for saltwell pumping in flammable gas tanks and documenting incorporation into the Authorization Basis.
Due Date: October 1996
- f. Letter reporting completion of AN Tank Farm ventilation upgrade.
Due Date: November 1996

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- g. Letter reporting completion of flammable gas safety screening of remaining passively ventilated SSTs to determine if steady-state vapors are less than 25% of the LFL. (If any tanks are greater than 25% of the LFL, the letter will include the schedule to evaluate corrective actions).**
Due Date: November 1996
- h. Letter reporting completion of supporting technical document on Flammable Gas Safety Issue. (This topical report will describe the current understanding of the issue and future work for resolution).**
Due Date: December 1996
- i. Letter reporting that external equipment spark sources in flammable gas tanks have been managed by controls or the equipment has been modified.**
Due Date: December 1996
- j. Letter reporting completion of voidmeter and viscometer readings in tanks AN-103, AN-104, and AN-105.**
Due Date: December 1996
- k. Letter reporting completion of retained gas sampling in tanks AW-101, AN-103, AN-104, AN-105, and U-103. If the retained gas sampling performance is satisfactory, include future deployment schedule.**
Due Date: March 1997
- l. Letter reporting refinement of flammable gas generation/retention models using void meter and retained gas sampling data.**
Due Date: May 1997

5.4.3.6 High Heat

Statement: Retrieve wastes from tank C-106.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Letter reporting completion of tank C-106 supernatant and sludge sampling and analysis.**
Due Date: October 1996
- b. Letter reporting completion of tank C-106 retrieval safety assessment.**
Due Date: July 1997
- c. Letter reporting initiation of tank C-106 waste retrieval.**
Due Date: October 1997
- d. Letter reporting completion of topical report to resolve the High Heat Safety Issue.**
Due Date: May 1998

5.4.3.7 Criticality

Statement: Resolve the Criticality Safety Issue.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Letter reporting completion of topical report to resolve the Criticality Safety Issue.**
Due Date: December 1996

5.5 ISSUE: DISPOSAL PROGRAM DATA REQUIREMENTS

This section describes the approach for acquiring information necessary for the Disposal Program process development.

5.5.1 Issue Description

Insufficient tank waste technical information exists and the pace of acquiring additional information is too slow to ensure that future Disposal Program data requirements can be met.

5.5.2 Current Status

Process testing with actual tank waste samples is necessary to provide data to support process definition for the TWRS Disposal Program functions listed below.

- *Retrieve tank waste.*
- *Pretreat sludges/solids.*
- *Immobilize Low Level Waste (LLW).*
- *Immobilize HLW/transuranic waste.*

Testing of waste samples will also aid with identification of the safety basis for process design. The basis for the Disposal Program tank waste sampling strategy and the information obtained to date is summarized below.

*The document **Strategy for Sampling Hanford Site Tank Wastes for Development of Disposal Technology, Revision 1** (Kupfer et al. 1995) presents the proposed strategy for sampling SST and DST waste to provide information necessary to satisfactorily support the disposal process development mission. Experimental and information needs were obtained from the following reports: **Data Needs and Attendant Data Quality Objectives for Tank Waste Pretreatment and Disposal** (Slankas et al. 1995), **Characterization Data Needs for Development, Design, and Operations of Retrieval Equipment Developed Through the DQO Process** (Bloom and Nguyen 1995), and the draft document for Privatization DQOs. The sampling strategy uses a tank grouping concept to define a limited number of tanks to be sampled. The waste tanks are grouped based on similarities in waste streams that entered the tanks (i.e., waste types that originated from common separations processes) and known waste transaction records. Samples of waste materials from these tanks will provide material representative of bounding waste types that will prove limiting for the process.*

The Disposal Program process development strategy recommends sampling a total of 47 SSTs and 12 DSTs. These will provide a variety of tanks representative of bounding waste types necessary for process design. The strategy also provides information for tank retrieval sequencing and blending requirements. Sampling requirements were developed based on several major criteria, including those that can influence process definition for

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waste pretreatment, and those that can influence the quantity of the HLW vitrification product.

The Tank Waste Characterization Program sampled tanks in FY 1994 and FY 1995 to support resolution of safety issues and operational needs. For efficiency, the sampling requirements to support Disposal Program process development needs were integrated with these Characterization Project requirements. A total of 22 of the SST samples and two DST samples were selected for process development testing because they represented several different waste types. Testing was completed by the end of FY 1995 for 18 of the SST samples and for the two DST samples. The 18 SST samples provide the basis for understanding the sludge washing behavior for approximately 50% of all SST sludges based on the tank grouping concept. Column tests to evaluate ion exchange methods for removing ¹³⁷Cs were performed on the supernatant from two DSTs. These DSTs represent 33% of waste volume for the complexant concentrate waste type (approximately 10% of the volume of waste in the DSTs).

5.5.3 Resolution Plan and Timing

5.5.3.1 Issue Resolution

The key tenet of the sampling strategy to support the Disposal Program process development is that tanks can be grouped based on similarities in the waste streams that entered the tanks. Historical information (i.e., models including transfer records, flowsheets, etc.) has been and can be used to establish the waste groupings and to prioritize tanks for sampling. Samples of waste materials from selected key tanks will provide material representative of major waste types and representative of bounding waste types that will prove limiting for the chemical and physical process. Information about the processing characteristics of the waste in the remaining tanks in the group can be deduced from the information obtained by the analysis of the samples from the representative tank or from a selected number of representative tanks.

Based on the tank grouping concept, the resolution plan outlines the Disposal Program process development data for essentially all of the DST tank waste and more than 90% of the SST waste by sampling only 12 DSTs and 47 SSTs. The sampling logic is summarized in Tables 2 and 3. As mentioned above, 22 of the SSTs and two DSTs have already been sampled.

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Table 2. Summary of DST Sampling Strategy to Support Disposal Program

	Number of Double-Shell Tanks	Percent of Waste Volume Sampled	Percent of Waste Volume Based on Tank Grouping Concept
Tanks sampled and tested to-date (1994, 1995) ¹	2	10	33
Planned for FY 1996	4	20	35
Planned for out-years	6	29	32
Total	12	59	100

¹ Tank samples that have been tested to evaluate waste pretreatment process behavior.

Table 3. Summary of SST Sampling Strategy to Support Disposal Program

	Number of Single-Shell Tanks	Percent of Sludge Volume Sampled	Percent of Sludge Volume Based on Tank Grouping Concept
Tanks sampled and tested to-date (1994, 1995) ¹	22	24	50
Planned for FY 1996	4	10	13
Planned for out years	21	18	30
Total	47	52	93²

¹ Of the 22 SSTs sampled in FY 1994/1995, 18 were tested to evaluate waste pretreatment (sludge washing) behavior. The additional four samples are scheduled to be tested in FY 1996 along with four additional tanks scheduled to be sampled in FY 1996.

² Seven percent of the sludge in the SSTs are not represented by the SWORT groups. The associated tanks contain unique mixtures of the various waste types. However, these tanks are not expected to contain substantial amounts of key analytes such as chromium, aluminum, or phosphate.

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Disposal Program process development needs relate primarily to determining how a key waste type (e.g., REDOX process waste) will respond to separations processes using the baseline pretreatment processes, such as sludge washing. For Disposal Program process development purposes, sampling all tanks is not necessary, since the major goal is to establish process behaviors for the bounding waste types (i.e., those that impact process feasibility, facility design, and processing schedules). The sampling strategy emphasizes data for sludges because they are the most difficult portion of the waste to process. Understanding the process chemistry of sludges (because of their different origins, compositions, and physical form) is central to the development of pretreatment and HLW vitrification process requirements. The Disposal Program process development needs also include determining the process definition and capability for removing certain key radionuclides such as ^{137}Cs , ^{90}Sr , and Technetium 99 (^{99}Tc) from waste supernatants. Waste composition information is also needed for the proposed DST waste supernatants to be treated using the Phase I Privatization approach. This waste composition information will be used to determine inventories of constituents that can impact glass volumes for vitrification of Low Activity Waste (LAW).

The major criteria used for the identification of the tank wastes to be sampled are listed below.

- Similarities in composition among tanks are expected to be observed for like waste types. The Sort-on-Radioactive Waste Type (SORWT) (Hill et al. 1995) grouping scheme was used to ensure that all major waste types are represented and to determine candidate tanks within the same group. The SORWT scheme groups tanks based on the type(s) of waste introduced into the tanks and their subsequent process history. Information about the character of the waste in the rest of the tanks in the group can be deduced from the information obtained by the analysis of the samples from the representative tank. For SST waste, the SORWT groups selected for sampling encompass 93% of the total sludge volume. The remaining 7% represent minor waste types that have minimal impact on pretreatment processing or on HLW glass volumes.
- Tanks with large waste volumes are preferred (both sludges and saltcakes) because of their significant contributions to the waste stream.
- For tanks that contain both saltcake and sludge, tanks with higher sludge contents are considered potentially bounding, because the sludge mass to be vitrified relates directly to the volume of HLW glass produced.
- Tanks with a single waste type or uncomplicated process histories are more desirable because this better ensures obtaining samples that represent the desired waste type.
- All six major waste types in the DSTs were considered.
- Tanks with bounding saltcake forms from different separations process flowsheets were sought (e.g., REDOX process, PUREX process, and BiPO_4 process).

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- Choices of tanks were influenced by the quantity and concentrations of components known to limit waste loading for both HLW glass and LLW glass such as chromium, aluminum, sodium, potassium, and iron suspected to be in the tank based on historical models.

Seven of the 12 DST waste samples listed in Table 2 represent the Phase I waste supernatants to be treated using the Privatization approach for cleanup of the waste tanks at the Hanford Site. Nine of the 12 DST samples also are needed for enhanced sludge washing evaluation experiments to support waste pretreatment and immobilization strategies. The liquid samples required to support the Privatization requirements can be obtained using grab or push mode sample techniques. Therefore, the liquid samples were not prioritized with tanks requiring core sampling as defined in the *Tank Waste Characterization Basis* (Brown et al. 1995).

The sampling requirements to support the TWRS Disposal Program process development program needs have been integrated with sampling needs defined in other DQO documents including those for safety issues, waste operations, and for waste contents model evaluation. This ensures that the prioritized tank waste sample scheme defined in the *Tank Waste Characterization Basis* will satisfy the needs for the Disposal Program process development. In addition, the tank grouping criteria that were used for selecting tanks to sample for disposal process development allow for meaningful substitutions for a recommended tank. As a result, the disposal sampling needs (Kupfer et al. 1995) are well represented by the High Priority Tanks in the *Tank Waste Characterization Basis*.

Based on historical documentation (flowsheets, waste transfers, etc.), models can be used to classify the tank wastes based on waste types and to estimate waste inventories. As indicated above, the SORWT model was used as the basis for selecting representative groups of tanks for sampling to support Disposal Program requirements. The SORWT model provides a simplified method, based on process histories and waste transfers for classifying the wastes into characteristic groups. A model developed by LANL scientists uses *Waste Status and Transaction Record Summary* reports (Agnew 1994c and 1994d), the *Tank Layer Model (TLM) Spreadsheet* (Agnew 1994a and 1994b), and *Hanford Defined Wastes (HDW)* (Agnew 1995) to provide waste compositions used to develop the *Historical Tank Content Estimates (HTCEs)* (Brevick et al. 1994a, 1994b, and Brevick 1995a, 1995b). Efforts are presently underway to evaluate and reconcile the historical records that are the basis for the LANL model. Upon completion of these efforts, the LANL model may be used to improve the tank grouping concept that in turn could result in modification to the Disposal Program process development sampling requirements.

5.5.3.2 Timing

Sampling of 22 of the 47 SSTs has been completed through the end of FY 1995. Sampling and process development testing of the remaining 25 SSTs supports Disposal Program process development requirements. During the 20 month design for Phase I Privatization, it is expected that further sampling of DST supernatants will be requested by the vendor to support process development and safety basis development.

5.5.4 Characterization Needs

The behavior of essentially all the wastes to be used in the proposed pretreatment processing schemes will be known by sampling and testing waste from 10 additional DSTs and 25 additional SSTs (see Tables 2 and 3). The sampling/characterization strategy for Disposal Program will provide information needed to define waste retrieval and pretreatment process feasibility, obtain facility design basis information, and ensure that the feed to the LAW and HLW vitrification processes will meet glass composition and regulatory specification criteria for these processes.

Information used to select these samples relied heavily on historical records and their analysis to identify the various waste types. Additional information is needed from wastes in S and SX SST Tank Farms because these wastes contain large masses of sludge that can affect the volumes of expensive HLW glass. The wastes are thought to contain significant quantities of certain components, such as chromium, that are expected to reduce waste loading in HLW glass, thus increasing HLW glass volume. These characterization requirements are defined in *Strategy for Sampling Hanford Site Tank Wastes for Development of Disposal Technology* (Kupfer et al. 1995).

The sampling strategy for the Disposal Program must be applied iteratively to work most effectively. Success of the process tests, combined with the variability of process test results for particular waste types, will dictate the level of additional testing on other waste samples that may be required to provide high confidence that a robust process will result. Incorporation of Privatization experience and company-specific technology may dictate changes to both Phase I and Phase II Privatization sampling requirements.

Knowledge of the characteristics of tank waste is required to define the safety basis for waste retrieval, waste processing, and disposal activities. Major safety issues associated with facility design and operations include nuclear criticality potential, radiation dose minimization, hazardous materials' exposure control, and potential chemical (e.g., exothermic) reactions during processing. Because the design process for the waste processing facilities is in its early stages, data requirements have not reached maturity; for example, waste retrieval, blending, and processing strategies have not yet been well defined. Safety and hazard analyses need to be performed. Upon completion of these activities, the data requirements for the safety issues should be developed during the facility design process using DQOs.

5.5.5 Impact of Uncertainties

Tank samples for waste disposal process development serve two purposes. For Phase I Privatization, tank samples of DST waste supernatants will be the primary sources for defining reference waste compositions and tank inventories. These inventories will be evaluated by the prospective vendor to enable development and construction of proper processes for treatment of LAW. Because of the comparatively homogenous nature of DST waste supernatants, there is confidence that DST waste inventories can be based on analytical data.

The second purpose for sampling is to assess pretreatment process behavior for representative waste types in SSTs and DSTs. For example, important information needed to evaluate the effectiveness of sludge washing is the chemistry (chemical form/chemical species) of the waste, which can be related to how effectively the waste can be separated under reference process conditions. The solubility of the tank sludges will depend critically on the chemical composition and speciation of the tank sludges.

