Department of Energy

Richland Operations Office
P.O. Box 550
Richland, Washington 99352

JAN 0 8 1996

95-CHD-111

Mr. John T. Conway, Chairman
Defense Nuclear Facilities Safety Board
625 Indiana Avenue NW, Suite 700
Washington, D.C. 20004

Dear Mr. Conway:

STATUS OF DEFENSE NUCLEAR FACILITIES SAFETY BOARD (DNFSB) RECOMMENDATION 93-5
IMPLEMENTATION PLAN COMMITMENTS 1.5, 1.23

References: 1)   "DNFSB Recommendation 93-5 Implementation Plan," U.S.
                 Department of Energy (DOE), Richland Operations Office (RL),
                 DOE/RL 94-0001, January 1994.

            2)   Letter, T. R. Sheridan, RL, to J. T. Conway, DNFSB,
                 "Transmittal of Westinghouse Hanford Company (WHC) Documents
                 Demonstrating WHC Efforts to Improve Characterization
                 Program Technical Staff Competencies, in Accordance with
                 Commitment 1.4 of the U.S. Department of Energy
                 Implementation Plan for Board Recommendation 93-5,"
                 #94-OCH-063, dated July 12, 1994.

The purpose of this letter is to give an update of the status regarding the
DNFSB Recommendation 93-5 Implementation Plan commitments that are due
December 31, 1995 (see Reference 1).

• Commitment 1.5, "Complete Implementation of the Westinghouse Hanford
  Company Characterization Program Plan to Improve Staff Competencies."

      The 93-5 Implementation Plan contains two commitments with the goal of
      improving Characterization Program staff competency, i.e.,
      Commitment 1.5 to implement a plan, and Commitment 1.4 to develop a
      plan. The results of the staff competency review (Commitment 1.4) were
      sent to the DNFSB on July 12, 1994 (see Reference 2).

      Subsequent to the WHC staff competency review, the Characterization
      Project has expanded dramatically, expanding from fewer than twenty
      people to more than four hundred. In conjunction with the expansion, a
      Hanford Sitewide Training Requirements Matrix (TMX) system has been
      implemented. Rather than revise and resubmit the plan transmitted to
      DNFSB on July 12, 1994, RL requests that the TMX system be considered as
      meeting the intent of Commitment 1.5.

The required training for all personnel is scheduled to be complete by
May 31, 1996. RL proposes that closure of this commitment occur when RL
transmits a letter report to the DNFSB indicating that personnel in the
Characterization Project have completed training requirements. This is
projected to occur by May 31, 1996. On this date, RL will submit
recommendation of closure of this commitment.

• Commitment 1.23, "Identify Bounding Tanks for Disposal."

  WHC Document WHC-SD-WM-TA-154, "Strategy for Sampling Hanford Site Tank
  Wastes for the Development of Disposal Technology, Rev. 1," has been
  reviewed by RL's Retrieval, Treatment and Immobilization Division staff
  and has been accepted as meeting Commitment 1.23 (see attachment).
  Therefore, RL considers this commitment closed.

RL will continue to keep the Board informed of any changes that come from the
ongoing work process.

If you have any questions, you may contact me at (509) 376-7395 or your staff
may contact Mr. Jackson Kinzer, Assistant Manager for Tank Waste Remediation
System, at (509) 376-7591.

                                    Sincerely,

                                    John D. Wagoner
CHD:SJZ   Manager

Attachment:
Strategy for Sampling Hanford
  Site Tank Wastes for Development
  of Disposal Technology

cc w/attach:
R. Guimond, EM-2
M. A. Hunemuller, EM-38
K. T. Lang, EM-36
S. L. Trine, RL DNFSB Liaison
J. C. Tseng, EM-4
M. B. Whitaker, EH-9

STRATEGY FOR SAMPLING HANFORD SITE TANK WASTES FOR DEVELOPMENT OF DISPOSAL TECHNOLOGY

June 1995

M. J. Kupfer
W. W. Schulz
Westinghouse Hanford Company

J. T. Slankas
Pacific Northwest Laboratory

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ACKNOWLEDGEMENTS

CONTENTS

LIST OF TABLES

LIST OF TERMS

ANOVA	Analysis-of-Variance
CC	Complexed concentrate
DN	Dilute noncomplexed
DNFSB	Defense Nuclear Facilities Safety Board
DOE	U.S. Department of Energy
DQO	Data Quality Objectives
DSSF	Double-Shell Slurry Feed
DST	Double-shell tank
FY	Fiscal Year
HLW	High-level waste
ITS	In-Tank Solidification
LLW	Low-level waste
NCAW	Neutralized Current Acid Waste
NCRW	Neutralized Cladding Removal Waste
PFP	Plutonium Finishing Plant
PNL	Pacific Northwest Laboratory
PUREX	Plutonium-Uranium Extraction
REDOX	Reduction oxidation
SORWT	Sort on Radioactive Waste Type
SST	Single-shell tank
Tri-Party Agreement	*Hanford Federal Facility Agreement and Consent Order*
TRU	Transuranic
TWRS	Tank Waste Remediation System
USQ	Unreviewed Safety Question
WHC	Westinghouse Hanford Company
WSTRS	Waste Status and Transaction Record Summary

STRATEGY FOR SAMPLING HANFORD SITE TANK WASTES
FOR DEVELOPMENT OF DISPOSAL TECHNOLOGY

1.0 INTRODUCTION

This document updates Revision 0 of *Strategy for Sampling Hanford Site Tank Wastes for Development of Disposal Technology* (Kupfer et al. 1994) and presents a proposed strategy for sampling SST and DST waste to provide information necessary to satisfactorily support the Tank Waste Remediation System (TWRS) disposal mission. Information needs were obtained from preparation of the following reports: *Data Needs and Attendant Data Quality Objectives for Tank Waste Pretreatment and Disposal* (Slankas et al. 1995) and *Characterization Data Needs for Development, Design, and Operations of Retrieval Equipment Developed Through the DQO Process* (Bloom et al. 1995).

The tank sampling and process testing strategy defined in this report provides data and information needed to satisfactorily complete *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) (Ecology et al. 1994) Milestone M-50-03, "Complete Evaluation of Enhanced Sludge Washing to Determine Whether Advanced Sludge Processes are Required." Completion of this milestone is required by March, 1998.

The baseline approach (Jensen 1994) for the TWRS is to wash (pretreat) high-level waste (HLW) sludges using enhanced methods (e.g., leaching with NaOH, known as enhanced sludge washing) to remove certain key components from the sludge, such as aluminum, chromium, and phosphate. Removal of significant amounts of these components will reduce the volume of HLW glass that results from vitrification of the sludges. If enhanced sludge washing is ineffective, a larger volume of HLW glass will be produced, with associated increased operational and disposal costs. The response to Milestone M-50-03 will document if enhanced sludge washing is judged to be technically effective. If not, some alternative course of action may be desirable such as use of extensive separations techniques to reduce the volume of HLW feed to the vitrification process.

