WHC-SD-WM-DQO-011
Revision 1

Interim Data Quality Objectives for Waste Pretreatment and Vitrification

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Page 1 of 2

COMPLETE

1. ECN 144527

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Made Section 5.0 "Decision Rules" an appendix. Reduced list of required analytes. Improved justification for analytes (Table 2). Revised decisions and data requirements.

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13b. Justification Details
Significant comments were received that inappropriate decision based questions were in Revision 0 (Step 2 of the DQO process). These were revised. Other major comments received requested reduction to the list of analytes for tank samples. The list requiring QC was reduced and an additional list was requested that requires minimum QC.

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SDD/DD	☐	Seismic/Stress Analysis	☐	Tank Calibration Manual	☐
Functional Design Criteria	☐	Stress/Design Report	☐	Health Physics Procedure	☐
Operating Specification	☐	Interface Control Drawing	☐	Spares Multiple Unit Listing	☐
Criticality Specification	☐	Calibration Procedure	☐	Test Procedures/Specification	☐
Conceptual Design Report	☐	Installation Procedure	☐	Component Index	☐
Equipment Spec.	☐	Maintenance Procedure	☐	ASME Coded Item	☐
Const. Spec.	☐	Engineering Procedure	☐	Human Factor Consideration	☐
Procurement Spec.	☐	Operating Instruction	☐	Computer Software	☐
Vendor Information	☐	Operating Procedure	☐	Electric Circuit Schedule	☐
OM Manual	☐	Operational Safety Requirement	☐	ICRS Procedure	☐
FSAR/SAR	☐	IEFD Drawing	☐	Process Control Manual/Plan	☐
Safety Equipment List	☐	Cell Arrangement Drawing	☐	Process Flow Chart	☐
Radiation Work Permit	☐	Essential Material Specification	☐	Purchase Requisition	☐
Environmental Impact Statement	☐	Fac. Proc. Samp. Schedule	☐	_____	☐
Environmental Report	☐	Inspection Plan	☐	_____	☐
Environmental Permit	☐	Inventory Adjustment Request	☐	_____	☐

19. Other Affected Documents: (NOTE: Documents listed below will not be revised by this ECN.) Signatures below indicate that the signing organization has been notified of other affected documents listed below.

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7. Abstract

This Pretreatment Interim Data Quality Objective will identify and provide the basis for pretreatment and vitrification analytical requirements to be performed on waste samples collected prior to the release of the Pretreatment DQO in Support of High-Level and Low-Level Waste Feed (WHC-SD-WM-DQO-010). It will represent the needs of the Pretreatment program until document WHC-SD-WM-DQO-010 is released.

The objectives of waste pretreatment are to process waste retrieved from double-shell tanks and single-shell tanks to meet high-level waste and low-level waste requirements and to optimize the volumes of HLW and LLW for ultimate disposal. Characterization data are needed to support near-term strategic decisions regarding which pretreatment options to choose.

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Interim Data Quality Objectives for Waste Pretreatment and Vitrification

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August 1994

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Richland, Washington

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LIST OF TERMS

DOE	U.S. Department of Energy
DQO	Data Quality Objectives
ESW	enhanced sludge washing
FY	fiscal year
GEA	gamma energy analysis
HLW	High-Level Waste
HWVP	Hanford Waste Vitrification Plant
IC	ion chromatography
ICP	inductively coupled plasma
LLW	Low-Level Waste
PT	pretreatment
RCRA	*Resource Conservation and Recovery Act of 1976*
SREX	Strontium Extraction
TCR	Tank Characterization Reports
TRU	transuranic
TRUEX	transuranic extraction
TWRS	Tank Waste Remediation System

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Stakeholder Meeting Attendees
Ten stakeholders meetings were held in support of the final Pretreatment DQO during the months of March through May. Comments provided from the first draft of the final document have been incorporated into this interim DQO where applicable. The following were involved in the meetings and reviews.

Washington State Department of Ecology
Megan Lerchen (Characterization Oversight)
Mike Gordon (Characterization Oversight)

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PRETREATMENT INTERIM DATA QUALITY OBJECTIVES FOR WASTE PRETREATMENT AND VITRIFICATION

1.0 INTRODUCTION

The Tank Waste Remediation System (TWRS) is responsible for storing, processing, and immobilizing the Hanford Site tank wastes. Characterization information on the tank wastes is needed so that safety concerns can be addressed, and retrieval, pretreatment, and immobilization processes can be designed, permitted, and implemented. This document describes the near-term tank waste sampling and characterization needs of the Pretreatment, High-Level Waste (HLW) Disposal, and Low-Level Waste (LLW) Disposal Programs to support the TWRS disposal mission.

This report provides the pretreatment and vitrification characterization needs on an interim basis for samples taken from the tanks in fiscal year (FY) 1994 and early FY 1995. The final DQO document will use a DQO process to determine longer term TWRS characterization needs as required by the Characterization Program (Babad 1994), the Defense Nuclear Facilities Safety Board Recommendation 93-5 (DOE 1994), and the *Hanford Federal Facility Agreement and Consent Order* (Tri-Party Agreement) (Milestone M-44-02) (Ecology et al. 1994). This interim DQO identifies sampling and analytical requirements until the final DQO report is issued and its recommendations are addressed.

The final DQO will define specific waste tanks to be sampled, sample timing requirements, an appropriate analytical scheme, and a list of required analytes. This interim DQO, however, focuses primarily on the required analytes since the tanks to be sampled in FY 1994 and early FY 1995 are being driven most heavily by other considerations, particularly safety.

The complete DQO process, as described in Babad, et al. (1994) consists of seven steps:

1. State the problem.
2. Identify the decision.
3. Identify the inputs to the decision.
4. Define the boundaries.
5. Develop a decision rule.
6. Specify acceptable limits on decision errors.
7. Optimize the design.

The completeness of the later steps depends on the maturity of the program and decisions being considered. This DQO, addressing an early, exploratory stage in the Pretreatment/LLW/HLW program definition, will make a rough estimate of decision error tolerances as specified in step six. Data collected initially will allow these tolerances to be better specified in a later DQO. Design optimization is seriously constrained by the fact that sampling currently only occurs under existing tank risers. Thus, there will be little consideration of this step at this time.

Samples obtained and analyzed under this DQO will provide information that will allow refinement of the data requests in the final Pretreatment/ LLW/HLW Immobilization DQO. For this reason, the analyses are requested for samples recovered from two risers for each tank specified. Comparison of analytical results from two sample locations in each tank provides an estimate of the sampling error and the error stemming from spatial variability within the tank. For all analytes requested in this report, analysis shall be performed in duplicate. This provides an estimate of the error stemming from sample homogenization and analytical processes.

The major objective of this Interim DQO is to provide guidance for tank waste characterization requirements for samples taken before completion of the final DQO. The characterization data needs defined herein will support the final DQO to help perform the following:

- Support the TWRS technical strategy by identification of the chemical and physical composition of the waste in the tanks
- Guide development efforts to define waste pretreatment processes, which will in turn define HLW and LLW feed to vitrification processes.

2.0 BACKGROUND AND STATEMENT OF PROBLEM

2.1 BACKGROUND

The overall strategy of Waste Pretreatment is to deliver phased pretreatment capability, including solids and liquids separation; then liquid treatment for LLW immobilization, and then solids treatment for HLW immobilization as shown in Figure 1. A general goal is to have the LLW fraction contain the maximum volume of the tank waste and the minimum inventory of radionuclides. The HLW fraction shall contain the minimum volume of the tank waste and the maximum inventory of the radionuclides.

A simplified schematic of the processes and strategy being considered for use in pretreating Hanford Site tank wastes is given in Figure 2. Assumptions for these processes and a description of the strategy to be used are provided in Wodrich (1994) and Gasper (1994). The strategy adopted for pretreatment of the Hanford Site tank wastes assesses both baseline and alternative processes, indicated in Figure 2. Alternative processes and technologies will continue to be developed as contingencies until the baseline processes are shown to be adequate.

In the baseline case, the solids and liquids separation will be done by decanting liquid from double-shell tanks (including salt cake that has been dissolved in single-shell tanks and transferred to the double-shell tanks). The solids treatment will consist of in-tank processing (sludge washing with water and sodium hydroxide solution) to remove solubles, including some of the aluminum, chromium, and phosphate to reduce the volume of solids going to the HLW immobilization facility.

An important decision will be made by March 1998 (Tri-Party Agreement Milestone 50-03) to determine how extensive pretreatment will be. By this time, evaluation of enhanced sludge washing capabilities must be completed to determine whether more advanced sludge separation processes are required.

To the extent that additional facilities are needed for the solids treatment, they will be provided by a HLW pretreatment facility, which may be a stand alone facility or may be combined with the LLW pretreatment facility or with the HLW immobilization facility. This HLW pretreatment capability is scheduled to be operational by June 2008 (Tri-Party Agreement Milestone 50-04) to support the HLW immobilization activity.

The liquid treatment for LLW immobilization consists of solids and liquids feed clarification to avoid fouling of ion exchange columns and radionuclide removal. The baseline case identifies cesium ion exchange and strontium removal, if necessary, as the only required radionuclide removal operations. Strontium is most likely to be found complexed with organic species; therefore, if strontium removal is required, a complexant destruction step may be necessary. Technology development is underway to support this activity. Evaporation capability will also be included in the first pretreatment module. This module is known as the Initial Pretreatment Module or LLW Pretreatment Module 1 and is scheduled to be operational by December 2004 (Tri-Party Agreement Milestone 50-02).

Figure 1. TWRS Tank Waste Pretreatment Program.