A key question is whether actual tank waste samples (particularly SSTs) are representative of the tank contents. Several tank samples may be required to adequately define tank inventories (chemical masses, radionuclide content) (Jensen et al. 1995). One or two samples from a tank may be inadequate to define the chemistry of the waste inventory. However, the chemical and physical waste properties are likely to be quite representative of those properties from other areas in the tank. This is because the majority of the waste was exposed to similar conditions that define the waste chemistry (e.g., aging, heat, etc.). Thus, only one or two tank samples will likely provide a good understanding of the process chemistry of that waste. The use of historical information along with knowledge of the process chemistry, and the ability to predict waste types in tanks using models such as SORWT can allow extrapolation of the process chemistry knowledge of waste in one tank to others. The need for extensive sampling from each waste tank may thus be reduced; instead, taking one or two representative samples from several different tanks may be adequate.

The process behavior information will support definition of design parameters for pretreatment/disposal facilities. The design concept is robust enough to compensate for some uncertainties by using conservative engineering factors to compensate for waste composition uncertainties and other contingencies.

5.5.6 Milestones

Completion of the milestones listed below will close out DOE actions associated with the Recommendation 93-5 sub-elements on the Disposal Program.

5.5.6.1 Disposal Program Characterization

Statement: Complete sampling and analysis of *Tank Waste Characterization Basis* (Brown et al. 1995) tanks for disposal.

Responsible Manager: Assistant Manager, TWRS

Applicable Facilities and Programs: TWRS

Milestone deliverables/due date:

- a. Letter report completion of *Tank Waste Characterization Basis* (Brown et al. 1995) High Priority Tanks sampling and analysis for the Disposal Program.
Due Date: March 1998

5.6 TECHNICAL BASIS FOR CHARACTERIZATION

This section describes the approach for completing the Technical Basis for gathering and evaluating characterization information.

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The definition of the verb to characterize is "to describe the essential character or quality." In the technical arena, characterization denotes gathering sufficient information to describe the essential qualities of an entity when considered from a specific perspective. In this context, characterization has two key components: 1) identification of the essential information requirements; and 2) acquisition of that information. The strategy to acquire information will be driven by the essential information required and constrained by the nature of the entity to be characterized. The Technical Basis for Characterization consists of identification of the information required and how it will be acquired. The factors that define the Technical Basis for characterizing the Hanford Site tank wastes are described below.

The 177 Hanford Site waste tanks fall into one of five categories based on capacity. Sixteen small tanks (208,200 liters [55,000 gallons]) have a diameter of approximately 6 meters (20 feet). The remaining 161 tanks all have a diameter of 23 meters (75 feet) with capacities of 2,006,000 liters (530,000 gallons), 2,870,000 liters (758,000 gallons), 3,800,000 liters (1,000,000 gallons), or 4,390,000 liters (1,160,000 gallons) depending on height. The actual depth of waste stored in the tanks ranges from less than 0.3 meters (one foot) to more than 9 meters (30 feet). The bottoms of the tanks lie from 11 meters (37 feet) to 17 meters (55 feet) below the surface of the ground. Records indicate that the mass of waste in the tanks is on the order of 240,000 metric tons, non-uniformly distributed in the 177 tanks. Although the overall waste inventory of each tank is unique, the inventories are built up from a smaller set of primary waste types. It is possible to group tanks based on commonality of materials in the tanks. They also can be grouped by safety-compromising phenomena (e.g., ferrocyanide, flammable gas, etc.).

Characterization information is required for safe storage of the waste, to operate the tanks and their infrastructure safely, and to plan and implement retrieval and processing of the waste into durable solids suitable for disposal. Information is required on the waste content (chemical species and their physical condition) and on phenomena caused by the waste. The word phenomena refers to the important chemical or physical reactions that are capable of occurring within the mixture of chemicals. The means of characterizing waste content and phenomena associated with the waste are fundamentally different. The waste content can be determined by analytical chemistry or direct measurements of physical properties. Understanding the phenomena requires more extensive analysis of chemical and physical properties combined with experimental modeling.

The information requirements for each TWRS programmatic issue have been identified through the DQO process (EPA 1994). The DQO process provides a rigorous, disciplined approach for determining the information necessary to make a decision. The process was designed for regulatory compliance applications where only content information was required. As applied to Hanford Site tank waste, the DQO process has focused primarily on addressing waste content information needs, including composition (chemical and radiological), condition (physical parameters), and configuration (stratigraphy and heterogeneity). Characterization of phenomena caused by the waste has not generally been addressed through the DQO process, but has been pursued through experimentation using simulants and development of models. In most cases, waste content information is a prerequisite to the design of experiments to determine phenomenology. Physical samples of waste for testing are also required to adequately define the nature and boundaries of conditions that are necessary to support the phenomena that are occurring.

A fundamental step in characterization is to develop the strategy to acquire samples. In an unconstrained situation, a number of standard sampling schemes may be applied (random grids, sequential sampling etc.). The Hanford Site tank situation is different in that sampling is highly constrained because few tank access points (risers) are available and the waste under the risers may not be representative of the overall tank contents. A tank of 23 meters (75-foot) diameter tank has a plan view cross-section of more than 4,097,020 square centimeters (cm^2) (635,000 square inches [in.^2]). Sampling the waste in the tank with a 2.5 centimeters (1 in.) diameter coring tool, with a cross-section of 5.03 cm^2 (0.78 in.^2), provides the ability to sample about 1/800,000 of the cross-section. In round numbers, every core, extending completely through the waste material to the bottom of the tank, provides information on about one millionth of the tank's content. A meaningful, statistically defensible picture of the waste content cannot be provided through sampling alone.

Successful characterization of the tank waste requires understanding of the relationship between the waste at the available sampling sites and the overall tank contents. A complete picture of the three-dimensional waste composition is not generally required to address the essential information requirements. However, the effect of the limited sampling access on the key data requirements needs to be understood.

Samples of Hanford Site tank waste cannot be considered in isolation. A body of information exists, including process and transfer records, HTCEs, monitoring and surveillance data, photographs, and sample analysis information from related tanks. Models of waste behavior (chemical and physical) have been developed. This information is used to evaluate the existing sites available for sampling and to determine how the sample analysis results can be interpreted and extrapolated to an entire tank.

Appendix J summarizes key aspects of the Characterization Technical Basis. This section reviews the strategy to select the High Priority Tanks and key milestones to finalize the Technical Basis.

5.6.1 Strategy to Select High Priority Tanks for Sampling

The information needs identified through the DQO process and described in Sections 5.4 and 5.5 of this plan were integrated to form a single prioritized core sampling plan: *Tank Waste Characterization Basis* (Brown et al. 1995). This plan is reviewed and updated as the relative priorities among the issues changes. The key issues requiring characterization data were identified and prioritized. For each issue, criteria were identified to evaluate the importance of a tank in resolving the issue. Tanks were reviewed against these criteria and the most important tanks associated with each issue were identified. Issues were weighted so that tanks important for key issue resolution received higher priority weights. Tanks important for multiple issue resolution received the highest overall ranking. The outcome of the prioritization process was reviewed with the programs requesting data to ensure that their needs continue to be met.

Twenty-eight High Priority Tanks were selected for near-term core sampling. Analyses of samples from these tanks are expected to resolve or bound the key questions described in Sections 5.4 and 5.5. Appendix F shows which Watch List issues are associated with each of the High Priority Tanks and what primary waste types are contained in the tank (SSTs

only). The issues requiring characterization information are described, including whether the information addresses content or phenomena.

5.6.2 Summary of Characterization Approach and Key Actions

Sampling and analysis of the High Priority Tanks should provide information to increase the understanding of issues applying to all tanks, not just to those sampled. The information gained on waste content will be used to evaluate and update models on the content, waste type distribution and variability in multiple tanks. The information on phenomena caused by the waste will be used to resolve issues, better define screening parameters, determine appropriate controls and mitigative actions, and identify appropriate processes. The High Priority Tank results will also provide the basis to determine and schedule future sampling needs.

The strategy to focus on sampling the High Priority Tanks achieves the intent of the original recommendation to expedite characterization to resolve safety issues. Characterization that focuses on understanding phenomena so that issues may be resolved for groups of tanks is more effective than treating each tank individually. Sampling limitations may prevent resolution of safety issues solely by sampling individual tanks whereas addressing phenomena associated with groups of tanks may resolve the issue.

In parallel with sampling the High Priority Tanks, several key tasks will be accomplished to finalize the Technical Basis and improve tank safety screening. These include developing standard inventory estimates for all tanks, updating HTCEs, evaluating tank headspace homogeneity implementing Fourier Transform Infrared Spectroscopy (FTIR) percent moisture capability in the 222-S Laboratory (*Milestone 5.6.3.1b*), and documenting the comparison between truck and vapor sampling systems .

Recommendation 93-5 focused attention on the Watch List tanks. Table 4 shows the progress in sampling Watch List tanks as the sampling of the High Priority Tanks proceeds. It should be noted that the High Priority Tanks include many Watch List tanks and support resolution of the Watch List issues. However, the High Priority Tanks do not exclude non-Watch List tanks. Key safety questions may be answered through sampling of the High Priority Tanks sooner than they could be answered through sampling of Watch List tanks only. In particular, assumptions regarding the behavior of waste types not generally associated with Watch List tanks needs to be understood through sampling of several non-Watch List tanks.

Table 4: Watch List Tank Sampling Progress Under High Priority Tank Sampling Schedule

Watch List Tank Summary			Watch List Tanks Sampled and Analyzed² Prior to Starting High Priority Tank Sampling³			Watch List Tanks Sampled, and Analysis Complete or in Progress² as of January 31, 1996			Watch List Tanks That Will Be Sampled and Analyzed² When High Priority Tank Sampling is Completed		
Watch List	Total	HPTs¹	Core	Vapor	Grab	Core	Vapor	Grab	Core	Vapor	Grab

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<i>FeCN</i>	18	8	6	18	0	11	18	0	11(13)	18	0
<i>Organic</i>	20	6	8	16	3	9	20	4	12	20	4
<i>Flammable Gas</i>	25	14	3	9	3	6	21	4	13	21	4
<i>High Heat</i>	1	0	0	1	0	0	1	0	0	1	1

Notes:

1. *HPTs: the number of Watch List tanks included in the High Priority Tank (HPT) list. Six of these tanks are on two Watch Lists.*
2. *The term "sampled and analyzed" includes that period from removal of materials through publication of a Tank Characterization Report (TCR).*
3. *The sampling and analysis of several High Priority Tanks were in progress on June 1, 1995. These tanks are included in the numbers in this section, although sampling and analysis was not complete at that time.*
4. *The Ferrocyanide Program currently has information from 11 Watch List tanks. The need to sample the two remaining Ferrocyanide HPTs for resolution of the Ferrocyanide Issue is being reviewed by the Safety Program. However, the two remaining Ferrocyanide Watch List Tanks are scheduled to be sampled to provide the information to satisfy other programmatic DQOs.*

The information from the High Priority Tanks will be reviewed and evaluated. As adequate information is gained on each key issue, decisions will be made that may affect the scope of characterization required in the future. A tank-by-tank safety evaluation that assesses the safety status of each tank using a combination of characterization information from the HPT sampling and analyses and applicable items from the safety issue supporting technical documents will be developed and updated annually if sufficient new information is available. The proposed format and content outline for the evaluation is scheduled to be submitted in January 1997. The initial evaluation is scheduled for completion in July 1998 after completion of the HPT sampling and analysis.

5.6.3 MILESTONES

Completion of the milestones listed below will close out DOE actions associated with Recommendation 93-5 sub-element for characterizing the Hanford Site HLW tanks.

- 5.6.3.1 Complete Tank Waste Characterization Basis Sampling and Analysis**
Statement: Complete the sampling and analysis specified by the Tank Waste Characterization Basis (approximately 28 tanks) to provide the highest priority information requested by the programmatic DQOs.
Responsible Manager: Assistant Manager, TWRS
Applicable facilities and programs: TWRS
Milestone deliverables/due dates:
- a. Letter reporting completion of comparison between truck and cart vapor sampling systems.
Due Date: September 1996*
 - b. Letter reporting implementation of FTIR moisture analysis capability in 222-S Laboratory.
Due Date: November 1996*
 - c. Letter reporting submittal of proposed content and format for tank-by-tank safety status evaluation.
Due Date: January 1997*
 - d. Updated HTCEs.
Due Date: June 1997*
 - e. Letter reporting verification of headspace homogeneity and evaluation of variations in headspace vapor concentrations in passively ventilated tanks with changing atmospheric temperatures.
Due Date: October 1997*
 - f. Standard inventory estimates for all tanks.
Due Date: November 1997*
 - g. Letter report completion of Tank Waste Characterization Basis (Brown et al. 1995) High Priority Tanks sampling and analysis.
Due Date: March 1998*
 - h. Letter reporting completion of tank-by-tank safety status evaluation.
Due Date: July 1998*
 - i. Update Tank Content Models or define limitations of the models.
Due Date: December 1998*
 - j. Letter reporting completion of core sampling of all tanks (assumes no repeat sampling).
Due Date: December 2002*

6 ORGANIZATION AND MANAGEMENT

6.1 CHANGE CONTROL

Complex, long range plans require sufficient flexibility to accommodate changes in milestones, actions, or completion dates that may be necessary due to additional information, improvements, or changes in baseline assumptions. The Department's policy is to:

- bring to the Board 's attention any substantive changes to this implementation plan as soon as identified and prior to the passing of the milestone date
- have the Secretary approve all revisions to the scope and schedule of plan milestones
- clearly identify and describe the revisions, and bases for the revisions.

Fundamental changes to the plan's strategy or scope or schedule will be provided to the Board through formal revision of the implementation plan. Other changes to the scope or schedule of planned milestones will be formally documented in quarterly reports, along with the basis for the changes, and appropriate corrective actions.

6.2 REPORTING AND REVIEW

To assure that the various Department implementing elements and the Board remain informed of the status of the progress of plan implementation, the Department's policy is to provide periodic progress reports. For this plan, the Department will issue progress reports quarterly, within one month of the close of each quarter during plan implementation. Quarters will coincide with the calendar and fiscal year quarters: January-March; April-June; July-September; and October-December. Annual reviews of this Implementation Plan will be conducted.

