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7. Abstract

The document describes limits for key constituents in the LLW feed, and the bases for these limits. The potential variability in the stream is then estimated and compared to the limits. Approaches for accomodating uncertainty in feed inventory, processing strategies, and process design (melter and disposal system) are discussed. Finally, regulatory constraints are briefly addressed.

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PRELIMINARY LOW-LEVEL WASTE FEED DEFINITION GUIDANCE

LOW-LEVEL WASTE PRETREATMENT INTERFACE

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February 1995

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LIST OF TERMS

CFR	Code of Federal Regulations
DOE	U.S. Department of Energy
DSSF	double-shell slurry feed
DST	double-shell tank
DWPF	Defense Waste Processing Facility
Ecology	Washington Department of Ecology
EPA	U.S. Environmental Protection Agency
HDW-EIS	Hanford Defense Waste Environmental Impact Statement
HLW	high-level waste
HWVP	Hanford Waste Vitrification Plant
LANL	Los Alamos National Laboratory
LLW	low-level waste
Na_2O	sodium oxide
NCAW	neutralized current acid waste
NCRW	neutralized cladding removal waste
NRC	U.S. Nuclear Regulatory Commission
PCT	product consistency test
PFP	Plutonium Finishing Plant
PUREX	plutonium-uranium extraction
RCRA	*Resource Conservation and Recovery Act of 1976*
REDOX	reduction and oxidation
RL	DOE, Richland Operations Office
SST	single-shell tank
TCLP	Toxicity Characteristic Leach Procedure
TLM	Tank Layer Model
TRAC	Track Radioactive Component
TRU	transuranic
TWRS	Tank Waste Remediation System
WAC	Washington Administrative Code
WHC	Westinghouse Hanford Company

PRELIMINARY LOW-LEVEL WASTE FEED DEFINITION GUIDANCE

LOW-LEVEL WASTE PRETREATMENT INTERFACE

1.0 INTRODUCTION

The Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) (Ecology et al. 1994) signed January 25, 1994, indicates that both double-shell tank (DST) and single-shell tank (SST) wastes will be retrieved and separated into high-level waste (HLW) and low-level waste (LLW) fractions as part of a pretreatment process. Both streams will be incorporated into glass waste forms in vitrification facilities prior to disposal. There is a need to examine preliminary waste feed requirements for vitrification of both HLW and LLW in order to provide guidance for planning and design activities among various Tank Waste Remediation Systems (TWRS) waste processing operations and to provide a basis for integrating feed requirements between consecutive operations. These waste processing operations involve waste retrieval and characterization; pretreatment including sludge washing, blending, and ion exchange; and subsequently vitrification and disposal. This preliminary definition will address requirements for vitrification of only the LLW fraction of Hanford tank wastes. Requirements for HLW will be addressed separately or included in a later revision.

The functions and factors that can impact feed composition variability and acceptability for vitrification include types of melter system components, glass technology constraints, waste retrieval and pretreatment technology, and existing tank farm facility limitations. Melter system component considerations include the melter feed system; offgas system capacity and efficiency; corrosivity of refractories, electrodes, or other firing materials along with operating temperature range and recycle streams. Glass technology constraints include determining the glass-forming composition region with acceptable product durability requirements; limitations due to low solubility of certain minor components, metals, and volatiles; melt characteristics such as viscosity, pourability, and reduction and oxidation (redox) state; and product uniformity and packaging requirements. Waste processing technology constraints include retrieval sequence strategy, sludge-wash factors, blending, ion-exchange efficiency, evaporation, and any special separation requirements. Existing tank farm limitations include infrastructure limits, assumptions of processing DST followed by SST wastes, tank space availability changes with time along with blending and storage options. Collectively, these functions and factors are the major drivers, along with disposal system functions, that determine LLW feed composition ranges.

1.1 PURPOSE

This document is intended to identify factors in the glass processability, regulatory, product performance assessment, and product quality areas that contribute to the need for setting compositional limits on feed provided to the vitrification process. It provides an initial comparison of these factors with retrieval and pretreatment strategies to develop a

framework for evaluating the processability of LLW feed stream compositions that will be received by the LLW vitrification facility. The following considerations are included in this framework:

- A definition of a preliminary LLW glass composition envelope in terms of major glass-forming/modifying components that emphasizes sodium-rich glass compositions with a high probability of meeting low-level mixed waste regulatory and performance assessment durability requirements.

- Identification of selected components in the waste inventory that are known to have limited solubility in silicate-based glasses and may potentially result in vitrification process or product quality problems if solubility is exceeded in the melter and phase separation occurs. These components are designated as minor components.

- Recognition of potential feed compositional variability after retrieval and pretreatment that may occur over time and suggestions for an approach or options to accommodate the variability.

- The identification of uncertainties and limitations that may impact the vitrification process and the explanation of how they are being addressed.

- Identification of key radionuclides in the LLW that must be limited so that product glass meets regulations for shallow land disposal.

The current version of this document does not attempt to provide the more detailed feed compositional data which will be needed to support a Design Requirements Document or conceptual design activity for the LLW vitrification plant. (See Section 1.2, Use and Interfaces, for future plans.) This block of data, which some call a "design basis feed specification," would define nominal and bounding LLW feed compositions and properties and would include:

- A chemical compositional range that encompasses all known or suspected constituents present in even trace amounts.

- Listings of nominal and "maximum" concentrations of all radionuclides expected in LLW feed, for use in flowsheet, shielding design, and accident analysis work.

- A range for physical property values of the LLW feed (e.g., viscosity, density, percent solids, etc.).