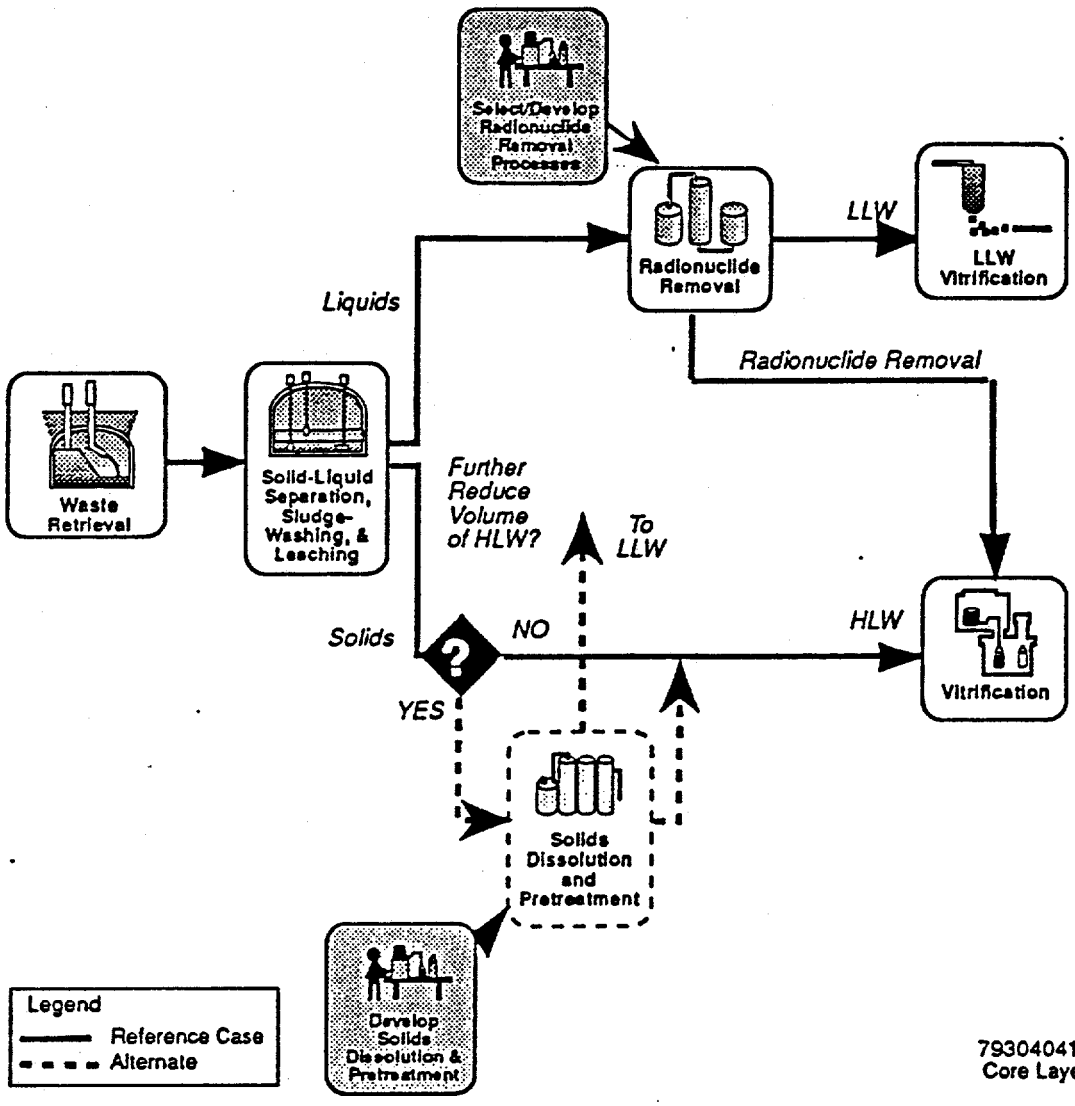
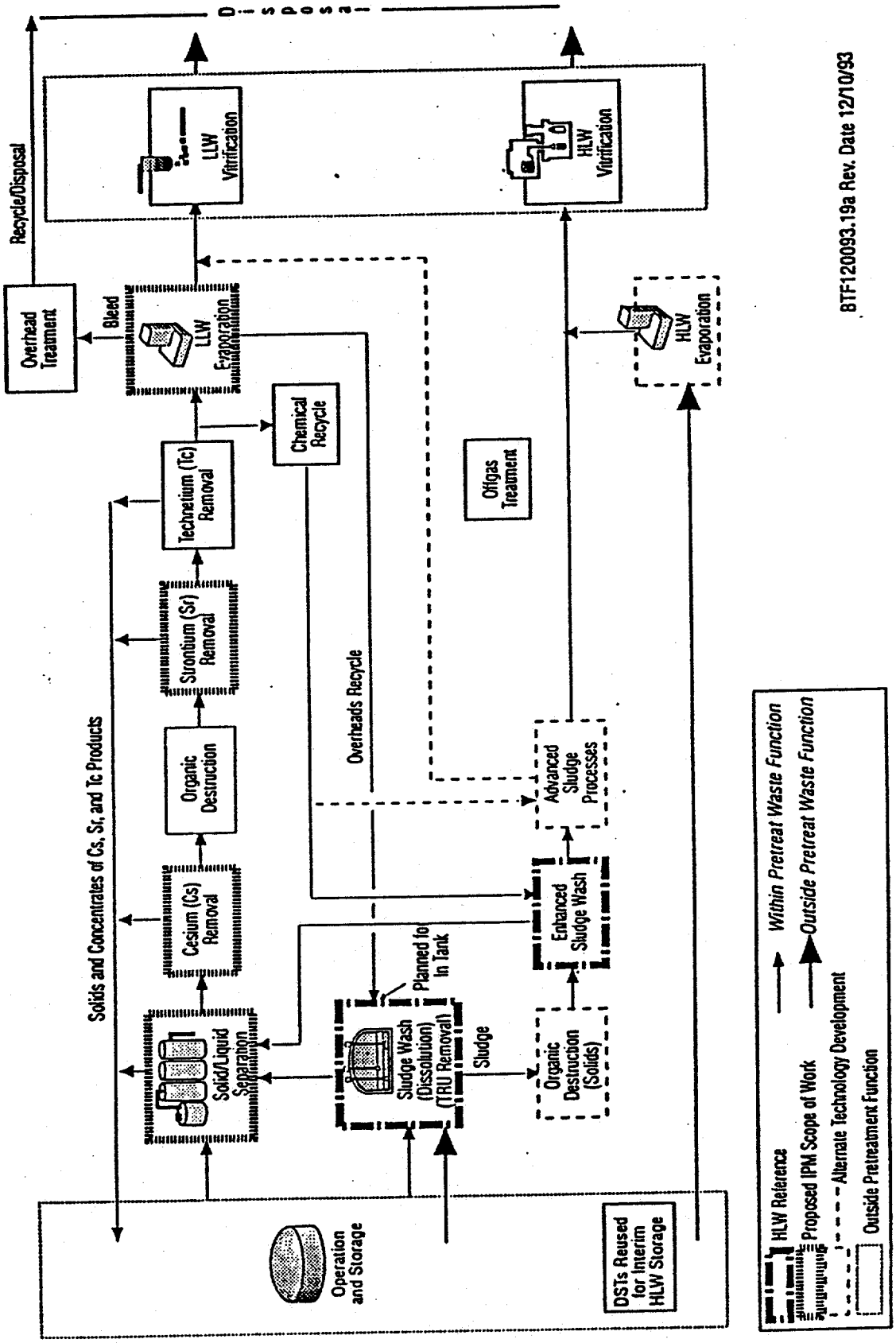


Figure 2. Schematic of Pretreatment Processes.



If the LLW performance assessment determines that other radionuclides need to be removed, the capability to remove these will be added to the second module of LLW pretreatment. (An exception to this may be technetium, which may be treated in Module 1.) LLW Pretreatment Module 2 is scheduled to be operational in January 2006. It provides additional capacity for pretreatment and may be an integral part of or co-located with Module 1.

2.2 PROBLEM STATEMENT

There are two underlying assumptions that must be verified (or modified) using a combination of characterization data and information from other sources:

Assumption 1. Relatively simple in-tank processes for pretreating the sludge will result in a reasonable volume of high-level waste requiring repository disposal.

Assumption 2. An acceptable LLW vitrification facility feed can be produced in the LLW pretreatment facility using feed clarification and ion exchange to remove cesium from the liquid stream.

The technology development and applied engineering strategy for waste pretreatment is to identify, evaluate, and test processes for development that will reduce the amount of vitrified HLW produced and also meet both the HLW and LLW vitrification feed requirements. Characterization data contributes to this strategy by providing bounding information about the analytes that will be found in the waste streams, and providing that information earlier than will be available from process development testing.

Characterization data obtained from this DQO will be combined with historical information regarding tank contents, knowledge of the reference and alternative processes and what analytes interfere with them, and information obtained from process development testing. This combined set of information will allow the programs to perform trade studies and select the most cost effective technologies and strategies for performing waste pretreatment and vitrification.

It is recognized that sampling and analysis from heterogeneous tanks results in incomplete information about average tank contents. It is the intention of the Pretreatment program to resample each tank following retrieval to determine the specific tank average concentrations of specific analytes of concern. This will allow decisions to be made regarding blending and treatment of the tank contents. It would be more costly and much less effective to attempt to obtain this information from samples collected from heterogeneous tanks before retrieval. The details of the analyses required at that time will be contained in a later DQO document.

3.0 QUESTIONS, INPUTS, AND BOUNDARIES

3.1 QUESTIONS AND INPUTS

Several key decisions must be made in the pretreatment program to support the strategy and objectives of providing pretreatment processing capability on-line to support retrieval, HLW Disposal and LLW Disposal objectives. Figure 2 indicates the process as presently envisioned. The baseline technology, as well as alternative and contingent technologies are indicated. The combined characterization data, historical data, and process development information will allow a decision to pursue the baseline course or, if necessary, a course that involves more extensive separations processes (Figure 2). The process-specific questions answered by characterization data obtained under this interim DQO are listed below.