Additionally, the strategy defines the tank sampling basis for supporting process definition and preliminary design information for other reference tank waste pretreatment functions such as removal of cesium from alkaline supernatants. Also included is the strategy to provide characterization information needed to define tank waste removal processes, perform solids/liquid separations operations, and to ensure that the characterization information for waste pretreatment will provide feed to the HLW and low-level waste (LLW) vitrification processes that meet the glass composition and regulatory specification criteria for these processes. The reference TWRS disposal strategy, as well as potential enhancements and alternatives to the reference case, are described in Slankas et al. (1995) and are also reviewed briefly in Appendix A.

Tank samples will provide material for TWRS process development testing. The information gained will be used to define the key constituent species in the 'sludges and supernatants that govern the design parameters for the pretreatment and vitrification processes. Primary analyses of samples will occur during process development testing studies. Selective analysis of some tank samples will also be used to supplement and confirm ongoing historical evaluations of tank contents to better understand individual tank inventories and physical and chemical properties of the waste.

1.1 INTEGRATION OF DISPOSAL SAMPLING STRATEGY WITH MASTER CHARACTERIZATION PLAN

This pretreatment/disposal sampling strategy report integrates sampling needs to the maximum extent possible with those sampling needs preliminarily identified as part of an integrated characterization basis. The integrated characterization basis will become the technical baseline for the characterization program (Dove et al. 1995, Brown et al. 1995). The sampling sequence for the characterization basis will address sampling needs defined in this report as well as in several recently issued Data Quality Objectives (DQO) documents. The DQO documents include those for pretreatment/disposal (Slankas et al. 1995), and for confirmation of historical predictions of tank waste characteristics (Simpson and McCain 1995), for tank safety issues (Babad and Hunt 1995, Buckley 1995, LeClair 1995, Osborne et al. 1995, Meacham and Cash 1995), and for waste operations (Fowler 1995).

1.2 INTEGRATION OF DISPOSAL SAMPLING STRATEGY WITH PRETREATMENT/DISPOSAL DQO DOCUMENT

Information and data needs for the pretreatment/disposal program of the Hanford Site TWRS are documented in the Pretreatment/Disposal program DQO document (Slankas et al. 995) and the Retrieval DQO document (Bloom et al. 1995). Although the DQO process addresses all informational sources, a key and useful outcome of the systematic application of · the DQO process to Hanford Site waste pretreatment problems is identification of specific waste types and waste tanks to sample to provide material for required laboratory-scale tests with actual wastes. However, Step 7 of the DQO process (optimize the study design) cannot be completed at this time for the pretreatment functions. Completion of this step would provide the capability for selecting specific tanks for sampling. Thus, the full benefit of the DQO process has not yet been applied to this sampling strategy report. Specific algorithms are provided in the present DQO document, however, that can be used to complete Steps 6 and 7 once the TWRS program definition and technology database are sufficiently mature and the required inputs from decision makers are available. In lieu of a completed DQO document this report provides an interim means of defining meaningful tanks to sample to support waste disposal process development needs. This sampling strategy document will

likely be modified at a later date to reflect the results of the completed DQO process. The tank selection strategy defined in this report is based on an evaluation of the experimental requirements as defined in Slankas et al. (1995), and utilizes historical information as a basis for defining representative and bounding conditions.

1.3 QUANTIFICATION OF HISTORICAL INFORMATION

The sampling strategy for support of pretreatment/disposal activities utilizes an iterative approach. The strategy will likely be revised based on: (1) the result of on-going laboratory-scale process development testing, (2) completion of the optimization step (Step 7) for the DQO process defined in Slankas et al. (1995), (3) evaluation of the historical models used for describing Hanford Site wastes.

Simpson and McCain (1995) describe a basis for quantification of historical data such as those predicted by Agnew (1994a, b, c, d, e). The basis for quantification of the historical estimates for distribution of the waste types and waste compositions involves a sampling and analysis scheme utilizing core samples and auger samples. The uncertainties will be defined using a statistical analysis of variability.

The recommended samples identified in Simpson and McCain (1995) support information needs for both tank storage safety and waste disposal activities. Although the data requirements for this sampling strategy for pretreatment/disposal document emphasize retrieval and pretreatment needs, a majority of the recommended samples are identical to those defined in Simpson and McCain (1995). The ability to integrate tank sampling needs for the Hanford master characterization plan (Section 1.1) will benefit from these complementary efforts.

This sampling strategy, the historical data evaluation, and the Pretreatment DQO all tie together in a unified development to define required tank waste samples and the scope of process behavior associated with the various sample investigations. Information is iteratively acquired and applied. This continuous process of review and input provides an optimized selection of tank waste samples that leads to a robust process technology database.

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2.0 DISCUSSION OF SAMPLING STRATEGY FOR PRETREATMENT/DISPOSAL INFORMATION NEEDS

The Disposal program requires sample material from representative waste types to determine and bound the performance of the candidate baseline processes, and contingent processes. Information derived from the process performance is being made available for disposal mission project design in the following areas:

- Process Viability (e.g., transuranic element contamination of the low-level waste stream via solids carryover, or resolubilization of sludges during the caustic leach step).

- Conceptual Process Design (e.g., materials performance for column, vessel, and line sizing, input to queuing modelling surge, rate, and availability decisions).

- Process Enhancements (e.g., efficiencies, selection of alternate processes to achieve enhanced performance).

- Verification of Historical Tank Content (e.g., test performance with actual waste versus predicted performance based on waste inventory modelling).

- Safety Envelope for Plant Operation (e.g., radiation source term, criticality safety analysis, bounding accident source term, hazardous materials source term, and operational safety requirements).

This sampling strategy report concentrates on providing information to support process viability, conceptual configurations for process design, and evaluating enhancements to the reference processes. Furthermore, immediate needs for experimental data in the Disposal program's technical development--pretreatment technology areas are addressed.

2.1 STRATEGY OVERVIEW

A phased iterative approach is used to perform initial sampling and to define additional sampling requirements. Phase I of the pretreatment/disposal sampling strategy is essentially complete. The tank waste characterization program sampled several tanks in Fiscal Year (FY) 1994 and FY 1995 to support resolution of safety issues and other characterization needs. Representative material has been obtained from selected samples for process development testing. To date a total of 22 single-shell tank (SST) samples and 2 double-shell tank (DST) samples were selected for process development testing because they represent bounding waste types of interest or were thought to support key tank selection criteria (see Section 2.2). The basis for selecting these tanks was also provided earlier in Kupfer et al. (1994), and utilized best estimates of tank waste knowledge based on historical

approaches. In particular, the Sort on Radioactive Waste Type (SORWT) (Hill and Simpson 1994) and information from Agnew (1994a, b, c, d, and e) was utilized.

To date, 7 of the 22 SST waste samples have been tested to evaluate the effectiveness of simple waste washing versus enhanced sludge washing (Slankas et al. 1995). Tests for 12 other samples are either complete or in final analysis with reports now being prepared. Two additional samples which provide a total of 21 for the year are scheduled for testing this year. By integrating the pretreatment/disposal sampling needs with those for the characterization/safety needs, significant sampling cost savings have been realized.