1.2 USE AND INTERFACES

This preliminary version of a LLW feed definition/guidance document should provide guidance to concerned parties (retrieval and pretreatment strategy developers) to ensure that waste compositions transferred between various process operations will result in LLW streams that meet vitrification requirements. In the event LLW stream compositions between pretreatment and the vitrification facility exceed vitrification limits, this document, along

Waste Vitrification Plant (HWVP) and the Defense Waste Processing Facility (DWPF) that used a statistical approach and a thermodynamic approach, respectively. Additional information from commercial glass-making experience with high-sodium glasses was also considered because waste glass compositions for HLW generally do not include high Na_2O content. Durability target requirements are based on preliminary performance assessment (Rawlins et al. 1994) analysis for LLW glass disposal and on experience from the grout performance assessment for DST LLW disposal (Kincaid et al. 1993). These durability requirements indicate a waste glass with good durability characteristics is needed to meet LLW disposal performance objectives if engineered barriers in the disposal system are minimized. Results from ongoing performance assessment activities are expected to provide additional guidance to product durability requirements and will be included in future revisions of this document.

Limits for minor components in glass are determined from HWVP and DWPF experience for HLW glass development and from a recent workshop involving both offsite and local researchers with waste glass experience currently working on high-sodium LLW glass formulations. These limits are generically applicable to other silicate-based glass systems and are adopted here pending results of current studies on minor component solubilities in LLW formulations.

Feed composition limit values for minor components may depend on the choice of glass melter. Currently, seven melter options are under consideration, and their individual differences in operating temperature or redox conditions will theoretically influence glass formulation and the solubility of certain minor components in the glass. Ideally, the scope of this feed limit definition should be broad enough to account for all possibilities in the future selection of a melter; however, lack of solubility data for some of the higher temperature conditions makes this goal impossible at this time.

As a fallback position, this feed composition limit definition was based partly on the relatively low-temperature, slightly reducing conditions typical of a cold-top, joule-heated melter with Inconel electrodes if results from current formulation investigations of melt properties and minor component limits in high-sodium LLW glass compositions were unavailable. This assumption is expected to be conservative for most minor components, in that solubility limits should be higher for other high-temperature melters. Thus, a pretreatment system and pretreated waste composition that is compatible with these bounding limits should not necessarily link the vitrification process in to any specific melter type.

Hazardous constituents will be regulated by the U.S. Environmental Protection Agency (EPA) (Title 40, Code of Federal Regulations, Part 260 [40 CFR 260]) and, as delegated, by the Washington Department of Ecology (Ecology) (Washington Administrative Code [WAC] 173-303).

1.4 ORGANIZATION

Chapter 2.0 summarizes LLW feed composition ranges and limits, emphasizing an interface with pretreatment activities. This chapter identifies selected feed constituents that are known to impact glass quality

with future cost tradeoff studies, will provide the framework for determining the most efficient point in the overall flowsheet at which to make process modifications.

In subsequent revisions this document will also be the primary definition of LLW nominal and bounding case feed compositions to be used as a reference for the LLW Vitrification Plant Design Bases Document (Swanson 1995). This document will also provide a reference for the LLW glass composition range for the TWRS Process Flowsheet (WHC-SD-WM-TI-613). It is intended that this document will be periodically revised as a baseline document as program development requires and as understanding of LLW glass chemistry and composition boundaries improves. The first revision is anticipated in August 1995, with subsequent revisions in 1996 and 1997.

1.3 SCOPE AND BASIS

This feed definition guidance is based on generic glass chemistry constraints and product performance requirements rather than on a specific vitrification system. A specific melter system has not been selected, so specific system constraints are not addressed.

The definition of LLW composition ranges and limits for LLW vitrification are based on glass product requirements emphasizing glass durability and glass melt processability. Both of these characteristics are strongly dependent on glass composition. Thus, preliminary LLW feed compositions acceptable for vitrification are derived from glass composition envelopes identified as glass-forming regions in high-sodium systems from commercial glass-making experience and from previous glass waste-form development studies. Updated feed definitions will be made when results are available from current waste glass formulation development activities.

Physical properties of melts are not considered in this definition because they are indirectly considered as part of glass composition constraints. Physical properties of melts will be considered in future revisions.

While this feed definition is based primarily on glass chemistry principles and vitrification process constraints, the application of these factors to defining glass composition envelopes and associated LLW feed composition envelopes also considers several other indirect requirements. As discussed below, glass durability requirements implied from disposal system performance assessments and regulatory requirements indirectly constrain acceptable glass composition envelopes. It is also assumed that a certain amount of compositional variability will occur during the overall retrieval and pretreatment history that requires accommodation by the glass composition envelope.

An initial glass composition envelope for LLW formulation studies has been defined with a nominal sodium oxide (Na_2O) composition of 20 wt% and a $\pm$5 wt% range although occasional compositions with Na_2O loadings up to 30% are being investigated to support glass composition modeling. This initial envelope was determined from extrapolating previous waste glass development work emphasizing composition versus property relationships from the Hanford

or melt processability in the melter and indicates compositional constraints in terms of ranges and limits in the glass. Subsequent chapters will include background information and provide additional details to support the definitions and bases summarized in Chapter 2.0. This will include reference to LLW inventory and recognition of TWRS flowsheet information that is relevant to LLW process stream compositions received by the vitrification facility. A brief discussion of relevant regulatory requirements will be included along with a summary of preliminary performance assessment guidance. Finally, issues of feed uniformity, limiting compositions in glass, and volatile components will be mentioned.