6.3 QUALITY ASSURANCE

The *Quality Assurance Program Plan* (Sparks 1995) outlines the Quality Management System for the Characterization Project. This system is designed to assure compliance with the quality requirements specified in 10 CFR 830.120, and the *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement [TPA]) (Ecology et al. 1994). This overall structure will include specific Quality Assurance Project Plans for the key characterization tasks, as well as existing procedures, sampling plans and reports, work instructions, and records.

APPENDIX A

ACRONYMS AND ABBREVIATIONS

BIO	Basis for Interim Operation
BiPO ₄	Bismuth Phosphate
Board	Defense Nuclear Facilities Safety Board
°C	degrees Celsius
CPS	Criticality Prevention Specification
¹³⁷ Cs	Cesium 137
CSER	Criticality Safety Evaluation Report
DNFSB	Defense Nuclear Facilities Safety Board
DOE	Department of Energy
DOE-HQ	Department of Energy, Headquarters
DOE-RL	Department of Energy, Richland Operations Office
DQO	Data Quality Objective
DST	Double-Shell Tank
EDTA	Ethylenediaminetetraaceticacid
FSAR	Final Safety Analysis Report
FTIR	Fourier Transform Infrared Spectroscopy
FY	Fiscal Year
HASQAP	Hanford Analytical Services Quality Assurance Plan
HDW	Hanford Defined Wastes
HLW	High Level Waste
HTCE	Historical Tank Content Estimates
IDA	Iminodiaceticacid
INEL	Idaho National Energy Laboratory
ISB	Interim Safety Basis
J/g	Joules/gram
k	Infinite critical multiplication factor
LANL	Los Alamos National Laboratory
LAW	Low Activity Waste
LFL	Lower Flammability Limit
LLW	Low Level Waste
NTA	Nitrilotriaceticacid
ORIGEN2	A revised and updated version of the <i>Oak Ridge Isotope Generation and Depletion Code</i> , ORNL-5621, (Croff 1980)
ORNL	Oak Ridge National Laboratory
PNNL	Pacific Northwest National Laboratory, formerly the Pacific Northwest Laboratory
PUREX	Plutonium/Uranium Extraction
REDOX	Reduction/Oxidation
SORWT	Sort on Radioactive Waste Types
SST	Single-Shell Tank
⁹⁰ Sr	Strontium 90
⁹⁹ Tc	Technetium 99
TCP	Tank Characterization Plan
TCR	Tank Characterization Report
TOC	Total Organic Carbon

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TPA	Tri-Party Agreement
TSR	Technical Safety Requirement
TWRS	Tank Waste Remediation System
USQ	Unreviewed Safety Question
WHC	Westinghouse Hanford Company
WSTRS	Waste Status and Transaction Record Summary
wt%	Weight percent

APPENDIX B

GLOSSARY

Administrative Controls. Provisions relating to organization and management, procedures, record keeping, assessment, and reporting necessary to ensure safe operation of a facility.

Aging. Decomposition of high energy compounds into lower energy products.

Authorization Basis. Those aspects of the facility design basis and operational requirements relied upon by DOE to authorize operation. These aspects are considered to be important to the safety of the facility operations. The Authorization Basis is described in documents such as the facility Safety Analysis Report and other safety analysis; Hazard Classification Documents, and TSRs, DOE-issued safety evaluation reports, and facility-specific commitments made in order to comply with DOE Orders or policies.

Bias. The difference between the mean of the measured parameter and the true value of the parameter. Characterization biases are introduced by factors such as tank heterogeneity, sampler selectivity, and laboratory analytic sub-sample size.

Bounding Gas Volume. A model-based estimate of the maximum concentration and composition of flammable gases retained in the condensed-phase wastes.

Characterization. Characterization is understanding the Hanford tank waste chemical, physical, and radiological properties to the extent necessary to insure safe storage and interim operation, and ultimate disposition of the waste.

Condensed-Phase Wastes. Hanford Site HLW tanks contain both vapor and condensed-phase wastes. The condensed-phase refers to the solid and liquid wastes.

Data Quality Objective (DQO). The DQO process provides a systematic method to determine what data are needed and the required accuracy to support a decision. Throughout this report the terms DQO and data requirements are used interchangeably.

Defense-in-Depth. An approach to facility safety that builds layers of defense against hazardous materials so that no one layer by itself, no matter how good, is completely relied upon. To compensate for potential human and mechanical failures, defense-in-depth is based on several layers of protection with successive barriers to prevent the release of hazardous material to the environment. This approach includes protection of the barriers to avert damage to the plant and to the barriers themselves. It includes further measures to protect the public, workers, and the environment from harm in case these barriers are not fully effective.

Design Basis. Design Basis is the set of requirements that bound the design of systems, structures, and components within the facility. These design requirements include consideration of safety, plant availability, efficiency, reliability, and maintainability. Some aspects of the design basis are important to safety. Others are not.

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Final Safety Analysis Report (FSAR). That report that documents the adequacy of safety analysis for a nuclear facility to ensure that the facility can be constructed, operated, maintained, shut down, and decommissioned safely and in compliance with applicable laws and regulations.

High Priority Tanks. The tanks determined to provide the highest value information from sampling and analysis for the satisfaction of programmatic needs. These tanks are defined by the *Tank Waste Characterization Basis* (Brown et al. 1995), Tables 9-2 through 9-4.

Infinite Multiplication Factor (k). The infinite multiplication factor is the ratio of the average number of thermal neutrons produced (and hence absorbed) in one generation to the number of thermal neutrons produced (or absorbed) in the preceding generation, in an infinite medium.

In-Situ. Measurements taken in their original place or position.

Interim Safety Basis. The document *Hanford Site Tank Farm Facilities Interim Safety Basis* (Stahl 1993) identifies the Tank Farms Safety Basis by referencing existing safety analysis documentation.

Manage Tank Waste Function. A functional area of TWRS. In particular, the management during storage, characterization, transfers, and concentration of existing and new tank wastes that are not the products of retrieval for final processing.

Off-Ramp Tank. Off Ramp (Eberlein 1996) tanks are alternate tanks that could be sampled to meet characterization needs as defined in the *Tank Waste Characterization Basis* (Brown et al, 1995) if the High Priority Tanks cannot be sampled.

Organic Complexants. Organic salts (such as EDTA) that were used to solubilize (complex) fissile material. Some of these complexants were sent to the Tank Farms.

Phenomena. Chemical or physical reactions that are capable of occurring within the mixture of tank chemicals.

Privatization. An approach to completing major work scope by industry experts using facilities that are privately developed, financed, constructed, owned, operated, decontaminated, decommissioned, and closed under the requirements of the Resource Conservation and Recovery Act.

Risk. The quantitative or qualitative expression of possible loss that considers both the probability that a hazard will cause harm and the consequences of that event.

Safety Analysis. A documented process: (1) to provide systematic identification of hazards within a given DOE operation; (2) to describe and analyze the adequacy of measures taken to eliminate, control, or mitigate identified hazards; and (3) to analyze and evaluate potential accidents and their associated risks.

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Safety Basis. The combination of information relating to the control of hazards at a nuclear facility (including design, engineering analyses, and administrative controls) upon which DOE depends for its conclusion that activities at the facility can be conducted safely.

Sampling and Analysis Plan. The Sampling and Analysis Plan integrates the DQOs applicable to a tank and specifies the sampling and laboratory analysis required to satisfy the information needs for the tank.

Simulant. A chemical replication of tank wastes using recipes derived from characterization data and/or from the Hanford Site processing facilities' flowsheets.

Source Terms. Estimates of the maximum possible concentrations of radionuclides and toxic constituents in the Hanford Site Tank Farms. This estimate is used to determine accident consequences.

Surrogate. A chemical mixture that contains the major chemically reactive compounds of a waste type (e.g., a mixture of EDTA and sodium nitrate).

Tank Characterization Database. A database that contains tank waste sampling data.

Tank Characterization Plan (TCP). The Tank Characterization Plans (TCPs) are developed for each tank and integrate the various decision-based DQOs which apply to that tank.

Tank Waste Characterization Basis. The document *Tank Waste Characterization Basis* (Brown et al. 1995), WHC-SD-WM-TA-164. This document describes the identification and prioritization of programmatic information needs to address various safety issues, historical/modeling confirmation, operations safety, and disposal system design and safety. The output from this document is a prioritized tank sampling list.

Technical Basis for Characterization. Called the "Technical Basis" throughout the document. The total body of technical information that defines the knowledge and actions necessary to characterize the Hanford Site HLW Tanks. This includes, but is not limited to, information needs for safety issue resolution such as found in Approach for Tank Safety Characterization of Hanford Site Waste, WHC-EP-0843 (Meacham et al. 1995c), programmatic DQOs, historical process information such as documented by the HTCE Reports, and tank sampling and analysis information such as documented by individual TCRs.

Technical Safety Requirements (TSRs). Those requirements that define the conditions, safe boundaries, and the management or administrative controls necessary to ensure the safe operation of a nuclear facility and to reduce the potential risk to the public and facility workers from uncontrolled releases of radioactive materials or from radiation exposure due to inadvertent criticality. A TSR consists of operating limits, surveillance requirements, administrative controls, use and application instructions, and the bases thereof.

Tri-Party Agreement (TPA). *Hanford Federal Facility Agreement and Consent Order* (Ecology et al. 1994).

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Watch List. Those tanks designated for special monitoring and controls under the Wyden Bill.

APPENDIX C

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APPENDIX D

SUMMARY OF MILESTONES AND SCHEDULE

MILESTONES. This Appendix summarizes the milestones contained in Sections 5.4, 5.5, and 5.6.

- 6.3.0.1 TWRS Manage Tank Waste Function Authorization Basis**
Statement: Upgrade the Authorization Basis for the TWRS Manage Tank Waste Function
Responsible Manager: Assistant Manager, TWRS
Applicable facilities and programs: TWRS
Milestone deliverables/due dates:
- a. Letter reporting completion of Comprehensive Source Terms Report.
Due Date: June 1996
 - b. Report on lightning evaluation, and if the probability exceeds 1×10^{-6} per year, evaluate potential mitigating options for lightning strikes.
Due Date: August 1996
 - c. Approved BIO.
Due Date: December 1996
 - d. Approved FSAR.
Due Date: June 1997
- 6.3.0.2 Ferrocyanide**
Statement: Analyze selected samples to reduce data uncertainties and issue final report.
Responsible Manager: Assistant Manager, TWRS
Applicable facilities and programs: TWRS
Milestone deliverables/due dates:
- a. Topical report on resolution of Ferrocyanide Safety Issue. This report will include the evaluation of sample analyses confirming ferrocyanide aging (If the results do not confirm that any remaining ferrocyanide is bounded by least favorable decomposition conditions, this Implementation Plan will be revised).
Due Date: January 1997
- 6.3.0.3 Organic Complexants**
Statement: Complete testing and evaluation confirming simulant results with real waste.
Responsible Manager: Assistant Manager, TWRS
Applicable facilities and programs: TWRS
Milestone deliverables/due dates:
- a. Letter reporting completion of supporting technical document on Organic Complexant Safety Issue. (This topical report will describe the current understanding of the issue and future work for resolution).
Due Date: December 1996
 - b. Letter reporting results of testing completion (using real waste samples) to confirm safe storage criteria, and organic solubility and aging effects on fuel

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content. If models are confirmed, an assessment of tank wastes compared to safe storage criteria will be scheduled.
Due Date: November 1998

6.3.0.4 Organic Solvents

Statement: Use vapor samples to identify organic solvent tanks.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Letter reporting completion of safety assessment covering pool and entrained organic solvent fires.
Due Date: October 1996
- b. Letter reporting completion of organic speciation of core samples for BY-108 and BY-110, and auger samples for C-102.
Due Date: October 1996
- c. Letter reporting completion of supporting technical document for Organic Solvent Safety Issue. (This topical report will describe the current understanding of the issue and future work for resolution).
Due Date: December 1996
- d. Letter reporting completion of vapor sampling of all SSTs.
Due Date: December 1999
- e. Letter reporting adequate vent path in all SSTs suspected of containing organic solvents.
Due Date: April 2000
- f. Letter reporting completion of vapor sampling of all DSTs.
Due Date: December 2000

6.3.0.5 Flammable Gas

Statement: Complete analytical evaluations and steady-state vapor samples to determine which flammable gas tanks require mitigative actions. Qualify saltwell pumping and rotary-mode core sampling for flammable gas environments.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Report documenting analyses to determine if additional tanks have potential to exceed 25% of the LFL.
Due Date: June 1996
- b. Letter reporting evaluation of gas monitoring instrumentation upgrade needs for additional tanks with the potential to exceed 25% of the LFL.
Due Date: August 1996
- c. Letter reporting approval of safety assessment for rotary mode core sampling in flammable gas tanks and documenting incorporation into the Authorization Basis.
Due Date: September 1996
- d. Letter reporting qualification of Rotary Mode Core Sampling System for use in Flammable Gas Tanks.
Due Date: September 1996

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- e. Letter reporting approval of safety assessment for saltwell pumping in flammable gas tanks and documenting incorporation into the Authorization Basis.
Due Date: October 1996
- f. Letter reporting completion of AN Tank Farm ventilation upgrade.
Due Date: November 1996
- g. Letter reporting completion of flammable gas safety screening of remaining passively ventilated SSTs to determine if steady-state vapors are less than 25% of the LFL. (If any tanks are greater than 25% of the LFL, the letter will include the schedule to evaluate corrective actions).
Due Date: November 1996
- h. Letter reporting completion of supporting technical document on Flammable Gas Safety Issue. (This topical report will describe the current understanding of the issue and future work for resolution).
Due Date: December 1996
- i. Letter reporting that external equipment spark sources in flammable gas tanks have been managed by controls or the equipment has been modified.
Due Date: December 1996
- j. Letter reporting completion of voidmeter and viscometer readings in tanks AN-103, AN-104, and AN-105.
Due Date: December 1996
- k. Letter reporting completion of retained gas sampling in tanks AW-101, AN-103, AN-104, AN-105, and U-103. If the retained gas sampling performance is satisfactory, include future deployment schedule.
Due Date: March 1997
- l. Letter reporting refinement of flammable gas generation/retention models using void meter and retained gas sampling data.
Due Date: May 1997

6.3.0.6 High Heat

Statement: Retrieve wastes from tank C-106.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Letter reporting completion of tank C-106 supernatant and sludge sampling and analysis.
Due Date: October 1996
- b. Letter reporting completion of tank C-106 retrieval safety assessment.
Due Date: July 1997
- c. Letter reporting initiation of tank C-106 waste retrieval.
Due Date: October 1997
- d. Letter reporting completion of topical report to resolve the High Heat Safety Issue.
Due Date: May 1998

6.3.0.7 Criticality

Statement: Resolve the Criticality Safety Issue.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

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Milestone deliverables/due dates:

- a. Letter reporting completion of topical report to resolve the Criticality Safety Issue.
Due Date: December 1996

6.3.0.8 Disposal Program Characterization

Statement: Complete sampling and analysis of *Tank Waste Characterization Basis* (Brown et al. 1995) tanks for disposal.