The strategy for Phase II sampling is again applied in an iterative manner. Information/data already obtained to date from process development tests are evaluated to determine the data necessary to satisfy needs and to ascertain missing data. Again, information used to select Phase II samples relies heavily on historical knowledge of the waste types. As mentioned in Section 1.3, utilization of the historical sources as a basis for tank sample selections is being confirmed by the Historical Data Evaluation DQO (Simpson and McCain 1995). Phase II sampling must be completed by approximately December 1997 to support the Tri-Party Agreement Milestone M-50-03.

The historical information is used to select tanks targeted to provide a representation of the waste types of interest. Tanks are grouped based on similarities of waste streams that entered the tanks. Selected process development studies will provide confidence in the grouping for the primary analytes of concern to the pretreatment/disposal programs. A combination of selective process testing and analyses to confirm historical predictions will allow extrapolation of process testing results to other waste tanks known to contain similar waste types. Success of the process tests combined with the reliability of process tests results will dictate how much additional testing is needed to provide high confidence that a robust process will result.

In Phase II a total of 25 additional SSTs and 10 additional DSTs are recommended for sampling. Significant additional information is needed from wastes in 241-S and 241-SX tank farms since these wastes combine large quantities (masses) of sludge that can result in large volumes of expensive HLW glass. They also contain significant quantities of certain components such as chromium that are expected to reduce waste loading in HLW glass, thus increasing HLW glass volume. Section 2.2.1 expands on the need for these samples.

Table 1 (sheet 1) shows the list of SST samples already taken and presently undergoing testing (Phase I). Also listed are the proposed 25 additional SST samples for Phase II (sheet 2). If one or more of the recommended tanks cannot be sampled, then alternative tanks should be prudently chosen for sampling using the selection criteria stated in Section 2.2. Table 2 shows a recommended list of DST tanks to sample. Additional discussion of the recommended SST and DST samples is provided in Sections 2.2 and 2.3.

Table 1. Sampling of Single-Shell Tanks for Pretreatment/Disposal
Process Development. (Sheet 1 of 2)

Tank	SORWT Group	% of Total Sludge Volume	% of Sludge Volume by SORWT Group[c]
PHASE 1 (Samples Already Taken)			
241-U-110	10	1.5	6.03
241-B-110	16	1.97	4.11
241-B-201	7	0.23	2.22
241-C-109	13	0.5	2.32
241-C-112	13	0.84	DUPLICATION
241-T-104	25-I[a]	3.56	3.56
241-S-104	4	2.36	9.88
241-B-111	16	1.9	DUPLICATION
241-B-202	7	0.22	DUPLICATION
241-BX-107	12	0.93	5.56
241-T-107	10	1.38	DUPLICATION
241-T-111	15	3.67	7.18
241-C-108	13	0.53	DUPLICATION
241-BX-105	5	0.35	5.45
241-C-103	20	0.5	2.08
241-C-105	25-H[a]	1.21	1.21
241-C-107	10	2.21	DUPLICATION
241-TY-104	22	0.35	1.65
241-SX-113	24	0.21	1.19
241-BX-109	5	1.54	DUPLICATION
241-B-104	25-E[a]	2.42	2.42
241-B-103	6	0.91	2.53
SUB-TOTAL	13/25[b]	29.3	57.4

[a] Group 25 is a miscellaneous group subdivided into this category.

[b] Number of SORWT groups represented out of the 25 total SORWT groups.

[c] "Duplication" notes that a tank from this SORWT group has already been accounted for.

Table 1. Sampling of Single-Shell Tanks for Pretreatment/Disposal
Process Development. (Sheet 2 of 2)

Tank	SORWT Group	% of Total Sludge Volume	% of Sludge Volume by SORWT Group[c]
PHASE 2 (RECOMMENDED SAMPLES: 1995-1996)			
241-BY-108	3	1.24	5.12
241-BY-110	3	0.83	DUPLICATION
241-BX-103	5	0.5	DUPLICATION
241-B-106	12	0.93	DUPLICATION
241-T-103	17	0.19	1.15
241-T-109	21	0.47	1.73
241-BX-110	8	1.52	6.48
241-SX-108	4	0.7	DUPLICATION
241-C-104	25-G[a]	2.37	2.37
241-BY-104	2	0.32	5.12
241-BY-105	2	0.35	DUPLICATION
241-S-101	1	1.96	11.57
241-S-107	1	2.36	DUPLICATION
241-SX-101	1	0.9	DUPLICATION
241-SX-104	1	1.09	DUPLICATION
241-SX-109	4	2.01	DUPLICATION
241-TX-111	2	0	0
241-U-109	6	0.39	DUPLICATION
241-TX-116	2	0	DUPLICATION
241-TX-118	6	0	DUPLICATION
241-TY-105	25-M[a]	1.86	1.86
241-S-110	1	1.05	DUPLICATION
241-SX-107	4	0.84	DUPLICATION
241-SX-110	4	0.5	DUPLICATION
241-A-101	11	0.02	0.02
TOTALS (Phase 1 and Phase 2)	21/25[b]	51.7	92.8

[a] Group 25 is a miscellaneous group subdivided into this category.

[b] Number of SORWT groups represented out of the 25 total SORWT groups.

[c] "Duplication" notes that a tank from this SORWT group has already been
accounted for.

2.2 CRITERIA UTILIZED FOR SELECTING SINGLE-SHELL TANKS FOR SAMPLING TO SUPPORT PRETREATMENT

The SST sampling strategy emphasizes the need to develop pretreatment process technology data for sludges. Sludges, because of their different origins and compositions, are central to the development of pretreatment and vitrification technology. This strategy also includes sampling a representative amount of salt cake. All salt cake in SSTs contains relatively large concentrations of water soluble $NaNO_3$, $NaNO_2$, NaOH, and Na_2CO_3, and smaller amounts of other sodium compounds (e.g., $NaAlO_2$, Na_2SO_4, and Na_3PO_4). The important radionuclides present in salt cake are ^{99}Tc and ^{137}Cs. Retrieval of the stored SST waste will result in the dissolution of the salt cake.

Following are the selection criteria employed for defining the Phase II SST samples in Table 1. The degree to which each criterion is met is also summarized. The basis and rationale for selecting the samples is further addressed in Section 2.2.1.

- Tanks with overall high waste volumes were preferred (both sludges and salt cakes) (Hanlon 1995).

- For tanks that contain both salt cake and sludge, tanks with higher sludge contents were identified as more desirable.

- Tanks with single waste types or uncomplicated process histories were identified as more desirable.

- Similarities in composition among tanks is expected to be observed. The 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 on the basis of the type(s) of waste introduced into the tanks and their subsequent process history.

  In addition, groups of tanks are represented based on distinct layers of waste types based on transaction history (Agnew 1994a, b, c, d, and e).

- Bounding salt cake forms from different separations process flowsheets were sought, e.g., REDOX, PUREX, $BiPO_4$.

- For tanks that have been previously sampled and where substantial characterization data exist, those data sets were used to their fullest extent. With few exceptions, revisiting previously sampled/analyzed tanks was avoided.