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2.0 SUMMARY OF LOW-LEVEL WASTE FEED DEFINITIONS

This chapter includes tables of composition envelopes of major LLW glass-forming constituents based on current LLW glass formulation activities and preliminary composition ranges and limits of minor components known to cause either processing problems or impact glass quality. In addition, tables defining preliminary limits for reducible metals and volatile/semivolatile constituents are included. Definitions of radionuclide limits based on either U.S. Nuclear Regulatory Commission (NRC) Class C or performance assessment considerations are included. It is anticipated that other physical properties such as feed density, percent solids, etc. will be included in future revisions of this section.

This chapter is intended to be a summary of various types of feed definition data based on current available information but with minimum discussion. It is intended for those who desire preliminary values for design or planning purposes but are not interested in background information. Details of the bases for these values and impacts on vitrification processes or products are given in Chapter 3.0. Discussion of the basis for radionuclide limits is given in Chapter 7.0. Limiting values for minor components, such as phosphorus, sulfur, chlorine, and fluorine, in LLW glass are based on current LLW glass formulation studies while values for other constituents, such as semivolatile metals are derived from HLW glass experience until appropriate LLW glass data are available. Values for minor components in LLW feed are considered conservative because they are derived from glass solubility limits and do not include additional increments from recycle streams, which are melter dependent.

2.1 MAJOR COMPONENTS

Table 2-1 lists the major component composition ranges in the LLW glass composition envelope in terms of component oxide ranges and as mole ratios with respect to moles of sodium in the glass for glass compositions of 20 wt% and 25 wt% Na_2O as an illustration for two different sodium loadings. These composition ranges include both constituents contributed by the LLW feed plus added glass-former constituents. Together, the LLW feed plus the glass-formers constitute the melter feed. Not all major glass-forming components are expected to be in the LLW feed in sufficient quantities to meet glass formulation requirements. Also, not all major components are expected to be at maximum concentrations at the same time. Mole ratio values with respect to sodium can be readily calculated for other waste loadings as desired. These ratios can be used as limiting ratios in the LLW feed assuming the LLW feed contributes the entire sodium loading to the glass.

2.2 MINOR COMPONENTS

The concentration of minor components in the LLW feed, such as phosphorus, sulfur, chlorine, fluorine, and chromium, that can cause either process or product problems will be small compared with sodium and can be limited in the

Table 2-1. Major Components.

Element	Oxide	Oxide in glass (wt%)	Element in glass (wt%)	Maximum mole ratio in glass (x/Na), Na_2O = 20 wt%	Maximum mole ratio in glass (x/Na), Na_2O = 25 wt%
Na	Na_2O	15 - 25	11 - 19	1.00	1.00
Si	SiO_2	50 - 70	23 - 33	1.82	1.46
Al	Al_2O_3	5 - 12	2.6 - 6.4	0.37	0.29
Ca + Mg	CaO + MgO	0 - 12	8.6 (all Ca)	0.34 (all Ca)	0.27 (all Ca)
B	B_2O_3	0 - 12	3.7	0.54	0.43
Fe	Fe_2O_3	0 - 12	8.4	0.24	0.19

Table 2-2. Minor Components (with Combinations).

Element	Oxide	Oxide in glass (wt%)	Element in glass (wt%)	Maximum mole ratio in glass (x/Na), Na_2O = 20 wt%	Maximum mole ratio in glass (x/Na), Na_2O = 25 wt%
P	P_2O_5	3.0	1.31	0.066	0.052
S	SO_3	1.0	0.40	0.019	0.015
Cl	--	1.0 (0.3 retained)	--	0.044	0.035
F	--	1.7	--	0.14	0.11
Cr	Cr_2O_3	0.5	0.34	0.010	0.0081
Cd	CdO	2.5	2.19	0.030	0.024
Noble metals	--	--	0.25	--	--
Rare earths	La_2O_3, Ce_2O_3, ...	2.0	1.7 (all La)	0.019 (all La)	0.015 (all La)
P + S	--	ND	ND	ND	ND
Ca + P	--	ND	ND	ND	ND
Cs + Cl	--	ND	ND	ND	ND
F + Cl	--	ND	ND	ND	ND

ND = not yet determined.

glass by adjusting waste loading. Table 2-2 lists the maximum concentration limits of the these constituents in LLW glass and their mole ratios with respect to sodium in the glass for two arbitrarily selected Na_2O loadings. These ratios can be used as limiting values in the LLW feed. Appropriate ratios for other sodium loadings can be calculated as desired. For any given Na_2O content in the glass, the ratio is determined by dividing the number of moles of sodium metal per 100 g of glass by the number of moles of the minor component element in the solubility limit for the glass.

2.3 SELECTED RADIONUCLIDES

Table 2-3 lists composition limits of selected radionuclides in LLW glass as required by either Class C requirements or performance assessment guidance. The ratio of curies to moles of sodium in the glass can be used to determine similar limiting ratios in the feed. An example for 25 wt% Na_2O glass is given.

Table 2-3. Selected Radionuclides.

Nuclide	Class C related limit (in glass)[a]	Performance assessment related limit (in glass)[b]	Limit in feed, Ci/mol Na (assumes 25 wt% Na_2O glass)
Short lived			
^{63}Ni	700 Ci/m^3	--	0.0347
^{90}Sr	7000 Ci/m^3	--	0.347
^{137}Cs	4600 Ci/m^3	--	0.228
Long lived			
^{14}C	8 Ci/m^3	--	0.000397
TRU	100 nCi/g	--	1.24 E-05
^{237}Np + ^{241}Am	N/A	ND	1.24 E-05
U	N/A	ND	1.24 E-05
^{99}Tc	3 Ci/m^3	ND	0.000149
^{129}I	0.08 Ci/m^3	ND	3.97 E-06

[a]A sum-of-fractions must be calculated for ^{63}Ni, ^{90}Sr, and ^{137}Cs to determine whether Class C is exceeded. A separate sum-of-fractions must be calculated for long-lived radionuclides to determine whether Class C is exceeded.