It is noteworthy that most decisions address the analyte content specific to the water soluble waste fraction (destined for LLW) or the insoluble fraction (destined for HLW) rather than total waste concentrations. For the sludge waste, process development testing will determine which materials go to which fraction following sludge washing and related treatments. Characterization data on the content of the supernatant and insoluble fractions following water washing will provide the preliminary bounding information requested in this DQO. The benefit of obtaining characterization data is that it will be available much sooner than the process development results.

The following sections outline decisions for which data are required and the types of information required from the Characterization Program to make the decisions. The analytical scheme is described in detail in Section 4.0.

3.2 DECISIONS AND DATA REQUIREMENTS

The decisions for which this DQO will enable supporting data to be gathered include:

Are there major uncertainties in the historical tank waste characterization records that need to be accommodated in the TWRS Process Flowsheet, which is used as a basis for the conceptual design of pretreatment processes and facilities? This question requires identification of analytes of importance which have not been well documented in historical records, and analytes for which there is large uncertainty in historical records. In addition, it is assumed that historical information provides a better overall estimate of average analyte values than does sampling and analysis. This assumption must be verified or modified, by measurement of key analytes and comparison to historic records. Many of the analytes measured based on this DQO will be used to verify the historic model predictions. However, the primary justification for the analyte requests is to address one of the questions below.

What radionuclides need to be removed from the liquid fraction (or water soluble fraction) of the tank waste to meet the emerging LLW immobilization feed specification? Specifically:

- *Are there chemical constituents in the waste that limit or interfere with the cesium removal process?* Measurement of cesium, as well as other alkali metals and cations are required to address this question.

- *Is technetium separation required in Module 1 or Module 2 or both of these LLW Pretreatment processing lines?* Measurement of technetium in the liquid waste fraction and water dissolution leachate is required to address this question.

- *Is strontium removal capability required in Module 1 or Module 2 or both of these LLW Pretreatment processing lines?* Measurement of strontium in the liquid waste fraction and water dissolution leachate is required to address this question.

- *Is neptunium or americium or other transuranic removal capability required in Module 1 or Module 2 or both of these LLW Pretreatment processing lines?* This question accounts for the remainder of the radionuclide analysis requests in the liquid waste fraction and water dissolution leachate fractions.

Is organic complexant destruction capability required in Module 1 or Module 2 or both of these LLW Pretreatment processing lines, either to ensure proper operation of the ion exchange columns or to ensure that strontium and transuranics do not pass through into the LLW Immobilization plant feed? To address this question, characterization data must be obtained regarding the organic complexants which remain in the water soluble fraction of the waste. This is the basis for requesting total organic carbon (TOC) in the liquid waste fraction and water dissolution leachate.

What kind of solids/liquids separation (feed clarification) processes will be required in Module 1 or Module 2 or both of these LLW Pretreatment processing lines to ensure that fouling of the ion exchange columns does not occur? Monitoring the solids/liquids separation step in the laboratory for volume settled solids, content of each fraction, and settling times will provide an indication of the effectiveness of decanting or centrifugation for solids/liquids separation. In addition, measurement is required in the water soluble and liquid waste fractions of the chemicals known to interfere with ion exchange. The analytes requested for this purpose are the specific metals and carbonate requested in the water soluble and liquid waste fractions as described in Section 4.0.

What are solids settling times and what is the solids content of the settled/separated fraction? The results of settling time measurements give an indication of the effectiveness of decanting as a solids/liquid separation step in the pretreatment process. The measurements required are the relative quantities of sample that go to the solid and liquid fractions following gravity settling and decanting and the time period over which gravity settling occurred. This question also motivates the request for weight percent solids

and specific gravity of the solid composite sample, and specific gravity of the liquid composite.

Are advanced sludge separation processes required in order to produce a "reasonable" volume of HLW requiring repository disposal? Specifically:

- *What is the water soluble portion of the composite waste samples from representative tanks?* This requires measurement of the weight percent residual solids and water remaining after water washing.

- *What is a reasonable assessment of the volume of HLW that will require repository disposal and what are the uncertainties related to these HLW volume predictions?* This will involve a combination of characterization and historic data. The analytical inputs include the weight percent residual solids following water washing, and measurement of the radionuclide content (both in total solid sample and in residual solid sample). Additional inputs include measurement of nonradioactive chemical constituents of the residual solids including components that can reduce the waste loading in glass.

- *Which areas of technology development should be pursued next to reduce the volume of HLW requiring repository disposal or to reduce the uncertainties related to these HLW volume predictions?* This can be answered by a combination of characterization data indicating the chemical content of insoluble sludge fraction and process development to define methods for dissolving greater portions of the sludge. The chemical analyses requested are indicated in footnote (a) of Figure 4 (residual solids fraction) as well as weight percent oxides.

What blending scenarios (which tanks and which retrieval sequence) are appropriate from a waste compatibility standpoint and useful for ensuring LLW and HLW Immobilization feed specifications are most cost effectively met? Development of a tank-by-tank retrieval and blending sequence is out of scope of this DQO, and will be developed in a later DQO with much of the sampling performed following waste retrieval. This interim DQO must provide some information regarding the specific chemicals that will be reduced in concentration by blending. This information will be used to determine which groups of tanks should be retrieved at the same time to facilitate blending. This question is the basis for the chemical analyses requested from the liquid composite and the solid composite before water washing.

Information for the pretreatment program is also needed on the behavior of waste material under different waste processing conditions. The quantities of sample material needed from the Characterization Program and any data needs associated with getting samples to organizations performing process development work are identified in this interim DQO to ensure that waste samples can be provided when needed.

3.3 BOUNDARIES

A priority list of 67 tanks has been identified for sampling and characterization to support the key TWRS decisions associated with pretreatment and vitrification (Table 1). Characterization and process development data from the sampling of these 67 tanks will provide sufficient information for making decisions and initiating designs. The 67 tanks selected contain 80 percent of the sludge in the waste tank farms. Also, the tanks selected are representative of the waste types in the tank farms, and compositions of the wastes in the other tanks can be inferred from waste tank groupings by waste type.

A number of tank waste, grab, and core samples are scheduled to be taken in FY 1994 and early FY 1995. Several of these samples can be tested to provide useful information for the TWRS pretreatment and vitrification functional areas. Analytical results are requested from all types of solid and liquid samples for the tanks listed in Table 1. Archiving and provision of material for process development are requested for these samples (see Section 4.0).

No auger samples are requested in the list of 67 tanks in Table 1. However, if a decision is made by the Characterization Program to sample a requested tank using the auger technique rather than core sampling, characterization of the homogenized auger sample is required as stated in Section 4.0 for solid core composites.

Table 1. List of 67 Prioritized Tanks. (3 Sheets)

Rank number	Tank number	Waste type	Sludge (m^3)	Cumulative sludge	Salt cake (m^3)	Cumulative salt cake	Sample type
1	C-106	SRS/PSS	746	746	0	0	Rotary mode
2	C-102	CW/TBP	1600	2346	0	0	Rotary mode
3	C-110	1C/TBP	708	3054	0	0	Push mode
4	C-104	CW/POS	1120	4174	0	0	Push mode
5	B-104	2C/EB	1140	5314	261	261	Rotary mode
6	S-107	REDOX	1110	6424	261	522	Rotary mode
7	S-101	REDOX/EB	924	7348	647	1169	Rotary mode
8	SX-109		946	8294	0	1169	Rotary mode
9	SX-108		435	8729	0	1169	Rotary mode
13	TY-105	TBP	874	9603	0	1169	Rotary mode
14	C-103	SRS/PSS	235	9838	0	1169	Rotary mode
15	C-107	Purex/SRS	1040	10878	0	1169	Push mode
16	C-105	TBP/PSS	588	11466	0	1169	Rotary mode
21	A-103	DSSF	1390	12856	0	1169	Push mode
22	BX-109	TBP/CW	731	13587	0	1169	Push mode
23	BX-110	1C/EB	715	14302	34	1203	Rotary mode
24	BX-112		621	14923	0	1203	Push/Rotary
25	BX-104	TBP/CW	363	15286	11	1214	Push mode
26	BX-102	TBP/CW	363	15649	0	1214	Push mode
27	BX-111		257	15906	613	1827	Rotary mode
29	SX-114	REDOX/IX	685	16591	0	1827	Rotary mode
30	SX-104		515	17106	1810	3637	Rotary mode
31	SX-111	REDOX/IX	473	17579	0	3637	Rotary mode
32	SX-102		443	18022	1610	5247	Rotary mode
33	SX-101		424	18446	1300	6547	Rotary mode
34	TX-103	TBP/EB	594	19040	0	6547	Rotary mode
35	TX-105		0	19040	2305	8852	Rotary mode
36	TX-106		0	19040	1711	10563	Rotary mode

Table 1. List of 67 Prioritized Tanks. (3 Sheets)