- Choices were influenced by the quantity and concentrations of components known to limit glass waste loading (i.e., HLW glass volume), such as chromium,

aluminum, phosphate, and iron suspected to be in the tank (Agnew 1994a, b, c, d, e, and Brevick 1994a, b and 1995).

The 22 tanks sampled from the first phase and the 25 tanks tentatively selected for sampling from the second phase have the following characteristics (Table 1):

- The tanks contain about 52 vol% of the total SST sludge inventory (based on sludge volume estimates from Hanlon 1995).

- The tanks contain about 43 vol% of the total SST salt cake inventory and are representative of all the evaporation processes that generated salt cake.

- The selected tanks include 21 of the 25 different SST waste groups identified by the SORWT model. These groups encompass approximately 94 percent of the total waste volume, 93 percent of the total sludge volume, and 97 percent of the total salt cake volume.

- The tanks contain, according to Agnew (1994e, b, c, d, e) and Brevick (1994a, b and 1995), large inventories of nonradioactive constituents (e.g., aluminum, chromium, phosphate) known to be highly important to development of viable pretreatment and/or vitrification technology.

- Of the 25 tanks recommended for sampling in the second phase, 18 are included in the priority tanks to be sampled to support the integrated characterization basis (Dove et al. 1995, Brown et al. 1995) and the plan to evaluate historical data (Hill et al. 1995).

2.2.1 Basis and Rationale for Single-Shell Tank Sample Selections

This section provides additional information on the basis and rationale for each selection criterion listed in Section 2.2, and defines the degree to which each criterion is met.

Classification On Basis of Waste Inventory. A straightforward method for selecting SSTs for sampling is on the basis of their inventory of sludge and salt cake. The baseline TWRS waste pretreatment process employs water and NaOH leaching of waste sludges prior to vitrification of the washed sludges. The volume of HLW glass that must be disposed of in a geologic repository is highly dependent upon the volume of sludge resulting from the washing operations. The cost of vitrification and disposal of the HLW is a key factor in the overall TWRS disposal mission costs.

The SSTs listed in Table 1 contain about 52 vol% of the total SST sludge inventory (Hanlon 1995). Approximately 29 vol% of the sludge volume is accounted for with the Phase I samples.

If sludge inventory were the only criterion used for selecting tanks for sampling, obtaining samples from only 50 tanks could encompass approximately 80 vol% of the sludge in SSTs. However, those SSTs (Hanlon 1995) that contain 80 percent of the total sludge inventory do not contain wastes representative of all of the various types known to have been introduced into the 149 SSTs. Additionally, such tanks contain only 16 percent of the total salt cake. Table 1 was compiled to address these selection criteria also.

The general uniformity in the composition of salt cake makes development of acceptable pretreatment and vitrification technology much easier than it is for sludges. Therefore, it is considered more important to sample SSTs that contain large inventories of sludge rather than large inventories of salt cake. However, representation from salt cake is important, e.g., to determine inventories of key analytes that can impact LLW glass volumes, to determine inventories of ^{137}Cs and test ^{137}Cs removal methods, and to determine physical properties that can impact the choice of salt cake retrieval techniques.

The 47 tanks in Table 1 contain about 43 vol% of the total SST salt cake inventory. The selected 47 tanks also represent all of the various evaporation processes that produced the salt cake. The potential number of required core samples is reduced where possible by selecting tanks that contain large volumes of both sludge and salt cake.

Classification of Single-Shell Tanks on Basis of Fill History. A second important way of classifying SSTs is to use historical fill data to sort the 149 SSTs into groups of tanks that contain the same type (or types) of wastes. Development of retrieval, pretreatment, and vitrification processes will require characterization and testing of a cross section of the various waste types. Several major chemical separations processes performed at the Hanford Site from 1943 through 1981 are recognized as generating different types of wastes that were introduced into the SSTs:

- $BiPO_4$ Process

- REDOX Process

- PUREX Process

- Metal Recovery (Tributyl Phosphate) Process

- Nickel Ferrocyanide Scavenging Process

- B Plant ^{90}Sr Recovery/Purification Process and ^{137}Cs separations process

- Waste Evaporation-Crystallization and In-Tank Solidification Processes

- Fuel Cladding Removal Processes.

Detailed chemical flowsheet and waste composition information for all of these processes are available in a number of sources (Anderson 1990, Swanson 1990, Cleveland 1970, Larowski 1955, Stevenson and Smith 1961).

A History of the 200 Area Tank Farms (Anderson 1990) classifies SSTs on the basis of their fill history. Anderson (1990) provides relatively complete historical data for the type and amount of each type of waste introduced into each SST.

Hill and Simpson (1994) and Hill et al. (1995) recently used Anderson's report and a database to develop a model--SORWT--to separate SSTs into characteristic groups. By applying Analysis-of-Variance (ANOVA) methods, they were able to confirm group effects are present. The SORWT model correctly reflects the fact that, during their active life, each of the SSTs received waste from several different chemical process operations but that underlying patterns from waste management activities exist and can be used to optimize the data gathering and assessment efforts.

The fundamental premise of the SORWT model is that SSTs received the same waste types in the same approximate proportion and had a similar processing history will be more similar to one another than SSTs that received several different waste types in varying amounts and had a relatively unique process history. In addition, waste types that are largely liquid do not have as significant an effect on the character of the waste in the tank as solid-forming waste types. Therefore, if the primary and secondary solid-forming waste types can be identified for each SST, the tanks can be grouped based on this criterion. Information about the character of the waste in the rest of the members 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.

Considerable use of the SORWT model classification system was made in this report to select SSTs for sampling and characterization. In particular, the SORWT tank groupings in Hill et al. (1995) provided a basis for ensuring that the recommended list of SSTs (Table 1) to sample contained solids representative of the entire spectrum of wastes present in the 149 SSTs. At least one tank from 21 of the 25 SORWT model groupings is recommended for sampling and characterization for disposal purposes.

The number of tanks in a SORWT group chosen for sampling was influenced by the total number of tanks within that SORWT group, e.g., SORWT group I contains 23 tanks and a total of 6 tanks in that group were chosen for sampling. In addition, the number of tanks chosen for sampling within a SORWT group was increased somewhat if that group contains a high percentage of the total SST sludge volume. The SORWT groups not included in the list of 47 SSTs to sample have potentially minimal significance, since they contain very small volumes of waste.

As previously stated, the composition of a waste within a SORWT group can be deduced from information contained from analysis of a representative tank within the group.

Thus, from the information gained from the 47 samples, the 21 SORWT groups represent approximately 94 percent of the total waste volume, 93 percent of the total sludge volume, and 97 percent of the total salt cake volume.

Classification of Single-Shell Tanks By Content of Key Analytes. A third way of classifying SSTs for sampling and characterization for disposal purposes is to select those tanks that are predicted to contain substantial amounts of the total inventory of certain key analytes. Of particular importance to vitrification of washed sludges are the analytes aluminum, chromium, and phosphate. Waste loadings that can be satisfactorily achieved when washed sludges are vitrified are strongly dependent upon the concentration of aluminum, chromium, and phosphate in the washed sludge. Certain other analytes, e.g., bismuth, uranium, and barium, impact the performance of various pretreatment processes for removing certain radionuclides from alkaline salt cake solutions and, possibly, acid sludge solutions.