[b]Performance assessment related items have not been established.

N/A = not applicable.

ND = not yet determined.

TRU = transuranic.

Table 2-4 contains the nominal concentrations of key radionuclides expected in the LLW glass. These data were extracted from stream 404 of the TWRS Process Flowsheet (Orme 1994).

Table 2-4. Nominal Concentrations for Key Radionuclides.

Nuclide*	Nominal concentration in glass, @25% Na_2O
^{137}Cs	1.3 Ci/m^3
^{90}Sr	3.8 Ci/m^3
^{99}Tc	0.41 Ci/m^3
TRU	19 nCi/g

*Data on other nuclides not included in Orme (1994). Other nuclides (^{63}Ni, ^{14}C, ^{129}I) not expected to be significant. In addition, carbon and iodine will volatilize in melter.

TRU = transuranic.

2.4 REDUCIBLE METALS, VOLATILES, SEMIVOLATILES

Table 2-5 lists limiting values for selected metals, semivolatiles, and volatile components that are expected to be present in small amounts in LLW feed.

Table 2-5. Other Components of Concern.

Element, oxide	Concern*	Preliminary limit of 2.0 wt% oxide in glass (X), or as indicated.	Preliminary limit not determined at this time
Ag, AgO	R, SV, SP	X	--
As, As_2O_3	R, V	X	--
Be, BeO	R, SV	--	ND
Bi, Bi_2O_3	R, SV	X	--
Cd, CdO	R, V	2.5	--
Co, CoO	R	X	--
Cu, CuO	R, SV, SP	X	--
Hg, HgO	R, V	0	--
Mo, MoO_3	R, SV	X	--
Ni, NiO	R, SP	X	--
Pb, PbO	R, SV, SP	X	--
Ru, Ru_2O_3	R, V	0.25	--
Rh	R	0.25 (as metal)	--
Sb, Sb_2O_3	V, SP	X	--
Se, SeO_2	R, V	<1% as oxide	ND
Sn, SnO	V	--	ND
Tc, TcO_4	R, V	--	ND
La,Nd; $(La,Nd)_2O_3$	R	X	--
Zn, ZnO	R, V	X	--

ND = not yet determined.
R = reducible.
V = volatile.
SV = semivolatile.
SP = secondary phase.

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3.0 LIMITING COMPOSITIONS IN GLASS

This chapter provides a preliminary definition of ranges and limits for major and minor components in LLW glass and discusses that basis for the ranges indicated. Potential impacts of feed composition limits on either the glass product quality or vitrification processing operations, if limits are exceeded, are also discussed.

3.1 MAJOR COMPONENTS IN LOW-LEVEL WASTE GLASS

The major glass-forming components are those that form the dominant molecular framework of the glass. Together they constitute the major component composition envelope. In Table 3-1 they are expressed as the major network-forming and network-modifying components. The complete LLW glass composition will consist of this major component envelope plus the addition of waste constituents.

The major component composition envelope was selected after considering several requirements. According to the baseline flowsheet and related tank waste inventory estimates it is generally accepted that the LLW stream composition will be dominated by sodium and that LLW glass compositions must be high in the Na_2O component. In addition, these high-sodium LLW glasses must have reasonably good durability characteristics to comply with regulatory and performance assessment requirements, but the melt compositions must also exhibit physical and chemical property characteristics that conform with processability requirements. These processability requirements include properties such as liquidus temperature, viscosity and pourability, electrical conductivity, and volatility/corrosivity.

Accordingly a literature survey was conducted of high-sodium commercial and waste glass compositions to select those whose properties showed promise of complying with the requirements described (Kim 1994; Cunnane et al. 1994). These, plus additional compositions estimated from general glass chemistry relationships of glass properties vs. composition, were used to define a series of LLW glass compositions for use in glass formulation studies. Oxide composition ranges of each individual major component from the current glass formulation study are given in Table 3-1. This study is still in progress, and future formulation studies will also include Na_2O loading exceeding 25 wt%. Preliminary results indicate that LLW glass formulations within the listed envelope have the best indication of meeting the desired requirements.

The range and a maximum value for each major component oxide is given in Table 3-1, but it should be recognized that all components cannot be at maximum values at the same time. Also, not all of these components will be derived from the LLW stream alone. Some, such as silica, will be supplied as glass-forming constituents as part of the melter feed system. To obtain desirable glass product and melt processing properties, component combination effects will be determined as part of the formulation effort. It is expected, however, that all sodium in the glass will be supplied by the LLW feed stream so that major component glass formulation constraints can be adjusted partially by waste loading.

Table 3-1. Major Component Envelope. (2 sheets)

Oxide system	Range in glass (wt%)	Basis for range	Comment
Na_2O	15 to 25 (a) Centroid for LLW Glass formulation studies is 20% Na_2O (b)	(a) Composition range being investigated for high-sodium LLW melter test glasses (Wilson 1994). (b) Based on best durability region for high-sodium glasses (Kim 1994; Das 1981).	Sum of oxides must equal 100%. High Na_2O content usually reduces durability, reduces melt viscosity, and increases electrical conductivity. Current preliminary performance assessment calculations indicate good glass durability is required to meet dose limits.
Al_2O_3	5 to 12	Composition range being investigated for melter test glasses (Wilson 1994). Also within the range for more durable commercial and high-sodium glasses (Tooley 1984; Kim 1994; Das 1981).	Aluminum increases glass durability and melt viscosity. High-aluminum glasses can have high liquids temperatures requiring high operating temperatures. Excess aluminum results in aluminosilicate crystallization that may reduce durability or cause processing problems.
SiO_2	50 to 70	Composition range being investigated for melter test glasses (Wilson 1994). Upper limits within the range for more durable commercial glasses (Tooley 1984). Durable high-sodium glasses often require silica above 60-65% (Kim 1994; Das 1981).	Increasing silica increases durability and melt viscosity. Very high silica can result in melt too viscous to process. Silica will be derived from frit or glass formers to melter feed, not from LLW streams and can be adjusted as needed.