Responsible Manager: Assistant Manager, TWRS

Applicable Facilities and Programs: TWRS

Milestone deliverables/due date:

- a. Letter report completion of *Tank Waste Characterization Basis* (Brown et al. 1995) High Priority Tanks sampling and analysis for the Disposal Program.
Due Date: March 1998

6.3.0.9 Complete Tank Waste Characterization Basis Sampling and Analysis

Statement: Complete the sampling and analysis specified by the Tank Waste Characterization Basis (approximately 28 tanks) to provide the highest priority information requested by the programmatic DQOs.

Responsible Manager: Assistant Manager, TWRS

Applicable facilities and programs: TWRS

Milestone deliverables/due dates:

- a. Letter reporting completion of comparison between truck and cart vapor sampling systems.
Due Date: September 1996
- b. Letter reporting implementation of FTIR moisture analysis capability in 222-S Laboratory.
Due Date: November 1996
- c. Letter reporting submittal of proposed content and format for tank-by-tank safety status evaluation.
Due Date: January 1997
- d. Updated HTCEs.
Due Date: June 1997
- e. Letter reporting verification of headspace homogeneity and evaluation of variations in headspace vapor concentrations in passively ventilated tanks with changing atmospheric temperatures.
Due Date: October 1997
- f. Standard inventory estimates for all tanks.
Due Date: November 1997
- g. Letter report completion of *Tank Waste Characterization Basis* (Brown et al. 1995) High Priority Tanks sampling and analysis.
Due Date: March 1998
- h. Letter reporting completion of tank-by-tank safety status evaluation.
Due Date: July 1998
- i. Update Tank Content Models or define limitations of the models.
Due Date: December 1998
- j. Letter reporting completion of core sampling of all tanks (assumes no repeat sampling).
Due Date: December 2002

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Figure D-1: Characterization Summary Schedule

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APPENDIX E

RECOMMENDATION 93-5 COMPLETED ACTIONS

The table below documents those completed actions that are credited to each Recommendation 93-5 element and sub-element. Where the sub-element is noted to be "Closed," the completion of the commitments listed are considered to be adequate to close that sub-element. Where the sub-element is noted to be "Open," the commitments listed and the completion of the milestones listed in Section 5 of this document are considered adequate to close this sub-element.

Table E-1: Recommendation 93-5 Original Implementation Plan Completed Actions Credited for Closure of the Recommendation

Commitment		Closure Document
#	Description	
Primary Element 1. (Open) - Undertake a comprehensive reexamination and restructuring of the characterization effort with the objectives of accelerating sampling schedules, strengthening technical management of the effort, and completing safety-related sampling and analysis of watch list tanks within a target period of two years, and the remainder of the tanks by a year later;		
1.1	Enhance Westinghouse Hanford Company (WHC) Characterization Program Management Staff.	DOE-RL letter 94-OCH-055 dated June 27, 1994
1.2	Reduce number of management layers in WHC TWRS to improve lines.	DOE-RL letter 94-OCH-056 dated June 30, 1994
3.1	Initiate construction of second and third rotary-mode core sampling trucks.	Reported closed as of November 1993 in the original Implementation Plan.
3.3	Complete qualification of first push-mode crew.	DOE-RL letter 94-OCH-021 dated June 30, 1994
3.5	Cognizant Engineer Training: Complete training and qualification requirements for sampling cognizant engineers.	DOE-RL letter 94-OCH-078 dated August 11, 1994
3.7	Complete qualification of first rotary-mode crews and vapor/grab/auger sampling crew.	DOE-RL letter 94-OCH-021 dated June 30, 1994
3.9	Develop detailed plans for acquiring and training additional crews for sampling trucks.	DOE-RL letter 94-OCH-021 dated June 30, 1994

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Table E-1: Recommendation 93-5 Original Implementation Plan Completed Actions Credited for Closure of the Recommendation

Commitment		Closure Document
#	Description	
3.11	<p>Deploy additional Rotary-Mode Core Sampling systems. Fabricate and/or procure new core sampling trucks and support equipment as indicated by Characterization Program needs. Current planning entails developing one complete system, and procuring one additional base drill rig. A design specification document and drawings, based on the design of the rotary-mode core sampling system, will be prepared. Documentation to initiate fabrication of equipment will be issued. Equipment for the Rotary Mode Core Sampling System includes a core sampling truck, nitrogen purge gas trailer, generator, support trailer, cask truck, and other ancillary equipment.</p>	DOE-RL letter 95-CHD-089 dated October 4, 1995
<p>Sub-Element 1.a (Open) - In accordance with the above, give priority in the schedule of tanks to be sampled to the watch list tanks and others with identified safety problems, and priority to the chemical analyses providing information important to ensuring safety in the near term during the period of custodial management. Other analyses, required by statutes such as the Resource Conservation and Recovery Act prior to final disposition of the waste, should not be cause for delay of safety-related analyses. In most cases, analyses needed for long term disposition may be postponed until more pressing safety-related analyses are completed.</p>		

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Table E-1: Recommendation 93-5 Original Implementation Plan Completed Actions Credited for Closure of the Recommendation

Commitment		Closure Document
#	Description	
1.21	Complete DQOs for all TWRS program elements that may need data.	<ol style="list-style-type: none"> 1. Ferrocyanide Safety Issue DQO Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 2. C-103 Vapor DQO Draft Report: DOE-RL letter 95-TSD-115 dated September 12, 1995 3. C-103 Dip Sample DQO Final Report: DOE-RL letter 95-TSD-115 dated September 12, 1995 4. C-106 High Heat DQO Report: DOE-RL letter 95-TSD-115 dated September 12, 1995 5. Organic Safety Issue DQO Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 6. Safety Screening Module DQO Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 7. Waste Compatibility DQO Report: DOE-RL letter 95-CHD-078 dated September 18, 1995 8. In-tank Generic Vapor DQO Final Draft Report: DOE-RL letter 95-TSD-123 dated September 29, 1995 9. Vapor Rotary Core DQO Final Draft Report: DOE-RL letter 95-CHD-078 dated September 18, 1995 10. Hydrogen Generating DQO Final Draft Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 11. Pretreatment DQO Draft Report: DOE-RL letter 94-CHD-113, dated November 4, 1994 12. HLW Immobilization DQO Draft Report: DOE-RL letter 95-CHD-078 dated September 18, 1995 13. LLW Immobilization DQO Draft Report: DOE-RL letter 95-CHD-078 dated September 18, 1995
2.1	Complete DQOs for all six safety issues.	DOE-RL letter 95-TSD-116 dated September 12, 1995
2.2	Complete the safety screening DQO.	DOE-RL letter 95-TSD-116 dated September 12, 1995
<p>Sub-Element 1.b (Closed) - Re-examine protocols for gaining access to the tanks for sampling with the objective of simplifying documentation and approval requirements.</p>		

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Table E-1: Recommendation 93-5 Original Implementation Plan Completed Actions Credited for Closure of the Recommendation

Commitment		Closure Document
#	Description	
4.1	Issue approved broad-based Environmental Assessment.	The Assessment, dated February 10, 1994, was signed out by Tara O'Toole, Assistant Secretary, on February 25, 1994
4.2	DOE-RL to submit a request for delegation of authority to DOE-HQ.	Request was submitted by DOE-RL on January 10, 1994. Approval was signed by Thomas Grumbly and Tara O'Toole on July 28, 1994
4.3	Obtain delegation of authority for DOE-RL to approve safety and environmental documentation for TWRS.	Request was submitted by DOE-RL on January 10, 1994. Approval was signed by Thomas Grumbly and Tara O'Toole on July 28, 1994
<p>Sub-Element 1.c (Closed) - Increase the laboratory capacity and activities dedicated to tank sample analysis:</p> <p>(i) Expedite efforts to obtain and begin utilizing additional sampling and analytical equipment now being procured, and the training of personnel needed for an enlarged through-put capacity.</p> <p>(ii) Explore availability and utility of laboratory services on- and off-site, such as Hanford's Fuel Materials and Examination Facility and the INEL and LANL laboratories, for accelerating the waste characterization effort.</p>		
5.3	New Extruder Operability.	DOE-RL letter 94-OCH-110 dated October 26, 1994
5.6	Evaluate Laboratory Staff Training.	DOE-RL letter 94-OCH-064 dated July 13, 1994
5.7	Develop and Implement Enhanced Training Plan for laboratory staff.	DOE-RL letter 94-OCH-064 dated July 13, 1994
5.9	Issue plan to upgrade INEL laboratory to ready-to-serve mode.	DOE-RL letter 94-OCH-046, dated June 28, 1994
5.10	Issue plan to upgrade Los Alamos National Laboratory (LANL) laboratory to ready-to-serve mode.	DOE-RL letter 94-OCH-045, dated June 30, 1994
5.12	Upgrade INEL Laboratory to ready-to-serve mode.	DOE-RL letter 94-CHD-127, dated November 4, 1994
5.13	Upgrade LANL Laboratory to ready-to-serve mode.	DOE-RL letter 95-CHD-025 to DNFSB dated April 10, 1995

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Table E-1: Recommendation 93-5 Original Implementation Plan Completed Actions Credited for Closure of the Recommendation

Commitment		Closure Document
#	Description	
Primary Element 2. (Open) - Integrate the characterization effort into the systems engineering effort for the Tank Waste Remediation System:		
1.12	All WHC Characterization Program management staff will complete Systems Engineering training.	DOE-RL letter 94-OCH-015, dated May 25, 1994
1.13	Detailed Functional Analysis Report.	DOE-RL letter 94-OCH-027, dated June 1, 1994
1.14	Complete characterization portions of the initial system engineering analysis result.	DOE-RL letter 94-OCH-066, dated June 30, 1994
Sub-Element 2.a (Open) - Schedule tank sampling consistent with engineering and planning for removal, pre-treatment, and vitrification of the tank wastes.		
	None	
Sub-Element 2.b (Closed) - Critically examine the list of chemical analyses done on samples to establish the smallest set needed to satisfy safety requirements.		

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Table E-1: Recommendation 93-5 Original Implementation Plan Completed Actions Credited for Closure of the Recommendation

Commitment		Closure Document
#	Description	
1.21	Complete DQOs for all TWRS program elements that may need data.	<ol style="list-style-type: none"> 1. Ferrocyanide Safety Issue DQO Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 2. C-103 Vapor DQO Draft Report: DOE-RL letter 95-TSD-115 dated September 12, 1995 3. C-103 Dip Sample DQO Final Report: DOE-RL letter 95-TSD-115 dated September 12, 1995 4. C-106 High Heat DQO Report: DOE-RL letter 95-TSD-115 dated September 12, 1995 5. Organic Safety Issue DQO Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 6. Safety Screening Module DQO Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 7. Waste Compatibility DQO Report: DOE-RL letter 95-CHD-078 dated September 18, 1995 8. In-tank Generic Vapor DQO Final Draft Report: DOE-RL letter 95-TSD-123 dated September 29, 1995 9. Vapor Rotary Core DQO Final Draft Report: DOE-RL letter 95-CHD-078 dated September 18, 1995 10. Hydrogen Generating DQO Final Draft Report: DOE-RL letter 95-TSD-116 dated September 12, 1995 11. Pretreatment DQO Draft Report: DOE-RL letter 94-CHD-113, dated November 4, 1994 12. HLW Immobilization DQO Draft Report: DOE-RL letter 95-CHD-078 dated September 18, 1995 13. LLW Immobilization DQO Draft Report: DOE-RL letter 95-CHD-078 dated September 18, 1995.
2.1	Complete DQOs for all six safety issues.	DOE-RL letter 95-TSD-116 dated September 12, 1995
2.2	Complete the safety screening DQO.	DOE-RL letter 95-TSD-116 dated September 12, 1995
Sub-Element 2.c (Closed) - Strengthen the management and conduct of the sampling operations.		
1.1	Enhance WHC Characterization Program Management Staff.	DOE-RL letter 94-OCH-055 dated June 27, 1994

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Table E-1: Recommendation 93-5 Original Implementation Plan Completed Actions Credited for Closure of the Recommendation

Commitment		Closure Document
#	Description	
1.2	Reduce number of management layers in WHC TWRS to improve lines of communication.	DOE-RL letter 94-OCH-056, dated June 30, 1994
1.3	Improve DOE-RL Oversight.	DOE-RL letter 94-OCH-023 dated May 26, 1994
1.6	Define responsibilities of key WHC managers associated with Characterization Program.	DOE-RL letter 94-OCH-068 dated June 12, 1994

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APPENDIX F

TABLE F-1: *TANK WASTE CHARACTERIZATION BASIS* HIGH PRIORITY TANKS

Table is on the succeeding pages.