The normalized Track Radioactive Components (TRAC) code has been used in the past for predicting the amount of key analytes in all the SSTs. However, in a cooperative effort, Los Alamos National Laboratory, ICF-Kaiser Hanford Company, and Ogden Environmental personnel have recently prepared Historical Tank Content Estimate documents. A primary purpose of these reports is to provide a tank-by-tank inventory of selected radioactive and non-radioactive waste constituents. Documentation is presently complete (Brevick 1994a, b, and 1995) for all tanks in the 12 SST farms.

Data contained in Brevick et al. (1994a, b, and 1995) documentation for the 12 SST Farms were used in conjunction with SORWT model considerations to guide selection of SSTs for sampling. Thus, of those 17 SSTs estimated to contain the largest amount of chromium, 11 are selected for sampling. Similarly, of those 15 SSTs estimated to contain the largest amounts of aluminum, 10 are selected for sampling.

Those tanks expected to exhibit various mineral forms of aluminum that could result from high temperatures and aging of the waste are also considered. The ability to dissolve aluminum in sludge using enhanced sludge washing is highly dependent on the aluminum mineral form.

2.3 STRATEGY FOR SAMPLING DOUBLE-SHELL TANK WASTES TO SUPPORT PRETREATMENT

Table 2 provides a preliminary list of 12 DSTs recommended for sampling and characterization for disposal purposes. Two of the 12 DSTs (241-SY-101 and 241-SY-103) have recently been sampled and the waste from those tanks has been (or is presently being) tested for development of pretreatment processes. Sampling of the 10 additional DSTs is recommended. Emphasis on DST sampling differs somewhat from SST sampling. The great majority of SST waste is solids that have been regularly inhomogenously mixed--little

supernate is involved. On the other hand, the great majority of DST waste contains relatively homogeneous supernatant and a small amount of sludge that contains minimal amounts of aluminum, chromium, and phosphorous. Sampling therefore puts additional emphasis on obtaining supernatant for DST waste.

Table 2. Recommended List of Double-Shell Tanks to Sample
for Disposal Purposes.

Selected tanks		Tank contents[a]	
Farm	Tank	Sludge (m³)	Supernate (m³)[b]
241-AN	AN-102	337	3,765
	AN-104[c]	999	3,028
	AN-107	507	3,536
241-AW	AW-101[c]	318	4,039
	AW-103	1,374	1,067
	AW-105	1,124	2,669
241-AY	AY-101	314	3,123
	AY-102	121	3,093
241-AZ	AZ-101	132	3,536
241-SY	SY-101[c,d]	0	4,155
	SY-102	269	2,491
	SY-103[c,d]	0	2,831
Total		5,363	37,337

[a]Data from Hanlon (1995).
[b]Also includes salt slurries.
[c]On Current Watch List (Hanlon 1995).
[d]Sampling complete - Testing underway.

The 12 DSTs meet the following criteria:

- The tanks contain all the five major types of DST waste:
  - Concentrated Complexed (CC) waste
  - Double-Shell Slurry Feed (DSSF)
  - Neutralized Current Acid Waste (NCAW)
  - Neutralized Cladding Removal Waste (NCRW)
  - Plutonium Finishing Plant (PFP) waste

- The tanks contain about 75 vol% of the total DST sludge inventory.

- The tanks contain about 52 vol% of the total DST supernatant liquid inventory.

- The tanks contain waste known to have high concentrations of certain components (e.g., chromium, organic carbon, sulfate, transuranic elements, ^{137}Cs) that could impact selection of pretreatment processes and HLW glass volumes (Shelton 1995).

Classification on Basis of Waste Type and Waste Inventory. Hanlon (1995) lists current inventories of solids (sludge) and supernatant liquid in each of the 28 DSTs. Collectively, the 28 DSTs contain 7 to 8 times more supernatant liquid than solids. Also, only 16 of the 28 DSTs contain significant amounts of solids; none of the 241-AP Tank Farm tanks contain solids. Planned pretreatment processing of DST waste includes enhanced sludge washing of solids and removal of ^{137}Cs from supernatant liquids and wash waters using ion exchange. The 12 DSTs listed in Table 2 include tanks containing all five major types of DST waste. All of the tanks containing NCRW, PFP, and CC wastes are recommended for sampling.

Supernatant liquids in all the DSTs are relatively well-mixed homogeneous liquids. They are all alkaline solutions containing large concentrations of sodium salts (e.g., $NaNO_3$, $NaNO_2$, $NaOH$, $NaAlO_2$, Na_2SO_4, Na_2CO_3, and Na_3PO_4). Supernatant liquid in five of the DSTs (CC waste) also contains substantial concentrations of water-soluble organic complexants (e.g., sodium ethylenediaminetetraacetate [EDTA], sodium nitriloacetate [NTA], sodium citrate, etc.).

The five waste types in DSTs listed in Table 2 (CC, DSSF, NCAW, NCRW, and PFP) are of particular importance to the development of pretreatment vitrification technology. These five wastes contribute almost all the solids to the DSTs. Sludges in the DSTs vary in chemical composition and properties depending upon the type of waste (e.g., NCAW, NCRW) from which they precipitated. Because of their different origins and compositions, DST sludges, analogous to SST sludges, are central to the development of pretreatment and vitrification technology. Unlike most SSTs, the DSTs contain sludges that have generally been segregated based on process origin.

Of the 13 DSTs that contain > 120 m³ of sludge, 10 are recommended (Table 2) for core sampling and characterization. These 10 DSTs contain approximately 75 percent of the total DST sludge inventory. Sludge washing tests were recently performed with solids from Tank 241-SY-103 (CC waste). However, results of these tests have not yet been reported.

Classification on Basis of Key Analytes. The DSTs selected for sampling (Table 2) contain significant concentrations of several important analytes that can directly impact the scope of the waste pretreatment processes chosen, as well as the volume of glass resulting from vitrification of pretreated waste. Previous waste samples from tanks 241-AY-101 and 241-SY-102 indicate high concentrations of chromium. Achievable waste loadings in glass can be limited by the chromium content of washed waste sludges. The performance of aqueous processes (e.g., NaOH leaching) to remove chromium from these wastes needs to be evaluated.

Other DSTs are believed to contain waste with high concentrations of zirconium, fluoride, chloride or sulfate that can influence glass waste loadings and melter performance. Wastes in tanks 241-AW-103, 241-AW-105, 241-AY-102, and 241-AZ-101 are representative of those with high concentrations of these analytes.

The DSTs in Table 2 address the range of process limiting components for cesium ion exchange expected in Hanford Site supernatant wastes (Slankas et al. 1995). Development of technology for removal of ¹³⁷Cs from alkaline waste solutions will be required from NCAW, CC and DSSF waste. Wastes in tanks 241-AN-107, 241-AN-102, 241-AW-101, 241-SY-101, 241-SY-103, and 241-AZ-101 represent these waste types. Tests with waste from 241-AW-101 will be particularly significant since this waste is known to contain high concentrations of potassium that can interfere with removal of ¹³⁷Cs. Laboratory tests of ¹³⁷Cs removal methods have recently been performed on supernatants from CC tanks 241-SY-101 and 241-SY-103 (Brown 1995).