Table 3-1. Major Component Envelope. (2 sheets)

Oxide system	Range in glass (wt%)	Basis for range	Comment
CaO+MgO	0 to 12	Composition range being investigated for LLW melter test glasses (Wilson 1994). This range is also within the range studied for HLW borosilicate glasses (Hrma and Piepel 1992).	These oxides are glass stabilizers and help improve durability (Tooley 1984). Limited substitution of B_2O_3 for CaO can be made to improve workability. Will be supplied by frit or glass formers to melter feed.
B_2O_3	0 to 12	Composition range being investigated for LLW melter test glasses (Wilson 1994). This range is also within the range studied for HLW borosilicate glasses (Hrma and Piepel 1992).	Boron oxide is a glass former and can substitute partially for CaO and SiO_2 in glass formulations (Tooley 1984). Will be supplied by frit or glass formers to melter feed.
Fe_2O_3	0 to 12	Based on HWVP composition for borosilicate glasses (Hrma and Piepel 1992).	Iron reduces melt viscosity, but excess iron increases crystallinity and phase separation potential reducing durability. Glass redox state measured in terms of Fe(II)/Fe(III) ratios. Low iron concentrations expected in LLW because of low solubility in basic solutions.

HLW = high-level waste.
HWVP = Hanford Waste Vitrification Plant.
LLW = low-level waste.
redox = reduction and oxidation.

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Table 3-1 provides a definition of ranges and limits of major oxide components in LLW glass, identifies the basis for selecting these compositions, and discusses the impacts if these limits are exceeded. The major oxide limits in LLW glass are not expected to be a significant constraint on LLW feed stream compositions because most of the major oxides will be added separately as glass-formers to the melter feed. Preliminary formulation results indicate that many compositions within this envelope can meet durability characteristics of 0.1 g/m^2/day mass loss rate using a product consistency test (PCT). This value is taken as a preliminary requirement pending additional performance assessment guidance. A liquidus temperature requirement between 1,000 °C and 1,400 °C is desired with 10 Pa-second (100 poise) viscosities within this range. For Joule-heated melters, electrical conductivity requirements are generally between 0.18 and 0.5 $(ohm\text{-}cm)^{-1}$. Formulations within the major component range listed in Table 3-1 are expected to meet these requirements.

3.2 MINOR COMPONENTS IN LOW-LEVEL WASTE GLASS

Certain constituents that, because of their low solubility in most silicate-based glass formulations, are known to cause either processing problems or adversely affect glass durability are designated minor components in the LLW waste glass. Concentrations of some of these constituents that exceed solubility limits in glass can result in processing problems that include molten salt layer buildup, intolerable volatility/corrosion, crystallized sludge accumulation that plugs drains, or metal reduction and accumulation that effects electrical fields. In addition, insoluble constituents can result in inhomogeneities in the glass product that affect durability.

The most significant insoluble constituents for LLW feed are P_2O_5, SO_3, fluorine, chlorine, and possibly Cr_2O_3. The majority of the existing inventory of these five constituents is expected to remain in the supernate after sludge washing and become part of the LLW feed stream. In addition, they are recognized to cause processing problems during vitrification because of limited solubility in glass. As a consequence, they may become the dominant constraints in LLW glass waste loading limits. Limiting values for these minor components in LLW glass are given in Table 3-2. These limits are based largely on experience with HLW glass formulations, some early results from LLW glass formulation development, and opinions presented in a recently held workshop consisting of glass chemistry experts from Westinghouse Hanford Company (WHC), Pacific Northwest Laboratory, and Savannah River Laboratory. The ranges and limits shown in Table 3-2 do not necessarily consider component interactive effects which may result in small adjustments to these limits in the future. Component interactive effects are included as part of the ongoing glass formulation development work.

Other minor components requiring consideration include volatile and semivolatile metals, reducible components, noble metals, and rare earth species. The potentially volatile or reducible constituents include silver, astatine, beryllium, bismuth, cadmium, mercury, potassium, molybdenum, lead, tin, selenium, ruthenium, rhodium, vanadium, and zinc, as well as chlorine and fluorine considered above. In general, these components, except for the halogens, are expected to be present in low concentrations in the LLW feed

streams either because of low initial inventory or because they will tend to remain in the sludge after the sludge-washing process. They are included in Table 3-2 to recognize that they could potentially lead to processing problems, perhaps through gradual accumulations. They are also included to recognize that uncertainty in inventory amounts and uncertain variability in LLW feed streams may require monitoring by the LLW vitrification facility. Many of the metal oxides have been tested up to 2.0 wt% in HLW glasses and at higher levels in some commercial glasses with negligible effects on glass properties. As specific metals are included in LLW glass formulation development studies, these limits will be updated.