Table F-1: Tank Waste Characterization Basis High Priority Tanks

Waste Types:

<i>BiPO₄ - Bismuth Phosphate</i>	<i>EB - Evaporator Bottom</i>	<i>TBP - Tributyl Phosphate</i>
<i>DSSF- Double Shell Slurry Feed</i>	<i>PUREX - Plutonium/Uranium Extraction</i>	<i>REDOX - Reduction/Oxidation</i>

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Table F-1: Tank Waste Characterization Basis High Priority Tanks

TANK PRIORITIZATION LIST			ISSUES		WASTE TYPE						WATCH LIST		
	Tank	Relative Value	PHENOMENON RELATED	COMPOSITION RELATED	BiPO ⁴	EB	TBP	DSSF	PUR-EX	RE-DOX	FeCN	Flam	Org
1	BY-105	100	Organic solubility; Organic aging; Ferrocyanide aging; Moisture retention/ distribution.	Organic fuel distribution; Ferrocyanide fuel distribution; Examine bounding saltcake forms; Examine bounding sludge forms; Determine spatial variability in complex tank;		X	X				X		
2	U-105	93	Organic solubility; Organic aging; Moisture retention/ distribution.	Organic fuel distribution; Spatially complex; Determine if metal waste type exists.	X	X						X	X
3	U-109	91	Organic solubility; Organic aging; Moisture retention/ distribution.	Organic fuel distribution; Determine spatial variability in simple tank; Range of variability in different saltcakes.		X						X	
4	BY-103	86	Organic solubility; Organic aging; Ferrocyanide aging; Minimum fuel concentration required to support propagation; Moisture retention/ distribution.	Organic fuel distribution; Ferrocyanide fuel distribution; Spatial variability in complex tank; Examine bounding saltcake forms; Examine bounding sludge forms.		X	X				X		
5	U-108	84	Organic solubility; Organic aging; Moisture retention/ distribution.	Organic fuel distribution; Spatially complex; Determine if metal waste type exists.		X				X		X	
6	U-107	76	Organic solubility; Organic aging; Moisture retention/ distribution.	Organic fuel distribution.	X	X						X	X

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Table F-1: Tank Waste Characterization Basis High Priority Tanks

TANK PRIORITIZATION LIST			ISSUES		WASTE TYPE						WATCH LIST		
	Tank	Relative Value	PHENOMENON RELATED	COMPOSITION RELATED	BiPO ⁴	EB	TBP	DSSF	PUR-EX	RE-DOX	FeCN	Flam	Org
7	BY-106	74	Organic solubility; Organic aging; ferrocyanide aging; Moisture retention/ distribution.	Organic fuel distribution; Ferrocyanide fuel distribution.		X	X				X		
8	S-102	74		Range of variability in different saltcakes; Spatial variability in simple tank.		X						X	X
9	SX-103	67		Confirm composition of REDOX sludge; Spatial variability in tank containing saltcake and sludge.		X				X		X	X
10	BY-108	65 C	Organic aging; Ferrocyanide aging; Organic solubility; Moisture retention/ distribution.	Organic fuel distribution; Ferrocyanide fuel distribution; vapor detection of organic solvent.		X	X				X		
11	A-101	62		Model of major saltcake composition; Spatial variability in simple tank.		X						X	X
12	TX-118	61		Resolve historical conflicts on saltcake, ferrocyanide, and organic waste.		X					X		X
13	SX-104	61		Confirm composition of REDOX sludge; spatial variability in tank containing saltcake and sludge.		X				X		X	

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Table F-1: Tank Waste Characterization Basis High Priority Tanks

TANK PRIORITIZATION LIST			ISSUES		WASTE TYPE						WATCH LIST		
	Tank	Relative Value	PHENOMENON RELATED	COMPOSITION RELATED	BiPO ⁴	EB	TBP	DSSF	PUR-EX	RE-DOX	FeCN	Flam	Org
14	BY-110	52 C	Ferrocyanide aging; Moisture retention/distribution.	Spatial variability in complex tank; Corroborate vapor detection of organic solvent; Examine bounding saltcake forms; Examine bounding sludge forms.		X	X				X		
15	TX-111	51		Confirm T2 saltcake waste composition.		X							
16	BY-104	51	Ferrocyanide aging; Minimum fuel concentration required to support propagating reaction; Moisture retention/distribution.	Spatial variability in complex tank; Examine bounding saltcake forms; Examine bounding sludge forms.		X	X				X		
17	C-104	50		Greatest vertical and horizontal variability. Contains minimum of eight waste types.					X				
18	S-107	50 C		Confirm REDOX waste composition; Spatially complex tank.		X				X			
19	S-101	50		Confirm saltcake waste composition; Confirm REDOX waste composition; Spatially complex tank.		X				X			
20	TY-103	50	Ferrocyanide aging; Moisture retention/distribution.	Ferrocyanide fuel distribution.			X				X		

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Table F-1: Tank Waste Characterization Basis High Priority Tanks

TANK PRIORITIZATION LIST			ISSUES		WASTE TYPE						WATCH LIST		
	Tank	Relative Value	PHENOMENON RELATED	COMPOSITION RELATED	BiPO ₄	EB	TBP	DSSF	PUR-EX	RE-DOX	FeCN	Flam	Org
21	SX-101	49	Sample material for pretreatment/ disposal studies.	Confirm saltcake waste composition; Confirm REDOX waste composition; Spatially complex tank.		X				X		X	
22	S-110	47		Confirm composition of REDOX sludge; Determine spatial variability in tank containing saltcake and sludge.		X				X			
23	AW-101	47	Flammable gas generation/ retention. Sample material for pretreatment/ disposal studies.					X				X	
24	AN-104	46	Flammable gas generation/ retention. Sample material for pretreatment/ disposal studies.					X				X	
25	AX-101	43		Confirm model of major saltcake composition; Spatial variability in simple tank.		X						X	
26	AN-105	37	Flammable gas generation/ retention. Sample material for pretreatment/ disposal studies.					X				X	
27	AN-103	36	Flammable gas generation/retention.					X				X	
28	B-104	15 C		Multiple waste types to be confirmed; Unknown waste type inputs; Spatially complex tank.	X	X							

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APPENDIX G

HIGH PRIORITY TANKS SCHEDULE

The schedule is on the succeeding pages.

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APPENDIX H

CROSS WALK TO BOARD RECOMMENDATIONS

The following table provides a cross-reference between the Recommendation 93-5 primary elements and sub-elements and the relevant sections in this revision to the plan.

<i>Table H-1: Crosswalk Between Recommendation 93-5 and Implementation Plan Revision 1 Sections.</i>	
<i>DNFSB Recommendation Element</i>	<i>Implementation Plan Revision 1 Section</i>
<i>1.</i>	<i>5.2, 5.4, 5.6, App E, J</i>
<i>1.a</i>	<i>5.4, 5.6, App E</i>
<i>1.b</i>	<i>App E</i>
<i>1.c</i>	<i>App E, J</i>
<i>2.</i>	<i>5.2, 5.6, App E</i>
<i>2.a</i>	<i>5.5, 5.6</i>
<i>2.b</i>	<i>5.4, App E, J</i>
<i>2.c</i>	<i>App E</i>

Figure I-1: Core Sampling Sequence 1994-1997

Phase A									
Phase B									
1Q 94	2Q 94	3Q 94	4Q 94	1Q 95	2Q 95	3Q 95	4Q 95		
	C-111	SY-103		BY-106 C-103 C-105 C-107 U-201 U-202	B-101 B-104 (HPT) BX-103 BX-109 U-203 U-204	B-106 BY-108 (HPT) S-107 (HPT)	B-203 B-204 BX-112 BY-104 (HPT) BY-106 (HPT) BY-110 (HPT)		
Phase A									
Phase B									
Phase C									
1Q 96	2Q 96	3Q 96	4Q 96	1Q 97	2Q 97	3Q 97	4Q 97		
BX-104 S-102 (HPT) U-105 (HPT) U-107 (HPT) U-109 (HPT)	AN-105 (HPT) AW-101 (HPT) S-101 (HPT) S-110 (HPT) S-111 (OR) U-102 (OR) U-106 (OR) U-108 (HPT)	AN-104 (HPT) S-103 (OR) S-109 (OR) TY-103 (HPT) U-103 (OR)	AN-103 (HPT) AZ-101 BY-103 (HPT) BY-105 (HPT) SX-103 (HPT) SY-102 TY-102 (OR)	A-101 (HPT) AW-105 C-104 (HPT) S-110 (HPT) SX-101 (HPT) SX-104 (HPT) TX-111 (HPT) TX-118 (HPT)	AW-103 AX-101 (HPT) B-108 C-102 S-110 (HPT) S-112 TX-116 U-107 (HPT)	S-105 S-10 SX-107 SX-109 TX-101 TX-105	S-108 SX-110 SX-111 TX-103 TX-10 U-111		

HPT = High Priority Tank
 OR = Off Ramp

NOTE: 2 Cores per tank, except HPT cores per tank are as required by Tank Waste Characterization Basis, WHC-SD-WM-TA-154, Rev. 1.

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APPENDIX I

FUTURE PACE OF SAMPLING PROGRAM

1 CORE SAMPLING

Core sampling to satisfy the intent of Recommendation 93-5 occurs in three phases. The three phases are conceptual in nature rather than strictly chronological.

- *Phase A: Includes tanks core sampled from January 1994 through July 31, 1996. This phase does not include High Priority Tanks.*
- *Phase B: Core sampling of the High Priority Tanks.*
- *Phase C: Core sampling of the remaining tanks after completion of the High Priority Tanks. This phase includes sampling of alternate tanks after July 31, 1996.*

It has occasionally been necessary to sample tanks other than High Priority Tanks. The need to sample alternate tanks has been driven by delays in deploying the retained gas sampler, imposition of flammability controls on all tanks, and the need to qualify the Rotary Mode Core Sampling Systems for operation in flammable gas atmospheres. Figure I-1 provides a summary chart that outlines tank core sampling plans from 1994 to 1997. Off Ramp tanks is a term for alternate tanks that could be sampled to meet characterization needs as defined in the Tank Waste Characterization Basis (Brown et al. 1995) if the High Priority Tanks cannot be sampled (Eberlein 1996).

Five sampling crews have been hired and trained. Because of the priority placed on completing the core samples from the High Priority Tanks, four of the sampling crews are devoted to obtaining core samples. Three of these four core sampling crews are used to sample on three shifts per day, five days a week, on one of the four trucks. The fourth core sampling crew is used to move and set-up the truck which has just completed a core. The fifth sampling crew is used to collect vapor, auger, and liquid grab samples.

Accelerating completion of the HPT sampling by increasing the number of sampling crews was considered. The existing schedule completes the HPT sampling in May 1997. Approximately six months would be required to hire and train additional crews. During the training phase, the field sampling rate would decrease due to diverting one sampling truck to complete operator training. The associated impact would delay the HPT sampling schedule by one to two months. By the end of November, the new crews would be ready for field deployment. Assuming that four additional sampling crews were deployed, the sampling rate could be doubled. This would allow completion of the HPT sampling in March rather than May. From January 1, 1994 until January 28, 1996, a total of 260 core segments (typically 48.3 cm [19 in] in length) was obtained, 106 core segments from the Phase A tanks and 154 core segments from the High Priority Tanks. Rotary mode core sampling testing was conducted from July 1995 through September 1995 to develop sampling protocols to allow effective production of rotary mode core samples. One of the most significant discoveries during this testing was that the push mode could successfully be used in many tanks previously thought to require the rotary mode. Twenty-two of the 28 High Priority Tanks were

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originally scheduled for rotary mode core sampling. Many of these tanks can be sampled by push mode; these tanks have been brought forward in the schedule. The tanks requiring rotary mode core sampling were delayed until after the Rotary Mode Core Sampling Systems are scheduled to be authorized for sampling in a flammable gas atmosphere.

The effect of using trucks #2, #3, and #4 in push mode exclusively was to improve the realized reliability of these trucks since the exhauster is not required to operate in the push mode. However, much of the High Priority Tank push mode sampling has been completed. Four of the High Priority Tanks remaining to be sampled require push mode sampling using truck #1 and the retained gas sampler. Therefore, six Off Ramp tanks may be sampled between March 1996 and September 1996 to allow time to qualify rotary mode core sampling for use in tanks with flammable atmospheres.

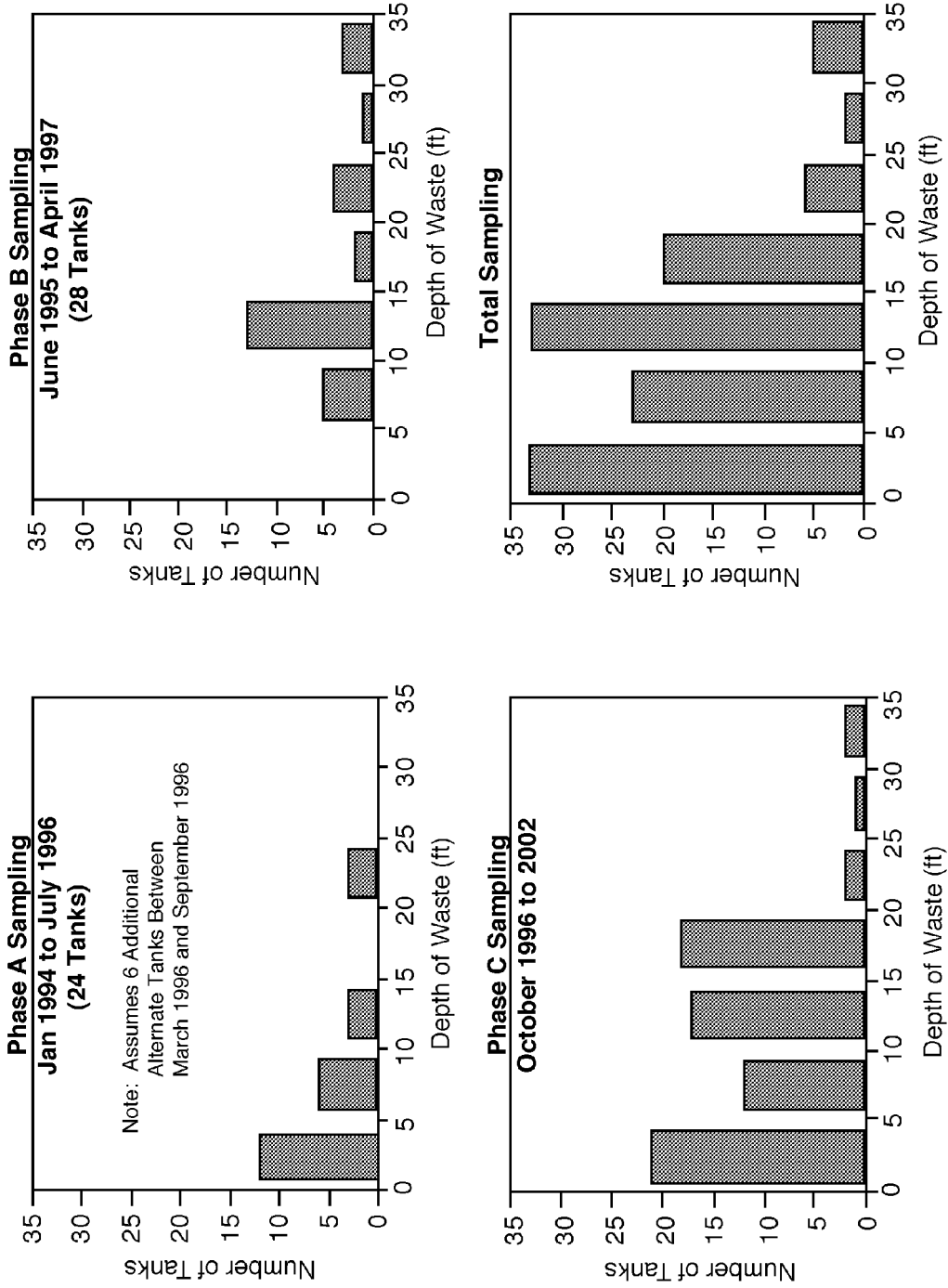
Thirty-nine core samples were obtained in FY 1995. It is anticipated that 52 core samples will be completed in FY 1996. Sixty core samples are scheduled for FY 1997. These increases represent a significant productivity achievement. The magnitude of this productivity increase is even more dramatic when the number of core sample segments are considered. The tanks which were sampled in FY 1995 were mostly shallow tanks, with less than 1.5 meters (5 feet) of waste. The time and effort required to complete the core sampling operation in a tank is strongly dependent on the depth of the waste which determines the number of segments. Figure I-2 displays a histogram of the waste depth in the tanks that have been sampled and the waste depth in tanks planned for future sampling. This figure illustrates that a higher number of deep cores are required in Phases B and C.