Removal of ⁹⁰Sr and TRU elements from waste supernatants also may be required. Wastes in tanks 241-AN-102, 241-AN-107, 241-SY-103, and 241-AN-104 are believed to contain high concentrations of these radionuclides (Shelton 1995). Tests also may be performed to evaluate methods to destroy organic complexants to precipitate ⁹⁰Sr and TRU. These tests will likely be performed on waste samples from tanks 241-AN-102, 241-AN-107 and 241-SY-103. Other DSTs containing DSSF (241-AW-101 and 241-AN-104) have significant quantities of sludges that have never been adequately characterized. Analysis and testing of these samples will determine any pretreatment requirements (e.g., removal of TRU elements and/or ⁹⁰Sr).

Existing chemical composition data from the 11 previously sampled DSTs (pre 1991) will complement and support the data obtained in the new characterization effort recommended in Table 2.

For DST waste, the use of grab sampling or combination of grab sampling and core sampling, may be appropriate rather than core sampling alone. An evaluation of less expensive (than core sampling) techniques for providing representative samples from DSTs, as well as SSTs, needs to be undertaken.

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3.0 DISCUSSION OF CHARACTERIZATION/SAMPLING REQUIREMENTS FOR WASTE RETRIEVAL

Characterization of actual tank waste is expensive and minimization of sampling requirements is an important method for reducing retrieval program costs. Methods used to reduce retrieval sampling requirements include utilizing historical data, using in situ instrumentation, minimizing the number of tanks that will be characterized and sampled, using the least expensive sampling method, and requesting only necessary analysis while obtaining adequate waste information for the identified decisions (Bloom et al. 1995). The historical information that will be utilized includes post sluicing records, Tank Characterization Reports, and information from Brevick et al. (1994a, b, and 1995).

Retrieval tank waste characterization requirements will be addressed in two phases to meet the intent of obtaining adequate waste information for the least cost. The first phase of tank waste characterization for retrieval will utilize historical data, development of in situ instrumentation, and use of data obtained for other programs to provide the necessary waste information.

Reevaluation of retrieval information needs will be required during the design of the retrieval systems to determine if safety or operational requirements require data in addition to that already available. The second phase of tank waste characterization will occur if the reevaluation determined that specific high impact information requirements are identified, a careful assessment of the available data completed and additional waste information found necessary. A revised retrieval DQO would be prepared during phase two.

During Phase I, slurry grab samples are required from DST 241-AZ-101. No additional new tank waste samples are requested for retrieval design, development, and operations in the current Phase I. Waste information required for retrieval system design and operation will be obtained from historical records, in situ instrumentation, documentation of operational experiences, and data obtained for other programs such as that required for the pretreatment and safety programs.

It is recognized that retrieval systems design and operations considerations could raise additional safety related questions concerning criticality, release of noxious gases, flammable gas accumulation, or others. Permitting and equipment disposal are additional considerations that require waste information during design of retrieval projects. Waste samples and analysis may be required in the future to provide information to resolve specific issues arising in these areas.

3.1 BOUNDING TANKS FOR SST DATA

During Phase I no new tank waste samples are requested for SST retrieval design, development, and operations. Historical data and documentation of operating experience in installation of salt well pumps and thermocouple trees in salt cake waste will be used to confirm past practice sluicing equipment design selection.

Tank waste data requirements for the initial sluicing demonstration in tank 241-C-106 are addressed in the 241-C-106 DQO document (Wang and Bell 1994). Safety and operations compatibility were evaluated and the results documented in the report *Chemical Compatibility of Tank Wastes in 241-C-106, 241-AY-101, and 241-AY-102* (Sederburg 1994).

Currently proposed SSTs to be retrieved by the Initial Single Shell Tank Retrieval System (ISSTRS) are 241-A-102, 241-A-106, 241-AX-101 and 241-AX-103. Other tanks in the 241-A, 241-AX, 241-TX, 241-BY, and 241-S farms are also being considered for retrieval and are assigned second priority. Historical tank waste data from all SSTs are desired but tanks in farms 241-TX, 241-A and 241-AX are given higher priority since they are being considered more likely for the initial SST retrieval at this time.

3.2 BOUNDING TANKS FOR DST DATA

Slurry grab samples are required from tank 241-AZ-101 to calibrate in situ instruments during the mixer pump test of Project W-151. However, no other new tank waste samples are requested for DST retrieval design, development, and operations during Phase I. Preliminary waste information requirements identified for DST retrieval will initially be addressed without new waste sampling specifically for retrieval. New waste samples may be required if specific data requirements are identified in phase two.

Characterization data obtained for the tank safety and pretreatment programs and historical data will be utilized to satisfy information needs required for retrieval system design during Phase I. Once the source and receiver tanks are identified for the initial retrieval project then available data will be assessed for meeting all the information needs including the criteria of the Compatibility DQO (Fowler 1995).

Operational tank waste data information requirements for the pumpability decision concerning waste transfers and the design information requirements for determining the number of mixer pumps for DSTs could be provided with in situ instruments that are currently proposed for development or demonstration. No waste sampling would be necessary if the identified in situ instruments are successfully deployed. Grab sampling of the mobilized waste in the waste recirculation lines during retrieval operations could continue to provide waste samples for limited analysis to assure the waste meets pumpability requirements if the in situ sensors are not developed.

Currently tanks 241-SY-102 and 241-AW-105 are considered the highest priority DSTs. However, all the DSTs will eventually be retrieved and tank waste information is required for all DSTs. Available compatibility information will be collected for these tanks from historical records tank characterization reports and data obtained for other programs.

The tank retrieval sequence is currently in development and the previous retrieval sequence for the initial retrieval of DSTs is being revised. Additional changes in the sequence are likely and historical data and data from other programs are adequate until a retrieval sequence is determined. Once the tanks to be retrieved are identified and confirmed, new data requirements will be determined after historical data are assessed.

The hazards analysis, preliminary safety evaluation, and safety assessment for initial retrieval of the DSTs are based on historical data. Specific detailed retrieval system design including safety mitigation equipment for each DST to be retrieved will also be based on historical data when it is sufficient. Safety mitigation equipment and retrieval system safety class requirements are determined in the safety assessment.

Safety and operations compatibility must be assured before waste transfer operations and any sampling requirements for operations will be identified once the tanks to be retrieved are determined.

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4.0 NUMBER OF SAMPLES REQUIRED FROM EACH TANK

The sampling strategy outlined in this document assumes that there is a significant degree of similarity in the behavior of wastes that fall into the same group. Analysis of the chemical properties of the waste groups show this to be true for chemical composition (Hill et al. 1995). However, minimal information is available regarding the variability in process test results for different samples of waste in the same group. As the strategy is applied, it will be necessary to determine the variability of wastes in a given group with respect to process testing. Although a relationship is expected between variability of chemical composition and variability of test results, the degree of correlation has not been established.