Rank number	Tank number	Waste type	Sludge (m^3)	Cumul-ative sludge	Salt cake (m^3)	Cumul-ative salt cake	Sample type
37	TX-101		318	19358	0	10563	Push mode
38	TY-103	TBP/IC-F	613	19971	0	10563	Rotary mode
39	TY-104	TBP/IC-F	163	20134	11	10574	Rotary/Auger
40	TY-101	EB	447	20581	0	10574	Rotary mode
45	T-110	2C/224	1420	22001	0	10574	Push mode
46	T-101	CW/Mix	390	22391	0	10574	Push mode
47	S-111		536	22917	1890	12464	Rotary mode
48	S-110		496	23413	980	13444	Rotary mode
49	B-107	1C/EB	621	24034	0	13444	Rotary mode
50	B-105		151	24185	1010	14454	Rotary mode
51	A-106	CC/NC/EB	473	24658	0	14454	Rotary mode
52	BY-108	TBP/EB	583	25241	280	14734	Rotary mode
53	BY-101		394	25635	0	14734	Rotary mode
54	BY-109		314	25949	1290	16024	Push/Rotary
55	BY-110		390	26339	1120	17144	Rotary mode
56	B-109	1C/EB	481	26820	0	17144	Rotary mode
57	B-101	CW/EB	428	27248	0	17144	Push mode
58	B-103	CW/EB	223	27471	0	17144	Rotary/Auger
59	B-110	2C/5-6	927	28398	0	17144	Push mode
60	B-111	2C/5-6	893	29291	0	17144	Push mode
61	U-104	REDOX/dia-e	462	29753	0	17144	Push mode
62	U-109		182	29935	1570	18714	Rotary mode
63	U-112		170	30105	15	18729	Rotary mode
64	U-103		121	30226	1650	20379	Rotary mode
65	U-106		98	30324	757	21136	Rotary mode
66	T-105	1C/CW	371	30695	0	21136	Push mode
67	SX-103		435	31130	2030	23166	Rotary mode
10	SY-103	CC	0	0	674	674	Push/wideBOS

Table 1. List of 67 Prioritized Tanks. (3 Sheets)

Rank number	Tank number	Waste type	Sludge (m^3)	Cumulative sludge	Salt cake (m^3)	Cumulative salt cake	Sample type
11	AY-101	CC	314	314	3123	3797	Push/wideBOS
12	AN-107	CC	507	821	3536	7333	Push/wideBOS
17	AY-102	NCAW	121	942	3093	10426	Push/wideBOS
18	SY-102	PFP	269	1211	2491	12917	Rotary mode
19	AN-104	DSSF	999	2210	3028	15945	Wide BOS
20	AW-101	DSSF	318	2528	4039	19984	Rotary mode
28	AZ-102	NCAW	360	2888	3274	23258	Push/wideBOS
41	AZ-101	NCAW	132	3020	3536	26794	Push/wideBOS
42	AW-103	NCRW	1374	4394	1067	27861	Push/wideBOS
43	AW-105	NCRW	1124	5518	2669	30530	Rotary mode
44	AW-102	DN	4	5522	3350	33880	Push/wideBOS

Waste type key:

BOS Bottle-on-a-string Sample
CC Concentrated Complexed (grab) waste
CW Cladding Waste
dia-e diatamaceous earth
DSSF Double-Shell Slurry Feed
EB Evaporator Bottom
Evap Evaporator Feed
F Ferrocyanide scavenged
HS Hot Semi Works
IX Ion Exchange Waste
NC Non-complexed Waste
NCAW Neutralized Current Acid Waste
NCRW Neutralized Cladding Removal Waste
POS Purex Organic Solvent
PSS Purex Sludge Supernatant
SRS Strontium Recovery Sludge
TBP Uranium Recovery
1C 1st Cycle, $BiPO_4$
2C 2nd Cycle, $BiPO_4$
224 Concentration Cycle, $BiPO_4$
5-6 Tank 5-6, B/T Plant

Total sludge for all tanks = 53,630 m^3. DSTs and SSTs listed represent 36,652-m^3 (9,683-kgal) sludge; 23,166-m^3 (6,120-kgal) salt cake; and 33,880-m^3 (8,950-kgal) supernate. Rank number is the integrated priority of SSTs and DSTs.

4.0 ANALYTICAL SCHEME

4.1 ANALYTICAL SCHEME FOR TANK WASTE SAMPLES

The sample handling and analytical scheme is shown in Figures 3, 4, and 5. The scheme may be summarized as follows: Note that the first three bullets are not addressed in Figures 3, 4, or 5. However, initial sample handling is described in Section 4.1.1.

- Drainable liquid is separated from solid material.
- In the solid fraction, solid material is further separated from liquid by gravity settling and decanting (note settling time and percent solids).
- Drainable liquid is combined with decanted liquid.
- A composite of solids and a composite of liquids are prepared.
- A portion of each composite is archived (for cores).
- A portion of each composite is transferred to a designated laboratory for process development tests (for cores).
- A portion of the solid composite is analyzed by the Characterization Program as outlined in Figure 4.
  - A subportion is allocated for direct analysis.
  - A subportion is allocated for fusion dissolution.
  - A subportion is allocated for water dissolution. Both the leachate and residual solids undergo analysis following water dissolution.
- A portion of the liquid composite is analyzed by the Characterization Program as outlined in Figure 5.
  - A subportion is allocated for chemical analysis.
  - A subportion is allocated for radiochemical analysis.

4.1.1 Preparation of Composites

Because homogenization of the waste is expected to occur during tank retrieval operations, characterization information to support waste pretreatment must be provided from a representative composite of the entire waste sample. When a core sample is taken, a single composite sample, representing all segments of the entire core, shall be prepared for the solid sample and for the liquid sample. This composite will consist of representative portions of each homogenized 48 m^3 segment. Both solid and liquid composites will be prepared as described in Figure 6-1 of Bell 1993.

The composites should be large enough to allow approximately 100-mL to be archived and an additional 25 to 100 mL of the composite to be transported to Pacific Northwest Laboratory (PNL) for process development tests. The composites shall be archived for a maximum of 5 years.

If an auger sample is taken rather than a core sample, a composite must be preparead from the homogenized sample. The analytical scheme would be the same as described for solid core composites (Section 4.1.2).

When a graph sample (bottle-on-a-string) is taken repreesentative liquid and solid composits must be prepared. The analytical scheme would be the same as describedin Sections 4.1.2 and 4.1.3.

4.1.2 Analytical Scheme For Solid Composites

Figure 3 shows the desired sample allocation for liquid and solid composites. As indicated in Figure 3, the core composite solids will be divided into three portions. One portion (approximately 100 mL) will be archived for possible future use to resolve unanswered questions pertaining to the TWRS technical strategy (box 1, Figure 3). A second portion (box 2) will be packaged and transported to the 325 Building, PNL, or an alternative laboratory for process development testing. A test plan will be developed for reference in Tank Characterization Plans that will define the receiving laboratory and the analyses to be performed on the process development portion. The third portion of the solids core composite (box 3) will be divided into subportions and analyzed by the Characterization Program to determine the chemical and radionuclide content of the solids core composite. Figure 4 shows the analysis scheme for the sample portion in box 3. If an insufficient sample is available to provide an archive and a sample for process development of the size just described, an attempt should be made to provide equal size archive and process development portions and a sufficiently sized portion to perform the analysis shown in Figure 4.

4.1.3 Analytical Scheme For Liquid Composites

The liquid composite (Figure 3) will be divided into three portions. One portion (box 4) will be archived (approximately 100 mL) for possible future use to resolve unanswered questions pertaining to the TWRS technical strategy. A second portion (box 5) will be transferred to the PNL 325 Building, or alternative laboratory for process development testing. A test plan will be prepared for reference in Tank Characterization Plans defining the receiving laboratory and the analyses that will be performed on this portion. The third portion (box 6) will be analyzed by the Characterization Program to determine the chemical and radionuclide content of the liquid composite. Figure 5 shows the analytical scheme for the portion in box 6.

4.1.4 Special Handling of Tank 241-C-106

The analytical scheme described above applies to each tank sample composite. Sampling requests to date for support of TWRS waste processing decisions (Section 5.0) have typically requested two core samples for each tank, preferably from different risers. However, for Tank 241-C-106, four core samples (two each from two different risers) were requested (Roal 1994a, Roal 1994b). The analytical scheme just described in Section 4.1 should be performed for two of the 241-C-106 core samples. The additional two core samples should be transported to the PNL 325 Building laboratory where the cores will be broken down and prepared for larger scale process development experiments. PNL will provide test plans to define the process development tests.

4.2 ANALYTES

The analytical scheme for the portion of the solids core composite to be analyzed by the Characterization Program is shown in Figure 4. The solid composite is divided into a portion for direct analysis, a portion for fusion dissolution analysis, and a portion for water dissolution. Figure 4 includes a listing of the analytes and properties required from the analyses. The results of the direct analysis and fusion dissolution analysis address the analytes and properties found in the total solid fraction of the waste before any pretreatment. The results of these analyses will act as a control check for the analyses performed following water dissolution, to ensure that all input materials are accounted for. In addition, in cases where most or all of the solid material is soluble in water washing, these analyses will provide information that would not be obtained from the leachate analyses following water wash.

Figure 4 also shows the properties and analytes requested for the residual solid portion following water washing of the solid composite. This information is particularly important for the Pretreatment and HLW programs because it bounds the analytes that may report to the HLW stream. It is possible to estimate the content of the residual solids by comparing the content of the total solid composite with the content of the leachate fraction. However, this comparison is very inaccurate for analytes that remain in the residual solids in small concentrations. Hence the residual solid analysis is requested. It is understood that procedures may not yet be in place to perform this analysis step. The Pretreatment program will accept the results of the unwashed solid composite analysis and the leachate analysis until the procedures are in place to provide residual solids analysis. Development of these procedures should be a high priority item.

Figure 4 also shows the properties and analytes required for the leachate analysis following water washing. This list is a subset of the list of analytes and properties required for the liquid composite fraction, and addresses the questions regarding the treatment that will have to be applied to the LLW stream.

Figure 5 shows the properties and analytes required for the liquid composite fraction. Again, these properties are requested to address the questions regarding the treatment that will have to be applied to the LLW stream.