From October 1995 through March 1996, an average of 0.64 segments was obtained each scheduled shift of core sampling operations. This rate was achieved while doing all push mode cores. When rotary core sampling resumes, maintaining the rate of productivity will be difficult due to several factors. The rotary mode core sampling equipment has an overall lower reliability than the simpler push mode. In rotary mode, a stream of nitrogen is used to cool the waste near the drill bit. Therefore, an exhauster must be operated to prevent an unfiltered release of headspace vapors. The exhauster and the associated emissions monitoring equipment decrease the overall system reliability. Modifications to qualify the rotary mode core systems for operation in Flammable Gas Watch List tanks may also increase system complexity and reduce reliability.

There are 522 segments scheduled for FY 1996 (average segments required 0.73 for 720 scheduled shifts) and 600 segments scheduled for FY 1997 (average segments required 0.83 for 720 shifts). Achieving 0.73 segments per scheduled shift during FY 1996 is an aggressive, achievable goal because of the large number of tanks which will be sampled in the push mode. The number of segments scheduled for FY 1997 is a significant productivity commitment. Assuming that six alternate tanks are push mode sampled between March 1996 and September 1996 and that rotary mode sampling resumes as scheduled in September 1996, sampling and analysis of the High Priority Tanks is scheduled to be completed in March.

Figure I-2: Depth of Waste Sampled During Phases of Core Sampling

Depth of Waste Sampled During Phases of Core Sampling



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Once Phases A and B are completed, 1302 segments will remain to be taken from 60 tanks (assuming three cores per tank and that it will be necessary to sample all tanks). There will be 600 scheduled core sampling shifts in FY 1998, 420 in FY 1999, and 240 in FY 2000. Assuming 3 cores per tank and 0.64 segments per scheduled shift, Phase C initial sampling, analysis, and report writing is scheduled to be completed in December 2002. . DOE plans to continue efforts to improve sampling productivity. These productivity gains could significantly shorten the overall time duration. As an example, assuming that the productivity can be raised from the current 0.64 segments per scheduled shift to 0.85 segments per scheduled shift, Phase C initial sampling, analysis, and report writing would be completed in March 2001. Assuming 3 cores required per tank and 0.75 segments (instead of the current 0.64) per scheduled shift, Phase C initial sampling, analysis, and report writing would be completed in January 2002. The date is also highly sensitive to the number of cores per tank. If 2 cores per tank could be justified and if productivity could be raised to 0.85 segments per shift, Phase C sampling, analysis, and report writing could be completed as early as August 1999. The above dates are all based on the assumption that no repeat sampling is required. If repeat sampling is required, the dates would be delayed.

2 HEADSPACE SAMPLING

As of February 1996, 63 tanks have been vapor sampled using the truck mounted Vapor Sampling System (truck system). There are 86 SSTs and 28 DSTs remaining to be vapor sampled. Thirty-two additional vapor samples are planned to be obtained from seven tanks. These samples will be used to confirm headspace homogeneity analyses (three SSTs) and to evaluate variations in headspace vapor concentrations in passively ventilated tanks with changing atmospheric temperatures (four SSTs) . The baseline planning rate for use of this system is 48 samples per year. Both sampling crew resources and laboratory throughput constrain this rate.

Approximately 50% of the field work associated with vapor sampling using the truck system is involved with installation, removal, and cleaning of the vapor probes. Installation and removal of the probes require a crane. Design and fabrication of a cart system to allow in-situ vapor sampling (without a heated vapor probe) is complete. Comparison samples have been obtained from three tanks (C-107, BY-108, and S-102) using both the truck and the cart systems. Laboratory analysis of these samples is in progress. Confirmation that the truck and cart systems provide essentially the same results is expected by September 1996. However, until the system is proven, schedules will be based on using the existing truck system. Once the cart system is accepted and if a screening method can be developed to reduce the laboratory analytical load, it should be possible to increase the vapor sampling rate with no increase in operator resources. Reduction in the number of tank samples for which organic speciation is accomplished is the only significant analysis reduction possible. The principal driver for the number of tanks which require organic speciation is the Rotary Mode Core Sampling System exhauster. The air permit for exhauster operation requires detailed organic analyses. Use of a screening method may result in the need to re-sample some tanks to satisfy permit requirements for the Rotary Mode Core Sampling System exhauster.

APPENDIX J

CHARACTERIZATION TECHNICAL BASIS

7 INTRODUCTION

This section describes the approach for completing the Technical Basis for gathering and evaluating characterization information.

Characterization information is required for safe storage of the waste, to operate the tanks and their infrastructure safely, and to plan and implement retrieval and processing of the waste into durable solids suitable for disposal. Information is required on the waste content (chemical species and their physical condition) and on phenomena caused by the waste. The word phenomena refers to the important chemical or physical reactions that are capable of occurring within the mixture of chemicals. The means of characterizing waste content and phenomena associated with the waste are fundamentally different. The waste content can be determined by analytical chemistry or direct measurements of physical properties. Understanding the phenomena requires more extensive analysis of chemical and physical properties combined with experimental modeling.

The information requirements for each TWRS programmatic issue have been identified through the DQO process (EPA 1994). The DQO process provides a rigorous, disciplined approach for determining the information necessary to make a decision. The process was designed for regulatory compliance applications where only content information was required. As applied to Hanford Site tank waste, the DQO process has focused primarily on addressing waste content information needs, including composition (chemical and radiological), condition (physical parameters), and configuration (stratigraphy and heterogeneity). Characterization of phenomena caused by the waste has not generally been addressed through the DQO process, but has been pursued through experimentation using simulants and development of models. In most cases, waste content information is a prerequisite to the design of experiments to determine phenomenology. Physical samples of waste for testing are also required to adequately define the nature and boundaries of conditions that are necessary to support the phenomena that are occurring.

A fundamental step in characterization is to develop the strategy to acquire samples. In an unconstrained situation, several standard sampling schemes may be applied (random grids, sequential sampling etc.). The Hanford Site tank situation is different in that sampling is highly constrained because few tank access points (risers) are available and the waste under the risers may not be representative of the overall tank contents. A tank of 23 meters (75-foot)-diameter tank has a plan view cross-section of more than 4,097,020 square centimeters (cm^2) (635,000 square inches [in.^2]). Sampling the waste in the tank with a 2.5 centimeters (1 in.)-diameter coring tool, with a cross-section of 5.03 cm^2 (0.78 in.^2), provides the ability to sample about 1/800,000 of the cross-section. In round numbers, every core, extending completely through the waste material to the bottom of the tank, provides information on about one millionth of the tank's content. A meaningful, statistically defensible picture of the waste content cannot be provided through sampling alone.

Successful characterization of the tank waste requires understanding of the relationship between the waste at the available sampling sites and the overall tank contents. A complete picture of the three-dimensional waste composition is not generally required to

address the essential information requirements. However, the effect of the limited sampling access on the key data requirements needs to be understood.

Samples of Hanford Site tank waste cannot be considered in isolation. A body of information exists, including process and transfer records, HTCEs, monitoring and surveillance data, photographs, and sample analysis information from related tanks. Models of waste behavior (chemical and physical) have been developed. This body of existing information is used to evaluate the existing sites available for sampling and determine how the sample analysis results can be interpreted and extrapolated to an entire tank.

The following sections describe:

- The essential information requirements driving the characterization effort and the effect of those requirements on the sampling needs*
- The available information sources, limitations of those sources, and how the information may be used to direct sampling schemes*
- The available sampling and analysis equipment, their capabilities and limitations*
- The approach used to evaluate sample analysis results in light of the other information sources and apply the results to addressing the information requirements for each tank*
- The approach used to extrapolate results of individual tanks to groups of related tanks, allowing issues to be addressed*
- Chemical and physical parameters for tank waste content*
- Chemical and physical phenomena associated with tank waste*
- The strategy for sampling High Priority Tanks that provide information about waste types or issues extending beyond the individual tank*
- The anticipated results of applying the approach described to the sampling and analysis of the priority tanks.*

8 ESSENTIAL INFORMATION REQUIREMENTS

Essential information requirements include waste content and nature of associated phenomena. Resolution of safety issues (as described in Section 5.4) depends heavily on understanding specific phenomena. In general, the mechanisms underlying phenomena can be understood by examining waste from a few bounding tanks and applying the understanding to other tanks. Once the phenomena and the conditions that drive them are understood, decisions may be made on appropriate treatment of specific tanks (e.g., decisions to mitigate or place controls on a tank). These decisions may involve tank specific characterization of content or characterization of a waste type applied to a group of tanks.

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Disposal Program information requirements (as described in Section 5.5) also involve both content and phenomena. Process testing of bounding waste samples provides an understanding of waste behavior during retrieval, waste separation, and conversion to durable waste forms. Waste content information supports decisions on how specific wastes will be treated and what resulting volume of final waste form is expected.

The DQO process was used to define data needs. The characterization needs listed in Sections 5.4 and 5.5 have been formally documented in DQOs (as examples: Babad et al. 1995, Bloom and Nguyen 1995, Dukelow et al. 1995, Fowler 1995, McDuffie 1995, Meacham et al. 1995a, Osborne et al. 1995, Simpson and McCain 1995, Slankas et al. 1995).

As described in Sections 5.4 and 5.5, characterization information plays a role in the overall plan to resolve safety and disposal program issues and make operational decisions. Characterization is seldom the sole factor supporting the decisions, and often plays only a supporting and confirmatory role in the process relative to many other factors (experimentation, models, controls, mitigative actions). This contrasts sharply with the types of problems for which the DQO process was originally developed. The traditional use of the DQO process involved problems where sampling data was the key decision determinant, and action levels and associated risks were clearly defined.

The characterization needs described in the DQO documents focus primarily on waste content information (composition, condition, configuration). Although the DQO process was originally designed to support acquiring content (specifically composition) information, many of the safety issues depend heavily on the characterization of phenomena. The DQO process was used as a vehicle to define the content information involved in understanding the phenomena caused by the tank waste. However, the process has required some adaptation to support the definition of information needs to resolve Hanford Site tank waste issues.

The first four steps of the DQO process have been successfully applied to the Hanford Site tank waste. The questions, decisions, decision inputs, and the boundaries were defined. The next three steps (develop a decision rule, specify tolerable limits on decision errors and optimize the design) apply when the information being sought is to determine waste content and make a specific decision. For example, these steps are appropriate for safety screening, where a decision must be made regarding the need for controls to maintain safe storage. However, the questions involved with understanding phenomena caused by the waste do not lend themselves to formulation as a hypothesis test. Even in cases where decisions can be specified, decisions cannot necessarily be made using sampling data only. The integration of risk acceptance criteria into the DQO process has been problematic because the majority of the factors controlling both the consequences and the probability of unfavorable events are not related to information derived from waste content characterization.

The successful path to using the DQO process for waste characterization involves the following:

- Define the overall approach to resolving an issue or making a decision, including the role of characterization information (see Section 5.4 and 5.5)*
- Perform the initial four steps of the process for the defined characterization needs*

- *Identify the impact of the characterization data on making a decision. If characterization data plays only a supporting role, incorporation of risk acceptance criteria and specification of quantitative error tolerances is not appropriate. If characterization data is the key element in the decision, completion of the DQO process should be pursued (action levels should be defined and sufficient analysis must be performed to provide an understanding of the statistical distribution of the data).*

9 AVAILABLE INFORMATION SOURCES

Characterization of tank contents combines information from several sources, including historic process records, modeling, monitoring, and sample analysis. This section reviews the current understanding of the quality of tank content models and waste configuration.

9.1 TANK CONTENTS MODEL

A valuable tool for characterization is an estimate of the tank contents developed from historical records of waste-generating processes and transfers. Integration and evaluation of this historical data are key to understanding the present condition and configuration of the tank waste contents.

A first step in the use of a model of tank contents to group tanks was the SORWT model (Hill et al. 1995) originally published in 1991. This model assigned the input streams to the SSTs to one of 26 waste types. The individual tanks were then assigned to groups based on the two largest-volume waste types in the tank. The approach did not attempt to predict the overall waste inventory in each tank and did not consider special attributes of smaller volume waste streams. Of the 149 SSTs, 133 could be placed into one of 24 groups with at least two tanks in each group. Sixteen tanks were unique in this grouping scheme.

A more complete model of the contents of the tanks developed from the historic records was completed in 1995 (Historical Tank Content Estimates [Brevick et al. 1994a, 1994b, Brevick 1995a, 1995b]). The waste types used in the latter approach are almost identical to those used in the original SORWT grouping. However, the HTCE tracks all contributing waste streams (not just the primary two streams) for each tank to predict the overall inventory.

To develop the HTCEs, a series of tasks was completed.

- *Chemical compositions for 48 process waste streams from four principal separations plants, several different radionuclide recovery operations, and eight different evaporator campaigns (Hanford Defined Wastes [HDW] [Agnew 1995]) were defined.*
- *Fifty years of process history and more than 40,000 documented transactions into a structured database (Waste Status and Transaction Record Summary [WSTRS] [Agnew 1994c, Agnew 1994d, Agnew et al. 1995a]) were organized.*
- *Volumes and locations of the various process wastes in the Tank Farms (Tank Layering Model [Agnew 1994a, Agnew 1994b, Agnew et al. 1995b]) were estimated.*

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- **Compositions of concentrated and non-concentrated supernatant mixtures (Supernatant Mixing Model [SMM] [Agnew et al. 1995c]) were calculated.**

The information provided by these tasks was integrated to produce a comprehensive model of the Historical Tank Content Estimate (Brevick et al. 1994a, 1994b, Brevick 1995a, 1995b). The waste contents models and resulting tank grouping models have been used to identify and prioritize tanks with regard to safety and disposal issues.