If initial test results show that great variability exists within waste type groupings or that the reaction of waste to process testing is not correlated with chemical composition in a predictable manner, the strategy for limiting the number of tanks to be sampled will be changed. Additional samples will be required to ensure that the range of possible waste types are covered. The value of the historic data on tank composition may decrease. This result is not anticipated, but contingency plans must address it.

Because the strategy is interested in behavior of defined targeted types of waste, rather than behavior of waste on a tank-by-tank basis, the number of samples required from a given tank is less important than the number of samples representing a waste type. For key waste types, several samples may be required. Obtaining those samples from several tanks will provide the most information about the possible range of variability within a waste type. On the whole, there is not a requirement for multiple samples within a single tank. However, if more than one sample is taken for other purposes, it would prove informative to perform testing and establish in-tank variability levels. If such sampling on several tanks shows that variability of process test results within a given tank is low, further sampling should be limited to one sample per tank. Exceptions may occur when multiple samples are required to achieve the necessary volume of material.

5.0 QUALITY ASSURANCE REQUIREMENTS

Process development tests with an appropriate selection of tank waste samples will provide information needed to support TWRS disposal decisions and to implement processes for final disposal of the waste. The strategy described in this report utilizes key selection criteria for choosing a minimum number of tank samples to adequately determine the required technical information. To assure that this strategy will achieve the TWRS goals with a low risk of failure, a quality assurance system must be in place. Quality must be assured through the following stages:

- Selected tanks must be sampled.

- Tank samples must be prepared for shipping to the performing laboratory (e.g., broken down, composited, archived).

- Controlled testing and analysis must be completed at the performing laboratory(ies).

- Testing results must be provided in a timely fashion to meet milestones necessary to support TWRS disposal plans.

The *TWRS Characterization Program Quality Assurance Program Plan* (Whelan et al. 1994) is the quality assurance program plan specific to the Characterization Program. This plan guides the program management activities for the Characterization Program. It establishes quality requirements for all Characterization Program work and provides a roadmap for implementing procedures.

An approved tank waste characterization plan (TCP) for implementing the sampling strategy will be issued before acquiring each tank sample. The TCP provides a description of the objectives achieved by sampling and analysis, e.g., support of relevant safety issues, and testing to support development of retrieval, pretreatment, and vitrification processes. Sample handling requirements and analytical needs are developed using the DQO process that provides input to the TCPs. The TCP defines appropriate operating procedures for sampling the tank, and quality assurance/quality control for handling and analysis of the samples.

The Westinghouse Hanford Company 222-S Laboratory has a quality assurance program plan (Meznarich 1994) and a quality assurance project plan (Taylor 1993) that provides the primary direction for the quality assurance/quality control for analyzing the waste tank samples at the 222-S Laboratory. If the Pacific Northwest Laboratory (PNL) 325 Laboratory is the performing laboratory, the analyses are guided by the 325 Laboratory quality assurance plan (Kuhl-Klinger 1994).

Procedures for performing process development tests with the tank samples are defined in Test Plans. Tests to be performed at the PNL 325 Laboratory are described in Lumetta and Rapko (1994). All process development work at PNL is done in accordance with requirements described in *TWRS Pretreatment Technology Development Project Quality Assurance Plan* (PNL 1994). Process development tests performed at laboratories other than PNL will utilize quality assurance project plans and test plans to assure that the work is done in a controlled manner.

The records associated with each test will be compiled into a data package. At a minimum, the data package will include the following:

- The test procedure used, including any notes taken during testing

- All analytical data reports

- A record of all calculations made in work-up and interpretation of the data

- A compilation of the test results that will form the basis for reporting of the data in annual status reports.

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APPENDIX A

TANK WASTE REMEDIATION SYSTEM

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A1.0 BACKGROUND INFORMATION

A1.1 TANK WASTE REMEDIATION SYSTEM

At the DOE Hanford Site, radioactive liquid and solid wastes are currently stored in 149 SSTs and 28 DSTs. DOE recently announced a decision (Ecology et al. 1994) to retrieve, for eventual final disposal, all the wastes from both the SSTs and DSTs. In response to this decision, the TWRS program was developed and documented (Johnson et al. 1993). The current technical strategy for accomplishing TWRS objectives also has been formulated (Wodrich 1994).

Principal functions of the TWRS include resolution of safety issues associated with interim storage of tank waste, tank waste characterization, waste retrieval, pretreatment of retrieved wastes to produce and/or separate LLW and HLW fractions, and vitrification of the LLW and HLW fractions. An important objective of the TWRS is to separate the retrieved wastes into a relatively small volume of HLW and a larger volume of LLW. Vitrified LLW will eventually be disposed of at the Hanford Site in a near-surface facility while vitrified HLW will be disposed of in a deep geologic repository.

A1.2 NEED FOR SAMPLING AND TESTING OF TANK WASTES

Tank sampling and testing of sampled wastes are needed to make key decisions necessary to support the TWRS disposal mission. Information on waste physical and chemical properties will help define the strategy for retrieval of tank waste, and the scope of waste pretreatment activities needed to provide suitable feed for waste vitrification. Of particular significance is a decision to be made by March 1998 that was established as part of the recently renegotiated Tri-Party Agreement (Ecology et al. 1994). This decision (Milestone M-50-03) will define the extent of waste pretreatment processes that must be utilized to prepare vitrification feed. The baseline approach (Jensen 1994) for the TWRS is to wash (pretreat) HLW sludges using enhanced methods (e.g., leaching with NaOH) to remove certain key components from the sludge such as aluminum, chromium, phosphate, etc. Removal of significant amounts of these components will reduce the volume of HLW glass that results from vitrification of the sludges. If enhanced sludge washing is ineffective, a larger volume of HLW glass will result, with associated increased operational and disposal costs. The response to Milestone M-50-03 will document if enhanced sludge washing is judged to be technically effective. If not, an additional course of action may be desirable to reduce the volume of HLW feed to the vitrification process (Jensen 1994).

The waste from any particular SST or DST certainly can be conveniently sampled and analyzed after retrieval to provide much more accurate and reliable needed information than can ever be obtained by analysis of one or two core samples from the tank. Thus,

preretrieval sampling and analysis for disposal purposes should be limited to that essential to develop needed retrieval, pretreatment, and vitrification technology. It is clear that some minimum amount of preretrieval core sampling and analysis of tank wastes is needed. Certain key pretreatment and vitrification technologies (e.g., sludge leaching, sludge dissolution, glass formulation development) cannot be developed without knowing the bounding chemical constituents and radionuclides in actual waste liquids and solids.

A1.3 FUNCTIONS AND SCOPE OF TANK WASTE CHARACTERIZATION

A1.3.1 Description of Tanks and Tank Waste

Between 1943 and 1964, 149 SSTs were built at the Hanford Site. These tanks were used to store radioactive waste generated at the Hanford Site. The 149 SSTs, located in 12 separate areas (tank farms) in the 200 East Area and 200 West Area, are currently estimated to contain 89,000 m³ of salt cake, 48,000 m³ of sludge, and 2,300 m³ of alkaline liquid (Hanlon 1995).