Table 3-2. Minor Component Ranges and Limits. (3 sheets)

Waste component	Range/limit in glass (wt%)	Basis for limit	Issues/impacts	Comments
P_2O_5	1.0(a) to 5.0(b) Recent Technical Interchange (WHC, PNL, SRL) indicates up to 3.0% possible if SO_4 <1% (b)	(a) 1.0 wt% solubility limit in borosilicate glass based on extrapolation of DWPF data (Bates 1987). Recent LLW glass formulation results suggest up to 3.0% with no phase separation. (b) Upper limit is estimated based on phosphorous substitute for fluorine in "opal glass" compositions (Tooley 1984). Requires evaluation of durability impacts of secondary calcium phosphate phases in glass.	A calcium/rare earth phosphate "scum" has been observed on the melt surface in some melters (Brouns et al. 1986; Jantzen 1986) depends on calcium-phosphorous ratio. Can slow production rates. Phosphorous can also increase melt corrosivity.	Secondary phase formation such as $Ca_5(PO_4)_3(F,Cl)$, a possible crystalline phase in "opal glass," may allow higher phosphorous limits, but impacts on durability unknown. Also "opal glass" production requires careful processing.
SO_3	0.5% in silicate glass Up to 1% SO_4 soluble in LLW glass in recent formulation work	Based on preliminary HWVP solubility limits for borosilicate glass (Hrma and Piepel 1992). Solubility greatest when ferrous/ferric ratios <0.3 (Bates et al. 1985).	Sulfate, SO_4^{-2}, solubility in melt related to calcium or iron under oxidizing or reducing state respectively. Excess SO_3 results in molten salt layer on melt surface and increased foaming potential. Also can affect glass durability.	Sulfate solubility is affected by melt redox state and melt temperature. Slight variability in sulfur solubility may be achieved through control of these parameters.

Table 3-2. Minor Component Ranges and Limits. (3 sheets)

Waste component	Range/limit in glass (wt%)	Basis for limit	Issues/impacts	Comments
Cr_2O_3	0.5% for silicate glass in Joule-heated melters. May be higher in others	Based on preliminary solubility limits in HWVP borosilicate glass (Bates 1987; Hrma and Piepel 1992).	Combines with iron and nickel to form spinel crystals which settle to melter floor - can cause electrical shorting or plug discharge ports.	Some melter designs may allow limit to be exceeded. Limit may be exceeded for LLW by reduced iron and nickel in feed. Testing required.
F	1.7(a) to 5.0(b) Preferred range is 0 to 1.7% in silicate glass.	(a) Based on preliminary solubility limits in HWVP borosilicate glass (Bates 1987; Hrma and Piepel 1992). (b) Upper limit based on fluorine content of "opal glass" (Tooley 1984) which contains CaF_2 phase. Requires evaluation of durability impacts of CaF_2 phase formation on glass product.	Fluorine tends to replace oxygen in the glass structure. Can reduce viscosity and cause phase separation affecting durability. All halogens tend to be volatile from melt and cause severe corrosion.	Formation of "opal glass" with CaF_2 may allow higher fluorine content, but bulk glass composition is limited and production process must be carefully controlled. May be too restrictive for waste glass production.
Cl	1.0% NaCl may be soluble in LLW glass. 0.3 g chlorine/100 g waste oxide was limit for HLW glass.	1% NaCl limit in glass derived from consensus of recent LLW glass workshop participants — requires testing. Lower limit based on HLW testing experience.	Chlorine effects corrosion and cesium volatility. Also has other interactive effects on melt chemistry.	Basis for limit not well understood. Chlorine is included in LLW glass minor component study.
Noble metals: Ru, Rh, Pd	0.25 wt% metal	Preliminary limit based on solubility in HLW glasses tested to date.	Noble metals can precipitate causing melter failure.	Metals tend to be insoluble in basic solutions. Only small amounts expected in LLW stream.

Table 3-2. Minor Component Ranges and Limits. (3 sheets)

Waste component	Range/limit in glass (wt%)	Basis for limit	Issues/impacts	Comments
Rare earths: (La, Nd)	2.0%	Preliminary limit based on glass compositions tested to date and commercial glass experience.	Rare earths have negligible impact on glasses. Limit may be expanded.	Rare earths tend to be insoluble in basic solutions. Only small amount expected in LLW feed.
Reducible/ semivolatile elements: Ag, As, Bi*, Cd*, Co, Cu, Hg*, Mo*, Ni*, Pb*, Sb*, Se, Sn, Zn*	Preliminary limit is 2.0 wt% as oxide. Except Hg = 0 CdO = 2.5% SeO_2 = <1%	Preliminary HWVP solubility limits in borosilicate glass (Bates 1987; Hrma and Piepel 1992) based only on the composition ranges tested to date. Many of these constituents are used as colorants in commercial glasses at <2.0%.	Cadmium is a hazardous element, but CdS is used as a colorant in specialty glasses. Impact is negligible unless low-solubility effects TCLP or other hazardous waste tests.	Most of these components tend to be insoluble in basic solutions and are likely to remain in sludge. Also the total inventory of some elements is small. Thus only small amounts are expected in LLW feed streams.

*May be present at 0.5 MT or more in tank inventory.
DWPF = Defense Waste Processing Facility.
HLW = high-level waste.
HWVP = Hanford Waste Vitrification Plant.
LLW = low-level waste.
PNL = Pacific Northwest Laboratory.
redox = reduction and oxidation.
SRL = Savannah River Laboratory.
TCLP = Toxicity Characteristic Leach Procedure.
WHC = Westinghouse Hanford Company.

4.0 FEED UNIFORMITY

It is anticipated that the LLW vitrification facility can accommodate limited variability in LLW feed composition through modifications in operating parameters or waste loading. This will require establishing sufficient lead time so that necessary changes in parameters such as melt temperature, glass-former additions (formulation and melter feed), feed rate, etc., can be made. While this chapter does not attempt to specify limits to LLW feed composition changes, it is intended to estimate some possible extremes, while acknowledging that the approaches used here oversimplify the dynamics of retrieval and processing.

4.1 POTENTIAL EXTREMES IN LOW-LEVEL WASTE FEED

Several different approaches were used to estimate the maximum concentrations in the LLW stream. These include output from a simplified flowsheet model of TWRS; estimates of the water soluble fraction of each waste tank; and estimates of the nominal concentration of the caustic leachate stream. These estimates are described in the following sections.