The waste types described in the HDW document are an enhancement of those used to generate the SORWT grouping model originally used by the Disposal Programs. No significant differences in the basic waste types exist between the two models, but the HDW document and the resulting HTCEs provide significantly more detailed information than the preliminary model used in SORWT. Now that the more complete historic information is available, the disposal process development strategy is being reviewed to allow adjustment in priority tanks for sampling.

9.2 EVALUATION OF THE TANK CONTENTS MODEL

The quality of the tank contents model information must be assessed to ensure that tank grouping activities have been performed adequately and that the most accurate site wide inventory is obtained. Records of past practices and processing, while extensive, are incomplete. The model of waste tank contents developed from these records contains certain assumptions about waste content and behavior. The resulting predictions have a range of potential inaccuracy that must be quantified. The historical data assessment task for model refinement includes the areas listed below.

- **Input information - identify and evaluate source term and systematic errors in the HDW and WSTRS on a global scale.**
- **Assumptions and sensitivity - evaluate physical and chemical constraints imposed by the model when the individual elements are linked, and determine whether the model introduces, damps, or exacerbates variability in the HTCE reported results.**
- **Output comparisons and uncertainty quantification - Statistically test selected sampling data and model estimates to examine the accuracy of the individual model elements. Estimate the magnitude of the uncertainty associated with the HTCEs and waste sampling information.**

Additional data requirements (waste composition) have been established to evaluate the extent of the understanding of the historical data and the underlying assumptions about the wastes (Simpson and McCain 1995). Five primary SST waste types (and several subtypes) have been identified to aid in grouping tanks (Brown et al. 1995). Models of tank contents are based on the predicted composition and distribution of these waste types. The quality of the waste content models can be determined by sampling and analysis to determine location and quantity of the key waste types within the tank farm system. Waste content model evaluation requires samples of each of the five primary waste types: REDOX process, saltcake (also called evaporator bottoms), PUREX process, uranium recovery process (also called Tri-butyl Phosphate process), and BiPO₄ process waste types. To date, only BiPO₄ waste types have been adequately characterized.

The Historic Model Evaluation DQO (Simpson and McCain 1995) identifies tanks that should contain large volumes of each of the key waste types. Samples of the waste types will be compared with the waste type recipe (as defined in the HDW document [Agnew 1995]) to determine the correctness of the recipe, and the variability observed within the waste type. This information will be used to correct the recipe (if systematic errors are observed) or to define the limitations of the model based on the observed variability.

The endpoint for the series of historic data assessment tasks will be a tank-by-tank best estimate of the tank contents. In addition, the HTCE will be updated to include confidence intervals for key waste constituents that are important to the Safety and Disposal Programs.

9.3 LIMITATIONS OF INFORMATION SOURCES DUE TO WASTE CONFIGURATION

Condensed-phase. Limited tank access prevents the use of random sampling schemes. Characterizing tanks is being pursued in the context of understanding problems that apply to multiple tanks, rather than in terms of focusing on the content of individual tanks. The approach to resolution of safety issues involves a combination of modeling, experiments to improve understanding of phenomena that cause the safety issue, and evaluating tank content information (including sample results, historical information, etc.). During the HPTs sampling, the number of core samples per tank was determined based on a balance of obtaining initial information to assess tank content variability and the number of tanks chosen to be sampled. As the issues and range of variability in different waste types are better understood, it should be possible to specify numbers of samples per tank to resolve specific tank issues. In the interim, planning and schedules have been based on three cores per tank.

Both vertical and horizontal variability is expected in the waste, and raises questions regarding the degree to which a few samples can be representative of the entire tank. Complete vertical profiles can be obtained. Therefore, vertical heterogeneity (layering) does not adversely affect the ability to characterize the tank through sampling.

Horizontal heterogeneity can be understood by obtaining many samples. Alternately, a model of the waste distribution may be developed from independent information sources (not sampling) and used to direct sampling. All historic records and photographs are being reviewed to develop an understanding of the horizontal heterogeneity of each tank and to determine if sampling beneath risers is likely to provide representative information. Risers have sometimes been used as access ports for waste addition, sampling, insertion of measurement devices, or other operations that may alter the waste below the riser. Careful examination of the riser history and photographs of the waste beneath each riser is being performed to improve understanding of the relationship between the sample and the overall tank contents. Grouping of tanks and analysis of samples from multiple tanks containing similar wastes may provide a statistical basis for making some decisions requiring multiple samples. Samples from specific tanks will be obtained to improve the understanding of spatial variability and the impact of limited sample numbers.

Headspace homogeneity. The headspace dynamics of most passively ventilated SSTs are dominated by thermally induced convection currents. Radioactive decay of the waste in these tanks results in waste surface temperatures that are higher than the temperatures of the tank dome and ground above the dome. Air warmed by contact with the waste surface consequently rises as cooler, denser air from near the dome displaces it. This convection

mixes the gases and vapors both vertically and horizontally within the headspace, limiting concentration gradients within this convection zone (Christensen 1995). In the regions very close to the waste surface, tank dome, or tank walls, concentration gradients are limited by molecular diffusion (Postma et al. 1994, Claybrook and Wood 1994).

However, for some tanks with low heat generation rates, there may be periods of the year when the ground temperature above the tank is warmer than the waste itself -- a situation that does not produce thermally induced convection. A survey of tank heat generation data has been performed. It is planned to use the heat generation data to select tanks for the testing discussed below.

The effect of thermally induced convection on the concentrations of semi-volatile organic vapors has been examined using a three-dimensional numerical model of tank C-103 (Claybrook and Wood 1994). From an initial condition of no organic vapors present in the headspace, the model evaluates the evaporation of organic liquid for three different tank dome temperatures. The model predicts that temperature differences as small as 1°C (2°F) will be sufficient to allow enough headspace gas mixing to prevent substantial concentration gradients.

Waste tank headspace stratification due to gas and vapor density differences has also been considered. Hydrogen and tributyl phosphate are the lightest and heaviest common gas phase constituents, respectively, of the tanks, and represent bounding cases for gravitationally induced concentration gradients. The calculated concentration gradients due to density differences are negligible to the collection, analysis, and interpretation of tank headspace samples (Wallace 1992, Claybrook and Wood 1994).

Empirical evidence supports the conclusion that there is no significant vertical stratification in the waste tank headspaces. Gas and vapor samples collected from three elevations of the tank C-103 headspace suggest no vertical stratification exists in that tank (Huckaby and Story 1994). Concentrations of several gases and vapors including ammonia, water vapor, hydrogen, and semi-volatile alkanes were measured at 0.79, 2.92, and 5.05 m above the waste surface, and no statistically significant difference due to elevation was observed. A similar result was found in tank C-111 (Huckaby 1994).

Given the modeling and empirical evidence that the headspaces of passively ventilated tanks are in general well mixed, only limited additional sampling and analysis will be conducted to confirm headspace homogeneity. The testing will be conducted in October 1996, when the ground and headspaces of the tanks to be sampled are at their warmest. Headspace vapors will be sampled down two risers, at three elevations, in three tanks. The headspace homogeneity results will be summarized by October 1997.

10 AVAILABLE SAMPLING AND ANALYSIS EQUIPMENT, CAPABILITIES, AND LIMITATIONS

Sampling and analysis of the waste in Hanford Site underground storage tanks is a complex undertaking. Application of existing commercial sampling techniques to the sampling effort is limited due to safety constraints and tank access limitations. Sampling in tanks where disruptive events can occur must be done within controls that ensure safety.

10.1 SAMPLING METHODS

Removal of liquid and solid phase waste samples from tanks is performed with one of four sampling methods: the grab sampler, the auger sampler, the push mode core sampler, and the rotary mode core sampler.

10.1.1 Core Sampler

Core samples are full depth solid and/or liquid samples of the waste materials. The core samplers are effective in retrieving sludge, cohesive solids (salt cake), and liquids. Four sampling trucks can be used to obtain core samples. Samples can be taken in either rotary mode or push mode. In rotary mode, a cutting bit is attached to the bottom of the drill rod assembly, and the drill rod assembly is rotated as it is pushed into the waste. Push mode pushes the drill string into the waste using a tapered push bit. Safety precautions include drill bits designed to preclude damaging the tank bottom, bottom detectors, rotational speed limits, and down force limits.

Three of the trucks (core sample trucks #2, #3, and #4) use a nitrogen purge to remove drilling fines, as a hydraulic fluid to balance the existing tank hydrostatic pressure, and to cool the bit. These trucks are used for both rotary and push mode sampling. The remaining truck, core sample truck #1, does not have a nitrogen purge capability. It is used exclusively for push mode sampling. Rotary mode sampling is currently not authorized in flammable gas tanks, but authorization is expected by September 1996.

The sampler for rotary and push mode coring obtains complete vertical profiles in 48-centimeters (cm) (19-in.) segments, approximately 2.5 cm (1 in.) diameter. The maximum volume is 300 milliliters (ml) for liquids and sludges and 245 ml for salt cake samples. This sampler can obtain samples to within 12.7 cm (5 in.) of the bottom of the tank.

10.1.2 Auger Sampler

Auger sampling equipment consists of an outer guide tube assembly and an inner auger sampler assembly. The complete auger assembly is approximately 15 meters (45-50 feet) long and requires the use of a crane during the sampling operation. The auger is contained within a metal sheath inside the guide tube, except during the sampling operation. The waste material is penetrated by turning the auger by hand and the waste is collected on the auger flutes. The auger samples waste to a maximum depth of 38 cm (15 in.) and is an appropriate method for recovering samples near the waste surface.

10.1.3 Liquid Grab Sampler

This sampler consists of a small bottle (wide or narrow mouths are available) fitted with a rubber stopper in a weighted holder. The sampler volumes range from 100 to 125 ml. The sampler is lowered into the tank until the bottle reaches the desired depth. The stopper is removed from the opening remotely, allowing waste material to flow into the bottle. The grab sampler is limited to a single-elevation sample.

10.1.4 Vapor Sampling

Three types of sampling devices can be used to sample the waste tank gases and vapors. One vapor sampling system draws tank vapors and gases through heated transfer tubing

into SUMMA¹ canisters or sorbent traps. SUMMATM canisters are used to collect certain gases and volatile organic vapors and sorbent traps are used to collect organic vapors and certain inorganic gases and vapors. A second newer vapor sampling system, the in-situ vapor sampling system, lowers the sampling devices (specifically sorbent traps) into the headspace of the tank. Side-by-side comparison testing by obtaining vapor samples from three tanks is in progress to confirm that the two vapor sampling systems yield equivalent results. A third sampling device, a combustible gas meter, is used to determine if the headspace combustible vapors are below 10% LFL. If they are above 10% LFL, then a vapor sample using either of the two vapor sampling systems must be used to obtain a more precise combustible gas measurement.

10.1.5 In-Situ Measurements

In-situ physical property measurements are most representative of the actual waste condition. In-situ measurements eliminate sample transport and laboratory costs and are frequently available in less time than laboratory analysis. DOE has developed several in-situ measurement systems to analyze the waste in Hanford Site tanks.

- *The void fraction instrument is designed to measure the volume fraction of free gas, or void, existing at specific locations in a tank.*
- *The ball rheometer (viscometer) is based upon classical "falling ball rheometry," where the time it takes a ball-shaped object to fall a known distance through the fluid is related to the fluid's rheology.*
- *Hydrogen monitoring systems provide continuous monitoring of the level of hydrogen in the tank headspace.*

In addition, several in-situ moisture monitoring systems are under development.

10.1.6 Condensed-Phase Sampling Limitations and Constraints

The sampling process is subject to limitations and constraints that impact the ability to collect representative samples which may bias the results of the sample/analysis effort. Potential sources of systematic bias include sampling methods that preferentially sample specific waste phases, handling methods that alter sample properties, and incomplete recovery of samples. Limited tank access, riser location, and waste heterogeneity may affect the representativeness of the samples. These biases and other constraints are identified (as applicable) in the TCRs.

The sampling method(s) chosen is(are) largely a function of the expected waste condition in the tank and the depth of the waste. There is no universal procedure and equipment configuration that allows sampling of a waste matrix with varying physical properties. Core samples are used when knowledge of the waste vertical distribution is required or the depth of the waste is more than 46 cm (18 in.). Core samples cannot acquire the bottom 12.7 cm (5 in.) of waste. Auger samples can only be effectively employed where a sample of the waste of 38 cm (15 in.) depth or less is required.

¹SUMMA is a registered trademark of the Summa Corporation.

A small number of risers are installed in each tank. Field conditions further limit those risers available for sampling. Operations must be performed in a manner that limits radiation exposure and radiation contamination. Flammable gases in the headspace of some tanks constrain equipment and procedures. Weather conditions can limit field operations. All these factors constrain the ability to obtain samples.

10.2 ANALYSIS AND MEASUREMENTS

10.2.1 Analytical Capabilities

Condensed-Phase. Laboratory capacity concerns were addressed in the original Implementation Plan. LANL and INEL capabilities were enhanced to provide characterization analyses of Hanford Site waste samples. The added capacity obtained with these laboratories was not required due to reduced numbers of analyses required as a result of applying the DQO process and a reduced sampling rate. These laboratories are no longer in standby to receive samples from the Hanford Site.

The 222-S Laboratory, operated by WHC, is the primary analytical facility supplying analytical data to the characterization effort. The 325 Analytical Chemistry Laboratory, operated by PNNL, has been used as a secondary analytical facility. However, the 222-S Laboratory has demonstrated the capability and capacity to meet the Characterization Program needs. Therefore, use of the 325 Analytical Chemistry Laboratory is being phased out of the Characterization Program.

Inorganic, organic, and radiochemical instruments are available in 222-S. These instruments are maintained to perform analyses according to accepted procedures adapted for operation on high level radiological samples of waste tank materials. Hot cells are available for receipt and extrusion of core segments, homogenization, aliquoting, and remote chemical analyses.

Multiple instruments for inorganic and organic chemistry analyses are available to minimize the impact of failure of an instrument. A full range of chemical separation procedures and instruments are available for quantification of radionuclide concentrations in waste materials. Several physical property measurement systems are used including thermogravimetry, differential and adiabatic calorimetry, flash point testing, viscometry, and density instruments. Limited mineralogical capabilities are available with scanning electron microscopy with X-ray characterization, and optical and polarized light microscopy.