For quality control, duplicate analyses will be required for each solid and liquid sample. Analytes for process development samples (boxes 2 and 5 of Figure 3) are not included in the scope of this DQO; however, the analytes will be described in specific process development test plans.

Table 2 summarizes the analytes and properties requested for the various steps in the analytical scheme shown in Figures 4 and 5. It also gives an indication of the bases for each request.

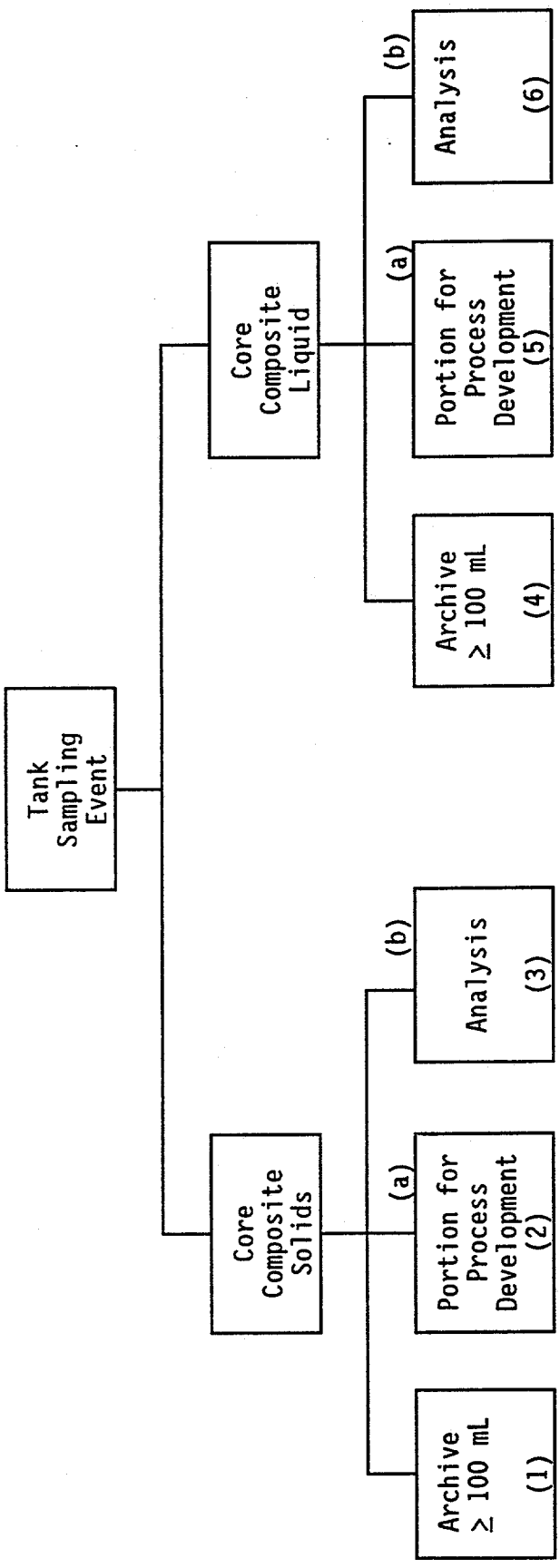
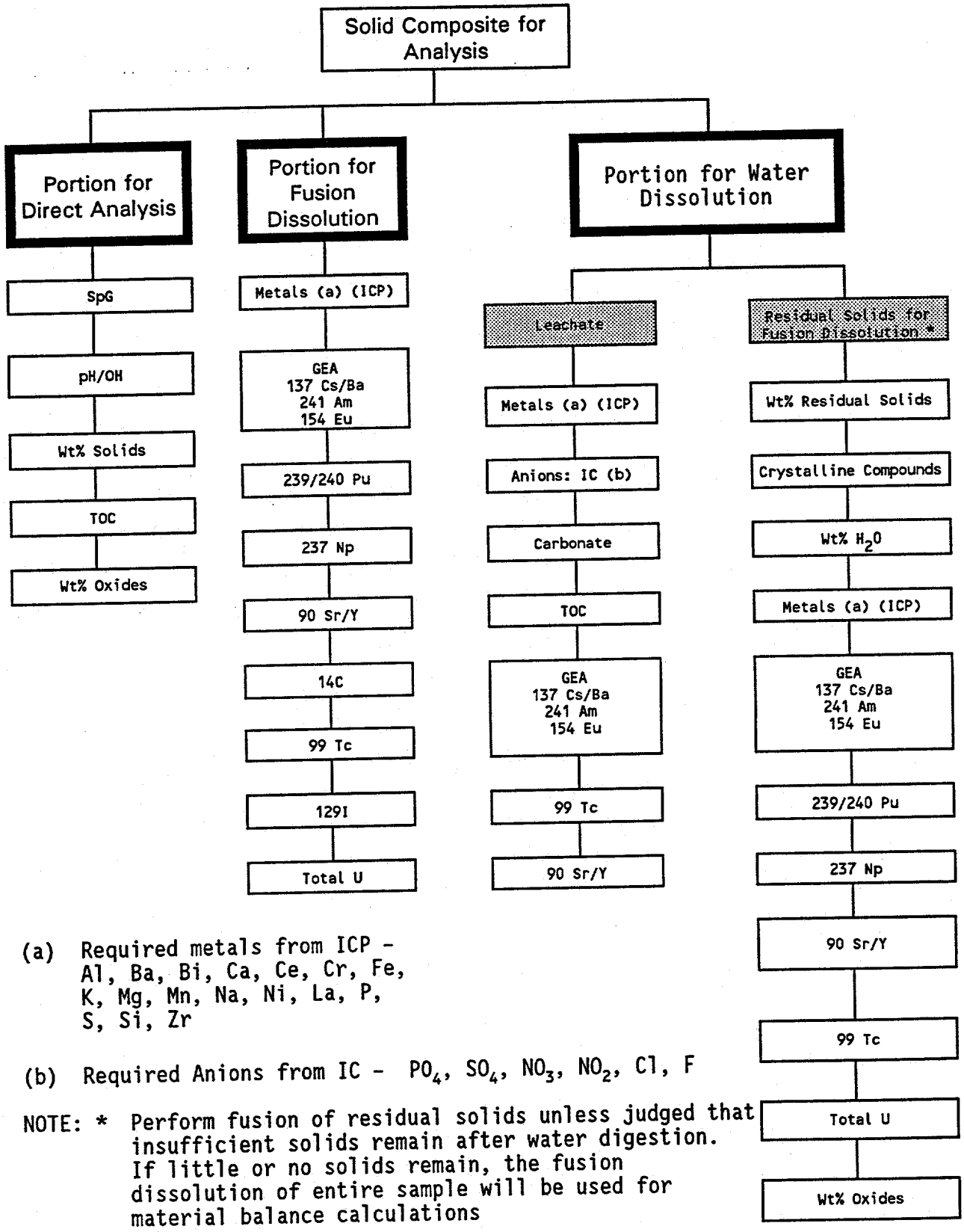


Figure 3. Composite Sample Allocation Scheme.

a) Sample size and analysis defined in process development test plans
b) See Figure 4 for analytical scheme of solids composite
c) See Figure 5 for analytical scheme of liquid composite

Figure 4. Analytical Scheme for Solid Composite.

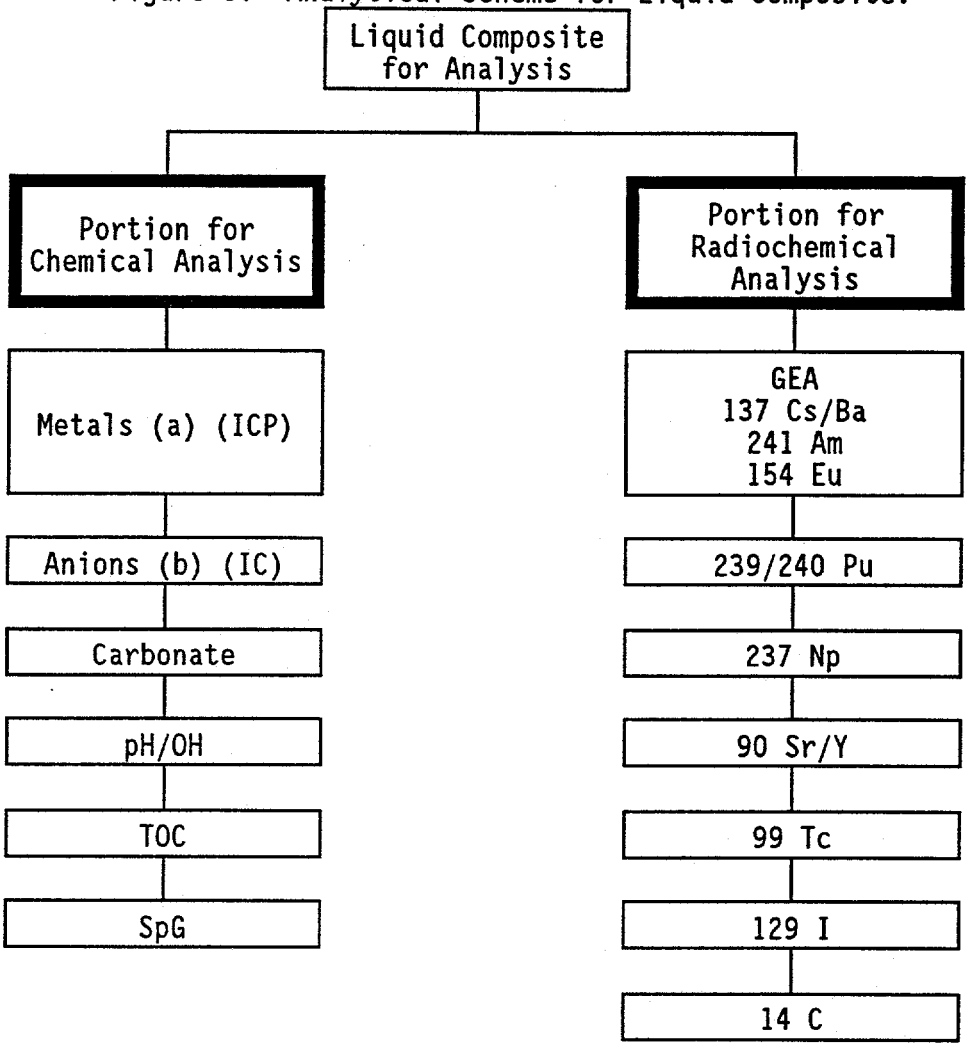


(a) Required metals from ICP - Al, Ba, Bi, Ca, Ce, Cr, Fe, K, Mg, Mn, Na, Ni, La, P, S, Si, Zr