Only the variability in certain key constituents is estimated. These are the constituents that are of most concern in caustic washing (aluminum, chromium, phosphorus) or are near glass processing limits (chlorine, chromium, fluorine, phosphorus, sulfur). For ease of comparison, all calculations in this chapter assume an Na_2O loading of 25 wt%. If 25 wt% sodium loading cannot be attained, then the glass must be diluted further with glass formers. In that case, the extreme concentrations predicted here would be lessened.

Variability in the concentration of radionuclides in the LLW stream is of less concern, as long as Class C limits are not exceeded (see Section 7.2) and the bounding inventory used for safety analyses (to be included in Swanson 1995) is not exceeded. At currently expected levels, variability in radionuclide concentrations should not affect the production of LLW glass (this assumes that cesium is removed from the LLW stream and transuranic (TRU) is removed from complexed wastes). Performance assessments (see Chapter 8.0) typically address the bulk inventory of certain radionuclides; variability is usually not considered.

4.2 FLOWSHEET PREDICTIONS FOR LOW-LEVEL WASTE FEED

The baseline model of the TWRS system was generated with a flowsheet program from ASPEN Technology, Inc. The ASPEN[1] model is a steady-state program. The TWRS flowsheet (Orme 1994) currently only assesses the nominal inventory. In reality, the feed to the LLW glass plant will vary due to differences in the compositions of tanks being retrieved. In an attempt to determine how variable the feed might be, different batches of waste were input as feed to a simplified version of the ASPEN flowsheet model (this

[1]Aspen is a trademark of ASPEN Technology, Inc., location:

simplified flowsheet includes all processing steps but ignores recycle and offgas streams from the melters). The feed batches to the simplified ASPEN model were average inventories for each SST tank farm and DST waste type. The normalized track radioactive component (TRAC) inventory (Boomer et al. 1993, Appendix D) was used. The minimum and maximum concentrations of key components of the LLW melter feed (from the simplified ASPEN runs) are presented in Table 4-1.

Table 4-1. Predicted Glass Concentrations for Nominal Low-Level Waste Feed (Orme 1994), and Minima and Maxima Predicted from ASPEN Runs with Farm-by-Farm Inventories (TRAC Data).

Wt % in glass	Al_2O_3	Cl	Cr_2O_3	F	Na_2O	P_2O_5	SO_3
Minimum	0.11	0.00007	0.0003	0.0015	25.0	0	0.006
Nominal	1.8	0.11	0.05	0.26	25.0	0.72	0.38
Maximum	6.1	0.51	2.5	10.3	25.0	6.76	2.24
Limit in glass (from Section 2.0)	12.0	1.0	0.5	1.7	25.0	3.0	1.0

This farm-by-farm approach is an oversimplification of what will really happen - farms will be retrieved and processed in parallel to some extent. The actual number of tanks contributing to one batch of decant material will be as little as one, but usually several. Thus, using the farm-by-farm batch approximation evens out some of the variability that might be observed in individual batches.

By excluding recycle streams, the simplified flowsheet model will underrepresent the concentration of semivolatile species in the melter. If the recycle stream is significantly enriched in problem species such as chlorine and fluorine, waste loadings might need to be reduced to avoid processing problems. Work is ongoing in this area. As retrieval sequences are generated, they will be used as input to a dynamic TWRS model which then predicts compositions of batches of retrieved waste. These batches are processed through the simplified ASPEN model, which predicts the LLW stream composition. This effort is expected to provide a more realistic estimate of LLW variability than the farm-by-farm approach described in this section.

4.2.1 Estimates of Variability from Water Washing

Another attempt to estimate the potential maximum concentrations of key components in the LLW feed used the TWRS flowsheet inventory (see Section 5.2.5). This inventory includes an estimate of the water soluble fraction of each tank. Using these data, glass compositions can be projected

Table 4-2. Potential Maximum Predicted Glass Concentrations Based on Water-Soluble Tank Data.

Component (wt%)	Al_2O_3	Cl	Cr_2O_3	F	Na_2O	P_2O_5	SO_3
Maximum (1 tank)	8.03	0.75	1.05	14.9	25.0	5.4	4.1
Average (top 10 tanks)	6.12	0.56	0.63	7.0	25.0	5.2	2.8
Overall average	1.32	0.09	0.07	0.3	25.0	0.7	0.5
Limit in glass (from Chapter 2.0)	12.0	1.0	0.5	1.7	25.0	3.0	1.0

NOTE: Tanks projected to contain <50,000 gal of feed (5*M* sodium) not included. Data derived from TWRS flowsheet working inventory, January 13, 1995.

on a tank-by-tank basis. Table 4-2 lists the maximum concentration of key components predicted from the water soluble tank data. Note that Tables 4-1 and 4-2 are based on different data sets.

Although aluminum concentrations do vary across the tanks, no tank exceeds the aluminum limit of 12 wt% stated in Chapter 2.0. Chlorine, being highly soluble, is concentrated in the DSTs. However, chlorine does not appear to be a problem by itself - all tanks are below the 1.0 wt% limit in glass. Fluorine is highly concentrated in neutralized cladding removal waste (NCRW) and is also found in LaF_3 wastes and in DSTs. A number of high fluorine tanks exceed the limit of 1.7 wt% stated in Chapter 2.0. Both chlorine and fluorine are semivolatile, and therefore, may build up in the recycle stream causing concentrations in the melter feed to be enriched beyond the levels predicted here. High concentrations of chromium are found mostly in 241-SX Tank Farm; a few tanks in 241-S and 241-SY Tank Farms exceed the 0.5 wt% Cr_2O_3 limit as well. PO_4 is well distributed in SSTs, with many tanks exceeding the P_2O_5 limit of 3.0 wt%. SO_4 is fairly well distributed across the tank farms, with generally higher concentrations in DSTs. Many tanks exceed the SO_3 limit of 1.0 wt%.