Vapor Phase. The Vapor Analytical Laboratory, operated by PNNL, is the primary analytical laboratory supplying laboratory analysis of vapor samples. The primary analyses include permanent gases, inorganic compounds, total organic compounds, and organic speciation on both thermal desorption trap and SUMMA™ canister samples. The ORNL operates the secondary vapor analytic facility and currently focuses on thermal desorption trap analysis of vapor samples. If required, both laboratories can perform analyses of radioactive samples.

Pacific Northwest National Laboratory. Although only one analytical system is available for inorganic, permanent gas, and total non-methane hydrocarbon analysis, the reliability of the systems is high and rapid repair options are available. Two gas

chromatograph/mass spectrometers are available for the more time consuming organic speciation. A third gas chromatograph/mass spectrometer is used for sorbent-based organic speciation analyses. In addition, the laboratory provides unexposed sorbent traps and SUMMA™ canisters to the sampling team before each sampling job.

Oak Ridge National Laboratory. One gas chromatograph/mass spectrometer system is configured for thermal desorption analysis of multisorbent traps. A second gas chromatograph/mass spectrometer acts as back up, but is being configured for analysis of SUMMA™ canister samples of permanent gases and organic species. In addition, ORNL provides unexposed solid sorbent sampling media (triple sorbent traps) to the sampling team, and will be providing unexposed SUMMA™ canisters, once Hanford Analytical Services Quality Assurance Plan (HASQAP) (DOE-RL 1995) compliance for the methodology has been confirmed.

10.2.2 Analytical Precision and Accuracy

Condensed-Phase. The 222-S Laboratory operates to the principles of the HASQAP. In the absence of a customer requested quality assurance/control tailored to meet specific goals and objectives of that program, the HASQAP guidance provides for control limits on analytes and technologies. It provides guidance consistent with the U.S. Environmental Protection Agency (EPA) in the use of blank, spikes, matrix spikes, calibration and control standards. Radiochemistry is also covered in the HASQAP and includes use of tracers and carriers to monitor the quality of radiochemical data generated.

Vapor. Analytical work in the two vapor laboratories is performed under a project specific quality assurance plan based on the HASQAP. Activity specific technical procedures for vapor analyses are developed, maintained, and used to assure the performance of analytical systems. To confirm data quality, the vapor program uses a series of analytical tests. These include field and lab blank samples, and surrogate standards for the multisorbent traps. The latter are spiked on the traps before the traps are provided to the sampling team; therefore, appropriate levels of surrogates on the returning traps confirm the validity of the entire sampling and analysis procedure.

11 INTERPRETATION OF ANALYSIS RESULTS

The interpretation of sample analysis results involves a reconstruction process where the analytical results are related to the state of the waste volume. Details of the process vary depending on the specific question being addressed. For example, the steps to extrapolate sample results to a mean tank value differ from those to extrapolate to a bounding value within a layer. The basic steps are listed below.

- Determine analytical variability observed in the data. This involves performance of appropriate statistical tests (problem specific) and consideration of any systematic analytic errors.*
- Determine how the observed measurements relate to the waste in the sampling location. This requires consideration of incomplete recovery and possible system biases as well as any changes introduced into the sample during the sampling process itself (e.g., physical parameters).*

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- *Determine how the estimated true values of parameters in the region sampled relate to the range of values in the waste region of interest. This may involve extrapolation to specific waste layers or to the entire tank volume. This step requires consideration of the history of the waste under the riser. In other words, was non-representative waste introduced under the riser? Evaluations must be completed on the means by which waste was put into the tank, the number of different waste types in the tank, previous sluicing or saltwell pumping, and other factors.*

The specific methodology to be applied in the last step depends on the question to be addressed and the available information about the waste model. Most questions do not require an understanding of the three-dimensional distribution of analytes within a tank. However, it is necessary to know when a specific sample may be bounding or non-representative for the entire tank. To address the relationship between the waste under a riser and the waste in the entire tank, riser histories have been compiled and photographs are examined.

12 EXTRAPOLATION OF TANK RESULTS TO GROUPS OR ISSUES

Sampling and analysis of waste content is performed on individual tanks. The information gained on phenomena caused by the waste and on specific waste type composition may be extrapolated to other tanks. As mentioned above, it is possible to group tanks that are related based on either compositional characteristics or common safety issues.

Waste content information can be extrapolated when bounding values for waste types can be established. A combination of process records and selected sampling is used to define the average and bounding values of key content parameters. This is the basis for the disposal process development program selection of a subset of tanks for sampling and process testing. The adequacy of this approach depends on the precision/accuracy required for the specific question and on how close the bounding waste value is to the threshold value.

Extrapolation of results from a few tanks to many tanks works very well when the detailed characterization is required to understand phenomena caused by the waste. If the phenomena can be understood through the study of tanks most likely to bound the behavior, conclusions can be drawn on groups of tanks. This is the basis for confirming ferrocyanide decomposition using limited samples from some ferrocyanide tanks. The requirement for selection of the High Priority Tanks was that they be those least likely to show decomposition. If aging of ferrocyanide is observed in these tanks, the chemical phenomenon is expected in all others.

If appropriate information is acquired regarding key bounding tanks, the need for sampling of individual tanks may be reduced. The tanks most likely to provide information about the phenomena and about waste type content associated with many tanks are highest priorities for early sampling.

13 CHEMICAL AND PHYSICAL PARAMETERS FOR TANK WASTE CONTENT

Essential information requirements include chemical and physical parameters that define the tank waste content and support making decisions regarding the waste in a specific tank. Content information falls into three broad categories: composition, condition, and configuration.

Determination of waste composition involves identification and quantification of chemical species (including radionuclides) in the waste. Parameters to be measured include elements, chemical compounds, radionuclides, pH, and vapor species. Total tank mass of key waste components and overall concentration of the components in the tank are values that are frequently required for safety and disposal planning purposes. These values are calculated with input from sample measurement data.

Waste condition addresses the physical state of the waste in the tank: is the waste present as a gas, liquid, or solid, and what are key physical characteristics? Parameters to be measured include shear strength, porosity, moisture content, hardness, abrasiveness, viscosity, specific gravity, particle size distribution, stored energy content, and temperature. These properties vary widely in the tank wastes that have been measured. Liquids can vary from thixotropic gels to low viscosity fluids. Solids can be as soft as putty or as hard as concrete. Measurements are required to understand the waste form. Solubility of the waste in water or other solvents and the ability to suspend particulate waste as a slurry (rather than a consolidated mass) are important parameters to understand waste retrieval requirements.

Waste configuration refers to the distribution and arrangement of material in the tank. It addresses the variability of the waste composition and condition in the vertical and horizontal dimensions. An understanding of the waste configuration is required to understand how limited sample measurements relate to the total waste in the tank. Specific Safety and Disposal Program issues must be addressed differently if certain materials (e.g., fissile) are concentrated in layers or local areas as opposed to being dispersed through larger regions. Configuration is understood through the measurement of key chemical or physical parameters at different locations and through the examination of photographs and other supporting information.

14 CHEMICAL AND PHYSICAL PHENOMENA ASSOCIATED WITH TANK WASTE

Tank wastes are not static, but are undergoing continuous chemical reactions. Some reactions are stimulated by the chemicals themselves. Others by the physical changes produced by the high energy radiation. Potential chemically driven phenomena may include thermally activated exothermic reactions, compound decomposition, and gas generation. Physically driven phenomena may include phase changes, precipitation, and gas adsorption. These phenomena need to be identified and understood because they have impacts on the safe storage of the waste and the safe and effective retrieval and disposal.

Measurement of waste properties plays a role in establishing and verifying the phenomena caused by the waste. However, full understanding of phenomena requires knowledge of a number of associated parameters and conditions, usually obtained through experimentation. A prime example is ferrocyanide. A model was developed for the

decomposition of ferrocyanide based on expected and observed properties of chemical compounds. Measurement of the energetics of the waste coincident with measurement of nickel (which was always added with the ferrocyanide) is being used to confirm that ferrocyanide decomposes to less reactive compounds. The presence of nickel confirms that ferrocyanide was added; the absence of energetics confirms that the ferrocyanide decomposed.

Other measurements associated with the evaluation of phenomena include measurement of energetics compared with total organic (or organic speciation) to understand organic decomposition, measurement of the distribution of organic complexants between the solid and liquid phases, measurement of the distribution of organic solvents between the vapor and condensed-phases, and measurement of the amount of water retained in various waste forms. The amount and composition of the flammable gases stored in the condensed-phase waste are measured, along with the content of the waste itself, to understand the phenomena associated with gas generation and retention.

In many cases, testing is performed on waste samples to understand phenomena. Reaction propagation is an example. The minimum energetics are measured in waste samples to determine what is required to support propagation. Waste samples are used to perform bench scale testing of waste separations and pretreatment processes. The phenomena associated with waste types are observed during testing. Waste content information is gathered to understand the ranges of wastes that are expected to demonstrate specific phenomena.

15 STRATEGY TO SELECT HIGH PRIORITY TANKS FOR SAMPLING

The information needs identified through the DQO process and described in Sections 5.4 and 5.5 of this plan were integrated to form a single prioritized sampling plan: Tank Waste Characterization Basis (Brown et al. 1995). This plan is reviewed and updated as the relative priorities among the issues changes. The key issues requiring characterization data were identified and prioritized. For each issue, criteria were identified to evaluate the importance of a tank in resolving the issue. Tanks were reviewed against these criteria and the most important tanks associated with each issue were identified. Issues were weighted so that tanks important for key issue resolution received higher priority weights. Tanks important for multiple issue resolution received the highest overall ranking. The outcome of the prioritization process was reviewed with the programs requesting data to ensure that their needs continue to be met.

Twenty-eight High Priority Tanks were selected for near-term core sampling. Analyses of samples from these tanks are expected to resolve or bound the key questions described in Sections 5.4 and 5.5. The issues requiring characterization information are described, including whether the information addresses content or phenomena.

16 ANTICIPATED RESULTS OF REVISED STRATEGY FOR SAMPLING PRIORITY TANKS

When the High Priority Tanks have been sampled and the analysis results reviewed as described above, a series of questions should be answered, allowing key decisions to be made.

16.1 SAFETY-RELATED QUESTIONS

The questions below relate to safety issues.

- *Does sample analysis confirm the model that ferrocyanide decomposes in the waste tanks into less reactive compounds?*

If the results confirm this model (and all sample results to date are consistent with the model), then the Ferrocyanide Safety Issue may be resolved for all tanks without further sampling.

- *Does sample analysis confirm the model that organic complexants decompose?*

If the results confirm the model and the degree of decomposition can be well enough modeled, reduction in some organic controls may be allowed. Additional tank by tank sampling for organics may be limited to far fewer tanks.

- *Does sample analysis confirm that organic complexants are soluble in water?*

Water solubility of the organics indicates that saltwell pumping will reduce the risk associated with a tank. If the degree of solubility can be bounded, this will provide guidance for determining the nature of controls required after saltwell pumping.

- *Does detection of organic solvents in the vapor phase correspond to presence of the solvents in the liquid or solid phases?*

Vapor sampling may be used as an indicator of condensed-phase solvents. Vapor sampling results may indicate the need for specific controls or actions without requiring a core sample. The comparison studies on the High Priority Tanks will reduce the number of false positives by confirming the relationship between vapor space concentration and condensed-phase concentration.

- *Does sample analysis confirm the anticipated locations of organic solvents within the liquid and solid waste (surface layers, interfaces, entrained)?*

Location of the organic solvents affects the hazard. The correct controls can be selected to match the consequence associated with the solvent distribution.

- *Does sample analysis establish an authoritative basis for understanding moisture retention in salt cake and in sludge?*

Models predicting moisture retention in salt cake and sludge may affect application of safety controls. These models will be evaluated with sample results.

- *Does sample analysis provide a basis for determining the amount and composition of retained gases in the bounding flammable gas tanks?*

The bounding tanks represent the worst conditions that must be controlled or mitigated. Specifying the correct action based on the results from these tanks ensures that all other flammable gas retaining tanks are conservatively controlled.

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- *Does the sample analysis confirm the postulated energetics and moisture criteria for propagation of fuel/oxidizer reactions?*

Confirming the postulated energetics and moisture criteria would allow revising the safety screening criteria.

- *Does the sample analysis confirm that the solvents found in tank C-103 are representative of solvents found in other tanks?*

Confirming solvent similarity would allow refinement of the screening criteria to determine if organic solvents were present.

16.2 DISPOSAL PROCESS DEVELOPMENT PLANNING RELATED QUESTIONS

The questions below relate to planning for the disposal process and its development.

- *What is the degree of spatial variability and level of resolution observed in a highly variable tank and in a homogeneous tank?*

These observations provide additional guidance on the number of samples that may be required to bound specific problems through sample analysis.

- *What is the range of compositional variability observed in saltcake?*

For disposal purposes, can all saltcakes be treated as similar or are there key differences among saltcakes resulting from different processes?

- *How well do the models of the key waste type compositions compare with the observed compositions?*

The composition estimates and the variability in composition within a key waste type determine whether wastes can be grouped and treated as similar with regard to any specific issue. Compositional variability determines the number of tanks that must be sampled to ensure that waste processing decisions address the majority of the waste. If composition and variability of waste types can be quantified, certain decisions may be made on specific tanks based on historic records and samples from related tanks without sampling each individual tank. The five primary waste types addressed in SSTs are BiPO₄ process waste, REDOX process waste, PUREX process waste, tri-butyl phosphate or uranium recovery process waste, and saltcake or evaporator bottoms.

17 SUMMARY OF APPROACH

Appendix F summarized the information that will be acquired through the sampling and analysis of each of the High Priority Tanks. The information will increase the understanding of issues applying to all tanks, not just to those sampled. The information gained on waste content will be used to evaluate models on the content, waste type distribution and variability in multiple tanks. The information on phenomena caused by the waste will be used to resolve issues, better define screening parameters, determine appropriate controls and mitigative actions, and identify appropriate processes.

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The strategy to focus on sampling the High Priority Tanks achieves the intent of the original recommendation to expedite characterization to resolve safety issues. Characterization that focuses on understanding phenomena so that issues may be resolved for groups of tanks is more effective than treating each tank individually. Sampling limitations may prevent resolution of safety issues solely by sampling individual tanks whereas addressing phenomena associated with groups of tanks may resolve the issue.

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