Between 1971 and 1986, 28 DSTs were constructed at the Hanford Site. Each of the DSTs was designed to contain, nominally, 4,000 m³ of waste. One of the DST tank farms (3 tanks) is located in the 200 West Area, the remaining 5 DST farms (25 tanks) are located in the 200 East area. As of January 1994, the 28 DSTs contained about 88,000 m³ of alkaline liquid and about 10,000 m³ of solid waste. A detailed description and status of Hanford tanks and tank waste are provided in Hanlon (1995). Additional information concerning the different types of wastes stored in the DSTs is presented in Section 2.0.

A1.3.2 Historical Characterization Methods

The various plans for final disposal of the wastes in the SSTs and DSTs, that have evolved over a decade or more, have all stressed the need to characterize the wastes. The TRAC computer code (Jungfleisch 1984) was an important initial step in characterizing wastes in both SSTs and DSTs. Input data to the TRAC code were derived from several sources: historical records of fuel irradiation conditions, fuel reprocessing chemical flowsheets, waste volumes, waste transfer routes and final destinations, and essential chemical purchases. Input data were coupled with computer code calculations of the radionuclide content of irradiated fuel at the time of reactor discharge and ORIGEN2 (Oak Ridge Isotope Generation and Depletion) code (Croft 1980) calculations of radionuclide decay. The final output of the TRAC code was a listing (as of 1984) of the quantities of 65 radionuclides and 30 nonradioactive chemicals in each SST and DST. The TRAC code predictions for nonradioactive chemicals were later adjusted or "normalized" (Boomer et al. 1993) to ensure that the total chemical inventories in all of the SSTs matched those in the *Hanford Defense Waste Environmental Impact Statement* (DOE 1987).

For various reasons (e.g., incomplete historical input data, incorrect assumptions concerning solubility of various waste components) the TRAC code predictions are quite uncertain. This has prompted a recent effort to expand the process to utilize historical tank content estimates as an important element in providing a basis for TWRS waste disposal decisions.

Los Alamos National Laboratory scientists, in association with personnel from ICF Kaiser Hanford Company, Westinghouse Hanford Company, and Ogden Environmental, as initiated by the Characterization Program Office in the TWRS, are currently developing the Historical Tank Content Estimate documents. These documents are being prepared from three separate elements: the Waste Status and Transaction Record Summary (WSTRS) reports (Agnew 1994b, c), the Tank Layer Models (Agnew 1994d, e), and the Defined Waste document (Agnew 1994a). The WSTRS is prepared from existing historical records such as the TRAC code transactions file and information in Anderson (1990) and is verified, as far as possible, from additional historical records. The WSTRS data concerning waste volumes and solids level measurements are used to provide a Tank Layer Model of the type and amounts of sludge and salt cake predicted to be in each tank. The third element, the Defined Waste List, is generated from historical process chemical flowsheet and essential materials purchase records. Combination of the WSTRS, Tank Layer Model, and Defined Waste List information provides an estimate of the types and inventories of waste components in each SST and DST and a framework for understanding and interpreting sample results. Estimates thus obtained will be compared to waste composition and inventory data defined by analysis of actual waste samples when such analytical data become available. The Historical Tank Content Estimate reports were recently issued (Brevick et al. 1994a and b, Brevick 1995). The methodology for sampling and analyzing tank wastes in order to better quantify values associated with the historical data models is provided in Simpson and McCain (1995).

A1.3.3 Tank Sampling

In addition to characterization information obtained from known purchase records, process knowledge, and tank transfer records, significant knowledge of tank waste has been obtained over the years through tank grab samples, direct process sampling, and process campaign reports (e.g., 242-A and 242-S Evaporator runs).

Concomitant with the development of the TRAC code, much effort was expended in the late 1970's and early 1980's to design and manufacture equipment to take full-depth core samples from SSTs and DSTs. This effort resulted in construction of the first core sample truck and associated equipment (Bell 1993). Currently this equipment is routinely used to take core samples from both SSTs and DSTs. Depending on the depth of waste in a particular tank, core samples up to 11.5-m long (22 48-cm long segments) can be taken. The "push type" equipment for taking core samples has recently been supplemented with new rotary drilling equipment. The new machinery will facilitate acquisition of core samples from certain SSTs that contain "hard pan-type" solids.

Procedures (Winters et al. 1990, Bell 1993) are currently in place to do the following:

- Receive up to 22 48-cm long core segments.

- Remove solid and liquid wastes from individual core sample segments.

- Sample solid and liquid wastes in each individual core segment.

- Composite wastes from several core sample segments.

- Sample composites of core sample segments.

Procedures are also in place for auger and grab sampling methods.

Analytical procedures also are in place for determining the radionuclide content of individual samples, subsamples, and composite samples as well as the concentration of most inorganic cations and anions. Specialized equipment and procedures for quantifying various organic materials in certain wastes also have been developed and applied. Considerable capability also exists for determining the physical properties of samples of solid wastes (Bell 1993).

A1.3.4 Characterization Plans and Reports

A detailed plan for characterization of SST and DST wastes was first published in 1990 (Winters et al. 1990). The plan was revised in 1993 and in 1994 (Bell 1993, 1994). The updated characterization planning documents focus on FY 1993 and outyear plans for sampling wastes in several important SSTs and DSTs. Various methods for sampling waste tanks and laboratory operations with the samples are described. A Quality Assurance Project Plan and a bibliography to various important waste characterization documents are also provided.

The recently amended Tri-Party Agreement, Amendment 4 (Ecology et al. 1994), establishes several new enforceable milestones for characterization of wastes in SSTs and DSTs. Tank characterization plans must be prepared before the tank sampling event. Tank characterization reports will be provided by 1999 for all 177 Hanford Site underground tanks. The scope of the reports will include information from tank waste samples as well as historical records of tank contents, flowsheets, etc.

A1.3.5 Data Quality Objectives

The requirements for characterization of tank wastes are being determined by a DQO process (Babad et al. 1994). The Tri-Party Agreement (Ecology et al. 1994) requires that the DQO process be used to support the completion of the required tank characterization

reports. The DQO process will result in identification and integration of data requirements needed for streamlined tank characterization efforts.

DQO documents have been prepared for the following functional areas of the TWRS Program:

- Waste Tanks Safety Programs

- Waste Compatibility (Operations)

- Retrieval

- Pretreatment/disposal

This approach is consistent with recommendations made by the DNFSB (DNFSB 1993) concerning the scope and objectives of the TWRS waste characterization program particularly as they relate to certain SSTs.

A DQO document that will evaluate characterization needs to support development of processes for retrieval of tank waste has been prepared (Bloom et al. 1995). Data quality objectives are already in place that address tank waste safety requirements during waste storage (Babad and Hunt 1995, Buckley 1995, LeClair 1995, Osborne et al. 1995, Meacham and Cash 1995, and Fowler 1995). A DQO document that addresses information needs to support waste pretreatment and disposal was recently issued (Slankas et al. 1995).

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