(b) Required Anions from IC - PO_4, SO_4, NO_3, NO_2, Cl, F

NOTE: * Perform fusion of residual solids unless judged that insufficient solids remain after water digestion. If little or no solids remain, the fusion dissolution of entire sample will be used for material balance calculations

Figure 5. Analytical Scheme for Liquid Composite.



a) Required metals from ICP - Al, Ba, Ca, Cr, Fe, K, Mg, Mn, Na, P, S, Si, Zr

b) Required Anions from IC - PO_4, SO_4, NO_3, NO_2, Cl, F

Table 3 lists additional analytes not listed in Table 2 or on the analytical scheme. These analytes may be obtained by performing Inductively Coupled Plasma (ICP) or Gamma Energy Analysis (GEA). These analyses are required to obtain other properties listed in Table 2. This DQO is requesting a reporting of the instrument results for the analytes in Table 3 with the caveats that:

- If instrument recalibration or running the instrument using different parameters is required to obtain the analyte result, the additional analysis is not required.
- No additional standards, spikes, or blanks should be prepared solely for the purpose of obtaining information on the analytes listed in Table 3.
- Duplicate analyses should be performed; however, preparation of special dilution sizes to analyze these components will not be required.

These analytical results will not be used to answer the questions defined in Section 3.0 needed for making TWRS disposal decisions. This information will, however, aid in detecting unexpected analyte concentrations, and could indicate the need for obtaining (at a later date) more extensive analyses from a core composite archive.

4.3 ERROR TOLERANCES

As stated in the introduction, samples are requested from two cores per tank to provide an estimate of the spatial variability within the tank and the sampling error. Duplicate analyses are requested to provide an estimate of the error stemming from the sample homogenization and analysis processes. Recent statistical analyses of existing core sample data (Jensen 1994, Jensen and Wilmarth 1994) have indicated that the majority of the statistical variability observed stems from spatial or sampling variability rather than analytical variability. Increasing the number of samples obtained from different locations within a tank will thus have a much greater impact on the confidence in the data than will increasing the number of duplicate analyses or reducing analytical error.

The data requested in this DQO will not be used to make a decision which is based on analytical data alone. Multiple inputs (several analytical inputs, historical information, process development testing information) will combine to drive the decisions. It is difficult to define the degree to which the decisions will depend on the analytical inputs. However, since analytical information is only one of a set of inputs, significant insight may be obtained even when the numbers measured vary from the actual values by a factor of two or three or perhaps more, depending on the analyte. The preliminary statistical studies cited above found that for most analytes studied, two or three core samples were required to obtain a 95 percent confidence level that the true mean value fell within plus or minus 100 percent of the measured value. For some analytes, two cores provided 95 percent confidence that the true mean fell within 50 percent of the measured value. Although these studies were preliminary, they suggest that a request for two cores per tank is a reasonable starting place for the Pretreatment/ HLW/LLW data needs.

Table 2. Complete List of Analytes for Core Composite Solids and Liquids. (5 sheets)

Analyte	Reason for Analyte Importance
Al	**PT**-Important for measuring effectiveness of enhanced sludge washing (ESW). **LLW**-Impacts melter performance; increases glass durability and raises the melt viscosity. **HLW**-Can increase glass durability and raise melt viscosity. Crystalline phase forms at high levels. Possible major component in washed sludge that directly impacts glass volume and quality.
Ba	**PT**-May interfere with strontium ion exchange.
Bi	**PT**-Needed to evaluate phosphate solubility with ESW; Bi interferes with TRU extraction for extensive separation option. **HLW**-Possible major component in washed sludge that directly impacts glass volume and quality.
Ca	**PT**-Affects efficiency of ESW process by forming insoluble phosphate. **LLW**-In the presence of P can form a sludge problem. Decreases melt viscosity; in excess it promotes de-vitrification. **HLW**-Decreases viscosity; excess promotes devitrification. Can impact HLW glass loading and product performance if present as phosphate.
Ce	**PT**-Can form insoluble phosphate and reduce efficiency of ESW. Would be concentrated with TRUs and impact TRU extraction. **HLW**-Affects melter performance. In the presence of P can form a sludge problem in glass.
Cr	**PT**-Important measure of effectiveness of enhanced sludge washing. **LLW**-Forms insoluble spinels with iron and nickel; these can accumulate in the melter. The melter would need to be modified for solids removal or the waste loading would have to be reduced or the frit composition could be modified. Also impacts performance assessment of glass. **HLW**-forms insoluble spinels with iron and nickel; these can accumulate in melter. Reduces glass quality. Low wt% limit in glass.
Fe	**LLW**-Known to affect glass durability and radionuclide release. **HLW**-Possible major component in washed sludge that directly impacts glass volume and quality. Required as buffer for uranium; excess reduces glass leach resistance.
K	**PT**-Interferes with ^{137}Cs ion exchange. **HLW**-Needed to ensure proper feed and final product. Increases electrical conductivity of the melt. Impacts total alkali metal limit in glass.

Table 2. Complete List of Analytes for Core Composite Solids and Liquids. (5 sheets)

Analyte	Reason for Analyte Importance
La	**HLW**-Melter performance. In the presence of P can form a sludge problem in the melter.
Mg	**LLW**-Known to affect glass durability and radionuclide release. **HLW**-Needed as input to glass performance model.
Mn	**PT**-May interfere with Sr ion exchange. Possible major component in washed sludge that directly impacts glass volume and quality.
Na	**PT**-Major component removed by sludge washing. Effectiveness of sodium removal from sludge by water washing impacts glass volume. Interferes with cesium ion exchange. **HLW**-Melter size and performance. Sodium will most likely be the limiting waste component. Will likely dictate HLW glass volume if sludge washing efficiency is poor.
Ni	**PT**-May interfere with Sr ion exchange. **HLW**-Needed to ensure proper feed and final product. Can form metal under reducing conditions if concentrations are sufficiently high.
P	**PT**-Important measure of effectiveness of enhanced sludge washing. **LLW**-Design and performance of the melter; increases corrosion and reduces leach resistance of glass. Limited solubility in glass, thus can reduce waste loading and increase glass volume. May form refractory solids with rare earths and calcium. Influences glass melting rate. **HLW**-Limited solubility in glass, thus can reduce waste loading and increase glass volume. Increases corrosion and reduces leach resistance. Influences melting rate.
S	**PT**-Directly affects efficiency of sludge washing or enhanced sludge washing process. **LLW**-Sulfur is not very soluble in the melt, causing separation. A separate sulfate phase can float to the top of the melt and increase volatilization of radionuclides from the melt. **HLW**-Not very soluble in melt; may cause phase separation and limit waste loading.
Si	**PT**-Directly affects efficiency of sludge washing or enhanced sludge washing process. **HLW**-Increases melt viscosity and glass quality. Impacts Si frit composition. Possible major component in washed sludge that directly impacts glass volume and quality.
Zr	**LLW**-Known to affect glass durability and radionuclide release. **HLW**-Increases melt viscosity and glass durability. Crystalline phase may form in glass if present in excessive amounts.

Table 2. Complete List of Analytes for Core Composite Solids and Liquids. (5 sheets)

Analyte	Reason for Analyte Importance
CO_3^{-2}	**PT**-Solubility modeling of tank waste sludges. **LLW**-Can cause foaming problems with melter.
Cl^-	**PT**-Impacts corrosivity of pretreatment process solutions on stainless equipment. **LLW**-Excess Chlorine promotes undescribable phase separation in glass and causes corrosion problems. Fission product volatility increases (e.g., CsCl).
F^-	**PT**-Impacts corrosivity of pretreatment process solutions. **LLW**-Excess fluorine promotes phase separation in glasses. May volatilize and corrode equipment.
SO_4^{-2}	**PT**-Directly affects efficiency of sludge washing or enhanced sludge washing process.Impacts corrosivity of pretreatment process solutions. **LLW**-Sulfur is not very soluble in the melt, causing separation. A separate sulfate phase can float to the top of the melt and increase volatilization of radionuclides from the melt.
NO_3^-	**PT**-Directly affects efficiency of sludge washing or enhanced sludge washing process.Impacts corrosivity of pretreatment process solutions. **LLW**-Affects melter performance. Major component in offgas; affects offgas system design.
NO_2^-	**PT**-Directly affects efficiency of sludge washing or enhanced sludge washing process.Impacts corrosivity of pretreatment process solutions. **LLW**-Affects melter performance. Major component in offgas; affects offgas system design.
PO_4^{-3}	**PT**-Important measure of effectiveness of enhanced sludge washing. **LLW**-Design and performance of the melter; increases corrosion and reduces leach resistance of glass. Limited solubility in glass, thus can reduce waste loading and increase glass volume. May form refractory solids with rare earths and calcium. Influences glass melting rate.
TOC (Total Organic Carbon)	**PT**-Needed for evaluating and testing organic destruction processes. **LLW**-Impacts melter performance; carbon is a reducing agent that can precipitate metals from the melt, form soot in the offgas system, and cause foaming in the feed tank. **HLW**-Impacts melter design and feed preparation (reducing agent).

Table 2. Complete List of Analytes for Core Composite Solids and Liquids. (5 sheets)

Analyte	Reason for Analyte Importance
Percent Oxides	**PT**-Directly affects efficiency of sludge washing or enhanced sludge washing process. **HLW**-Affects process design and performance; affects waste glass loading and glass volume.
Percent Water	**HLW**-Possible major component in washed sludge that directly impacts glass volume and quality.
Crystalline Compounds	**PT**-Knowledge of chemical species in solids (e.g., crystalline components) by x-ray diffraction will aid in defining solids dissolution methods.
Weight Percent Residual Solids	**PT**-Provides estimate of relative proportion of water soluble and water insoluble solids for defining facility design requirements.
Total U	**PT**-May affect TRUEX process solvent loading. **HLW**-Possible major component in washed sludge that directly impacts glass volume and quality.
SpG	**PT**-Mass balance calculations.
pH/OH^- [a]	**PT**-Mass balance calculations; sludge solubility modeling.
^{14}C	**LLW and HLW**-Affects melter offgas treatment system design.
^{99}Tc	**PT**-Needed to evaluate technetium removal capabilities. **LLW**-Affects melter offgas treatment system design. Requires glass of suitable durability to contain a very mobile (in environment) and long-lived radionuclide.
^{129}I	**LLW and HLW**-affects melter offgas treatment system design. Requires glass of suitable durability to contain a very mobile (in environment) and long-lived radionuclide.
^{137}Cs/Ba	**PT**-Cesium ion exchange system design; facility shielding design. **LLW**-Shielding design; the LLW vitrification plant is to be a lightly shielded facility and ^{137}Cs will be the main dose source. **HLW**-Exposure concerns, sizing of ion exchange facility.
^{154}Eu	**PT**-Affects solvent loading in extensive separations, TRU separations scheme. **LLW**-Shielding design; the LLW vitrification plant is to be a lightly shielded facility and ^{154}Eu may be a major dose source.

[a] OH^- only if pH > 13.

Table 2. Complete List of Analytes for Core Composite Solids and Liquids. (5 sheets)

Analyte	Reason for Analyte Importance
$^{90}Sr/Y$	PT-Needed to evaluate strontium removal. LLW-Strontium will be a major dose source in the lightly shielded facility.
$^{239,240}Pu$	PT-Needed to evaluate criticality concerns in pretreatment processes; Needed to evaluate methods of removal. LLW-TRU limits in glass. HLW-Criticality concern in HLW glass.
^{241}Am	PT-Needed to evaluate removal methods. LLW-TRU limits in glass. HLW-TRU limits in glass.
^{237}Np	PT-Needed to evaluate removal methods. LLW-Performance assessment of glass. Requires glass of suitable durability to contain a very mobile (in environment) and long-lived radionuclide. HLW-Product glass performance assessment.

Table 3. List of Analytes to be Reported With Minimum Quality Control Evaluation.

Analyte	Liquid Composite Method	Solid Composite Method
Ag	ICP	ICP
As	ICP	ICP
B	-	ICP
Be	-	ICP
Cd	ICP	ICP
Cu	ICP	ICP
Mo	ICP	ICP
Pb	ICP	ICP
Sb	-	ICP
Se	ICP	ICP
Sr	ICP	ICP
Zn	ICP	ICP
^{60}Co	GEA	GEA
^{155}Eu	GEA	GEA
^{125}Sb	GEA	GEA
^{123}Sn	GEA	GEA

The statistical studies previously mentioned (Jensen, 1994; Jensen and Wilmarth, 1994) found that laboratory error was a minor contributor to the total error. The precision and accuracy data in Table 4 are derived from data produced on several recent data packages of SST samples. These data included various types of prepared samples: drainable liquor, water and acid soluble fractions, and fusion/dissolution fractions. The precision expected on samples is derived from reproducibility of results, i.e., relative percent difference of replicated results from the same homogenized sample. The sample accuracy reflects how close the measured value is to the true value. Accuracy is based on analysis of samples and (as in this case) on matrix spike recovery data.

Both precision and accuracy are heavily dependent on the concentration of the analyte in the sample. Therefore, Table 4 lists the achieved precision and accuracy at two concentrations: far above the minimum detectable quantity detection limits and near (< 10 times) the minimum detectable quantity. Analytical precision and accuracy are poorer when a parameter is measured at or near its detection limit. Increased accuracy and precision can be achieved

if required through multiple sample analysis or additional controls. These additional steps may be costly and should be requested if they are required to meet programmatic objectives.

This DQO requires that the laboratories meet the accuracy and precision values listed in Table 4 for the analyses covered by this DQO. The adequacey of these requests will be reviewed and the requirements revised in the final DQO, following receipt of initial results.

Table 4. Required Accuracy and Precision for Sample Analytes. (3 sheets)

Analyte	Sample Accuracy in Percent	Sample Precision in Percent*
Al	20(1)	20
	50(2)	40
Ba	40(3)	40
	80	80
Bi	50	20
	120	50
Ca	20	20
	50	50
Ce	10	20
	20	40
Cr	20	20
	40	50
Fe	50	30
	50	60
K	20	20
	40	40
La	10	20
	50	70
Mg	20	30
	30	100
Mn	50	30
	70	100
Na	20	20
	20	30
P	Presence/absence only	Presence/absence only
	Presence/absence only	Presence/absence only
S	Presence/absence only	Presence/absence only
	Presence/absence only	Presence/absence only
Ni	20	10
	30	50

Table 4. Required Accuracy and Precision for Sample Analytes. (3 sheets)

Analyte	Sample Accuracy in Percent	Sample Precision in Percent*
Si	20	30
	30	80
Zr	20	30
	50	60
Cl	20	20
	50	30
F	30	30
	70	60
SO4	20	20
	60	30
NO3	20	20
	50	30
NO2	20	20
	50	30
PO4	20	20
	50	50
CO_3	20	20
	50	50
TOC	50	50
	100	100
acid H+ (pH)	10	20
	50	100
hydroxide OH-	10	20
	50	100
U (total)	20	20
	60	60
^{14}C	40	50
	50	200
^{99}Tc	60	20
	100	50

Table 4. Required Accuracy and Precision for Sample Analytes. (3 sheets)

Analyte	Sample Accuracy in Percent	Sample Precision in Percent*
^{129}I	60	100
	100	100
^{137}Cs	10	20
	40	60
^{90}Sr	20	30
	30	60
^{154}Eu	10	20
	40	60
$^{239/240}Pu$	20	40
	40	70
^{241}Am	20	30
	50	80
^{237}Np	60	40
	140	80

(1) The first row for an analyte lists the accuracy and precision at high concentrations (>10 times the detection limit)
(2) The second row gives the values at low concentrations (<10 times the detection limit)
(3) Those values in this table not reported or established by the labs will be estimated for the final DQO.

* Precision requirements are based on relative percent difference between duplicates rather than standard deviation of main value.

5.0 REFERENCES

Babad, H., 1994, *TWRS Data Quality Objectives Strategy*, WHC-EP-0732, Westinghouse Hanford Company, Richland, Washington.

Bell, K. E., 1993, *TWRS Tank Waste Characterization Plan*, WHC-SD-WM-PLN-047, Rev. 1, Westinghouse Hanford Company, Richland, Washington

DOE, 1994, *Recommendation 93-5 Implementation Plan*, DOE/RL 94-0001, U.S.Department of Energy, Washington, D.C.

Ecology, EPA, and DOE, 1994, *Hanford Federal Facility Agreement and Consent Order*, as amended, Washington State Department of Ecology, U.S. Environmental Protection Agency, U.S. Department of Energy, Olympia, Washington

Gasper, K. A., 1994, *Hanford Site Tank Waste Remediation Systems (TWRS) Waste Pretreatment Program Strategy and Issues*, WHC-SA-2140-FP, Westinghouse Hanford Company, Richland, Washington.

Jensen, Louis, 1994, *Confidence Interval Width as a Function of the Number of Core Samples, Composite Samples, and Replicate Analytes*, (Internal Memo to D. Washenfelder, 8E100-PLP94-050, August 1994), Westinghouse Hanford Company, Richland, Washington.

Jensen, Louis, and Steven R. Wilmarth, 1994, *Mean Concentrations, 95% Confidence Intervals and Sample Size Estimates for Total Organic Carbon and Percent Water from Single-Shell Tanks*, (Letter report to C. DeFigh-Price, 8E100-PLT94-056, August 1994), Westinghouse Hanford Company, Richland, Washington.

Roal, R. C., 1994a, *Revised Pretreatment Sampling Priority Schedule*, (Internal Memo, 7E360-94.003, to G. A. Stanton, May 16, 1994), Westinghouse Hanford Company, Richland Washington.

Roal, R. C., 1994b, *Revised Pretreatment Sampling Priority Schedule*, (Internal Memo, 7E360-94.004, to G. A. Stanton, June 27, 1994), Westinghouse Hanford Company, Richland Washington.

Wodrich, D. D., 1994, *The Hanford Site Tank Waste Remediation System Technical Strategy*, WHC-SA-2335-FP, Westinghouse Hanford Company, Richland, Washington.

APPENDIX A

PRETREATMENT PROGRAM DECISION PROCESS

This appendix describes the decision rules to which the tank characterization data will be applied. A logic diagram for the decision process is given in Figure A-1. The following text describes in more detail the logic diagram and refers to the box numbering in the diagram.

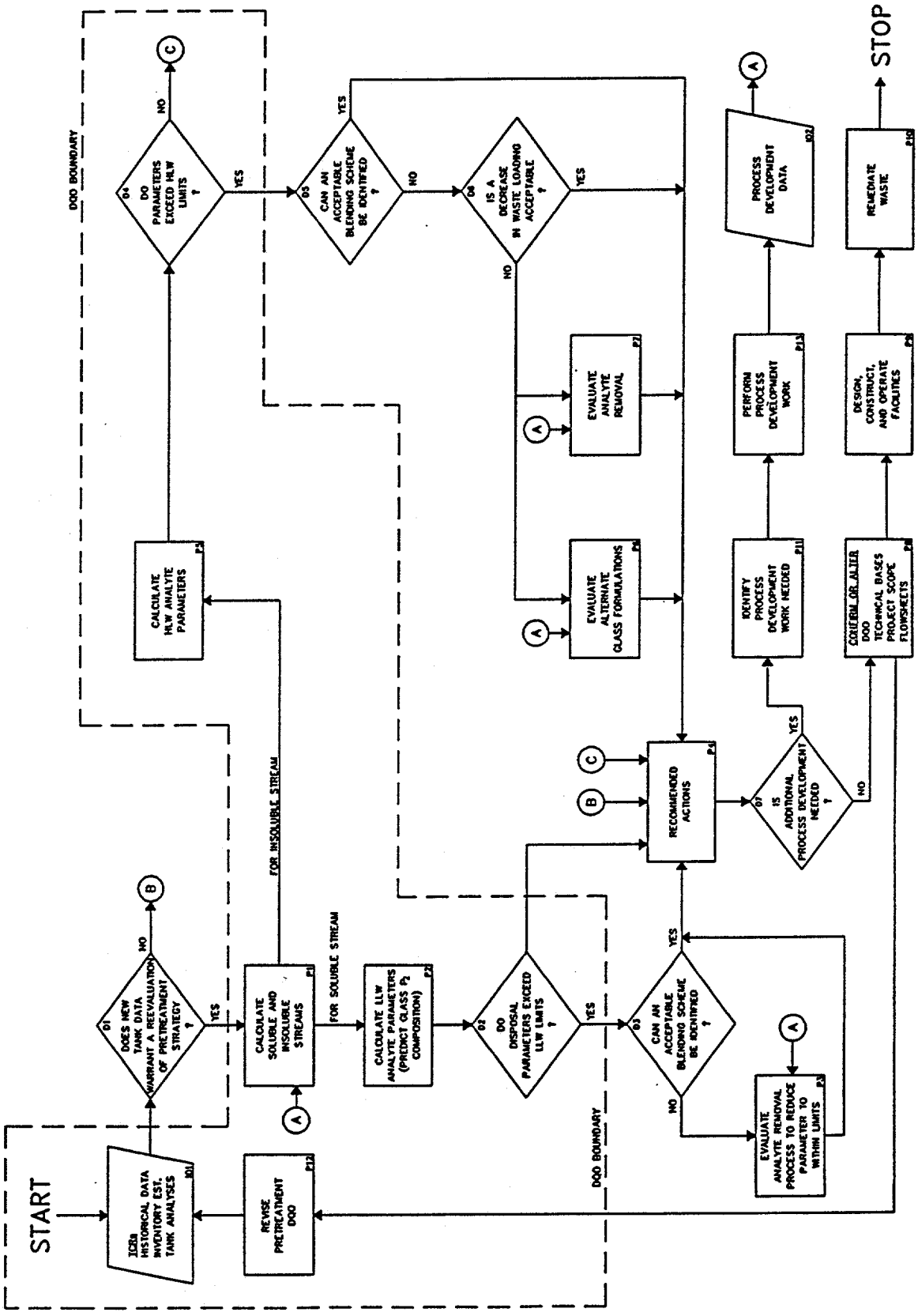
The pretreatment program will use historical data, tank characterization database information, and new tank analyses (input/output box I01) to prepare a pretreatment process flowsheet. As the tank characterization program obtains new data via tank sampling and characterization, that data is reviewed (decision box D1) by TWRS Process Engineering personnel against the available data to see if the new data appreciably changes the current understanding of the contents of the tank and the overall tank waste inventory. If the data does not change the understanding, the recommended action (process box P4) is to maintain the same strategy and the decision outcome confirms the technical bases upon which the strategy is based. If the new data is appreciably different from existing data, then the new data is incorporated into the tank waste inventory data used as input to the flowsheet model.

Flowsheet calculations are performed to predict the mass, flow, and composition of the soluble and insoluble streams that would result from the inhibited water washing performed during retrieval of the wastes (process box P1). These calculations are normally performed assuming uniform blending. That is, that all the wastes are retrieved and blended to provide a homogeneous feed stream to the pretreatment facilities. Separation factor data from process development testing is incorporated into the flowsheet to predict the split between soluble and insoluble fractions of the waste. Sometimes, as needed for process evaluations, the calculations will be performed for a particular tank or waste type to answer questions about processing selected waste types or tanks.

For the soluble stream resulting from retrieval (the LLW vitrification plant feed), calculations would be performed to predict the glass composition resulting from the vitrification of the stream (process box P2). The glass composition will be based on considerations of oxide loading in the vitreous product, type of melter used to produce the LLW vitrified product, and process development work on glass formulation. The LLW analyte parameters are next calculated and include such things as the concentration of various components in the glass and the concentration of chemicals and radionuclides in leach water to which the glass is exposed. The concentration of chemicals and radionuclides in leach waters will be based on a performance assessment of the glass and laboratory test data.

The analyte parameters are then compared (decision box D2) to LLW disposal limits to see if the parameters exceed the limits. Presently, the LLW disposal limits are identified in DOE Order 5820.2A and include such considerations as Nuclear Regulatory Commission class C limits for particular radionuclides and *Resource Conservation and Recovery Act (RCRA) of 1976* concentration limits for toxic metals. The final LLW disposal limits are being prepared by the LLW program office. If the LLW analyte parameters are below the limits, then the recommended action would be to vitrify the stream.

Figure A-1. Pretreatment DQO Decision Logic Diagram.



If the analyte parameters are above the limits, then blending of selected tanks would be considered (decision box D3) in an effort to reduce the parameters below the limits. If a successful blending scheme is identified, then adoption of that blending scheme would be identified as a recommended action and the technical bases altered to include that blending scheme. If blending selected tanks does not reduce the parameters below limits, then the program would evaluate whether a pretreatment process is needed (process box P3) to remove the analyte sufficiently to meet limits and would evaluate the success of the pretreatment process. Examples of pretreatment processes that would be used include cesium removal by ion exchange, strontium removal by ion exchange or by destruction of the organic complexants, and technetium removal by ion exchange or solvent extraction. Once a process is identified for use in removal, then a recommended action is to include that process in the technical bases. Data from process development testing will be used as part of the evaluation of analyte removal.

Part of the evaluation process involves the review of existing data to determine whether additional characterization or process development data is needed. This portion of the decision logic is depicted in Figure 4. The evaluator looks to see if additional characterization data are needed (decision block D8). If additional characterization data are required, the required data is identified (process block P14). A recommended action is also identified to revise the DQO requirements to get the additional data. This feeds back to the Revise Pretreatment DQO (process block P12, Figure 3) to provide revised direction to the characterization program. If no additional characterization data are needed or after identifying the DQO revisions needed, the evaluator checks to see whether additional process development data are needed (decision block D9). If additional process development data are needed, the required data are identified. A recommended action is also identified to communicate the need for additional data to the PNL Technology Development Program Office to identify the process development work (process block P11, Figure 3) needed to get the additional data. This feeds back to performance of the process development work (process block P13, Figure 3) with subsequent return of the data to the evaluation blocks. If no additional process development data are needed, the evaluator continues with the evaluation.

For the insoluble stream resulting from retrieval (the HLW vitrification plant feed), the analyte parameters would be calculated (process block P5) and compared to the HLW parameter limits (decision block D4). If the HLW analyte parameters are below the limits, then the insoluble stream can be vitrified and an action to vitrify the stream is recommended. The recommendation then becomes part of the pretreatment program planning basis. If the HLW analyte parameters exceed the limits, then blending of the wastes to reduce parameters below the limits is considered. If an acceptable blending scheme can be identified (decision block D5), then that blending scheme is recommended and becomes part of the technical bases. If an acceptable blending scheme cannot be identified, then the acceptability of a decreased waste loading in the vitrified product (more canisters) is evaluated. If a decrease in waste loading is acceptable, then an action to vitrify the waste at a lower waste loading is recommended. If a decreased waste loading is not acceptable, then the removal of the analyte to reduce the concentration below the limits (process block P7) and the use of an alternate vitrified product formulation

having a higher limit for the analyte (process block P6) are evaluated. The strategies resulting from these evaluations would result in recommended actions which in turn would be used to alter the baseline program documents (process block P8).

One possible outcome from the evaluation of analyte removal for the soluble and insoluble streams is that currently identified processes may not sufficiently reduce the analyte parameter to below the limits. In this case, a decision would be needed whether additional process development is needed to identify other pretreatment processes that could be used to remove or reduce the analyte parameter.

Once the technical bases are established with sufficient confidence, the information would feed into a project organization to design and construct (including startup) the LLW and HLW pretreatment and vitrification facilities. The information would also flow to the operations organization to operate the facilities.

Decisions D2 and D4 are the only decisions that can be reasonably defined now and as such are the only decisions included in the scope of the DQO. The rest of the decisions will be defined as the pretreatment program matures and as more information about the wastes becomes available. Decision D1 will be made by engineers experienced with the wastes and will be based on the degree of agreement between the characterization data and the knowledge available about the waste.

Figure A-2. Pretreatment DQO Decision Logic Diagram Detail.