4.2.2 Leachate from Caustic Wash

Another stream destined for LLW treatment and vitrification is the leachate that results from caustic washing of certain sludges to solubilize aluminum, chromium, and phosphorus. The average composition of the leachate, calculated from information in Orme (1994), is 3.9% Al_2O_3, 0.17% Cr_2O_3, and 1.6% P_2O_5 at 25% Na_2O (as waste oxides). However, due to variability in the sludges, the composition of the leachate will also vary. It is expected that the concentrations of chromium and phosphorus in this stream will at times exceed the limits stated in Chapter 2.0. The PO_4 in $BiPO_4$ wastes (B and T Tank Farms) should be readily leachable, resulting in high concentrations of PO_4. Large amounts of chromium are in certain 241-S and 241-SX Tank Farm

sludges, as well as 101-SY and 103-SY, which may result in high concentrations of chromium in leachate from these tanks. As additional tank samples are leached and analyzed, the variability of this stream can be better estimated.

4.3 FEED VARIABILITY ISSUES

The HLW stream will be blended to reduce the total amount of HLW glass produced. This is necessary to reduce expensive repository costs. The LLW supernate produced cannot be optimally blended to maximize waste loading due to the limited storage space and large throughput required. Therefore, the composition of the LLW stream will be variable. The preceding sections show that the LLW stream will at times exceed processing limits, meaning that either waste loading must be decreased, or that the feed must be blended to minimize LLW glass volume.

4.3.1 Handling Changes in Feed Composition

Since LLW lag storage is close coupled to the LLW pretreatment, waste will likely be batched through on a tank-by-tank basis, resulting in step changes in the feed as different feed tanks are brought online. Critical composition changes of one order of magnitude to the LLW melter would probably not be acceptable on a short-term basis. There would certainly be a loss of control of the melter, and a waste loading penalty (production loss) while the formulation was modified or a new formulation initiated.

4.3.2 Modifications/Blending Remedies

Several modifications can be suggested to reduce the impact of step changes in feed composition.

- Change in additives/modification to the formulation. Increasing glass formers if the component is being reduced in concentration should help ease the step change. For this option it is necessary that an immediately available inventory of glass formers be available, and the process control system available to accurately feed them to the process. This option may result in decreased waste oxide loading.

- Blending at the last moment. Blending at the last moment takes special process control and proper planning to mitigate the impact of the change on the system. This blending scenario would include transfers between the evaporator lag storage and LLW pretreatment lag storage to partly mitigate the composition change. A decrease in production rate may accompany the blending to help ease into the change.

- Increased lag storage volume. Another solution is increased lag storage volume outside the plant to allow additional blending when needed. This might include allocation of clean DST tanks for blending only when required. This would again tend to mitigate step changes in chemical composition.

4.3.3 Specifications/Requirements

To determine the requirements and specifications for composition changes it is required to determine at least the following:

- Melter type
- Lag storage volume
- Process control
- Sampling/characterization requirements
- Blending capability.

It is anticipated that a compositional change limit will be set up that will allow a set amount of change in critical waste compositions in a set time frame. These specifications will be flexible. In general the following should occur in operation of the system:

The magnitude and duration of the composition change should be established, and the timing of the change should be communicated to the vitrification plant as soon as possible. This will enable the plant to compensate for the changes in ordering raw material and in plant operation.

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5.0 TANK WASTE INVENTORY

Estimates of LLW feed variability as described in the Chapter 4.0 are strongly related to tank waste inventory estimates. This chapter describes the origin and principal characteristics of the Hanford Site wastes and summarizes the approach for estimating waste compositions. It is intended to provide background information on the sources of LLW compositions and possible variability in waste compositions since these estimates provided input to LLW feed composition calculations.

5.1 WASTE SOURCES

This information on waste sources was derived from Lambert and Kim (1994). Hanford Site wastes were primarily produced from the reprocessing of irradiated fuel from the plutonium production reactors in the bismuth phosphate process (1944 to 1956), redox process (1952 to 1966), and plutonium-uranium extraction (PUREX) solvent extraction process (1956 to 1972 and 1983 to 1988). Certain tank wastes, such as the metal waste stream from the bismuth phosphate process, were subsequently reworked to recover uranium (uranium recovery process, 1952 to 1957). During this same period, other supernate wastes were reworked to induce the precipitation of ^{137}Cs and ^{90}Sr before discharging the waste to cribs or trenches (nickel ferrocyanide scavenging operations). Later (1965 to 1976), high-heat PUREX waste sludges and general supernate wastes were reworked in B Plant to recover ^{137}Cs and ^{90}Sr by ion exchange and solvent extraction (cesium/strontium encapsulation operation).

Because tank space was severely limited, some wastes were concentrated by evaporation, with condensates being routed to cribs or trenches or treated for subsequent disposal. Through such processes, wastes in the SST tank farms were gradually converted into mixed sludges and salt cake, while most of the recent wastes from PUREX and supernates from the older wastes have been consolidated in the DST tank farms.

While site operations have caused some blending of semisoluble components in some wastes, the principal characteristics of other wastes such as the high-level redox waste (high chromium waste) and Zirflex cladding waste (high zirconium waste) are still relatively unique. In-tank precipitation and mineralization processes, however, may have altered the original solubility characteristics of some components or compounds by forming secondary phases, such as cancrinite ($2\ NaAlSiO_4 - 0.52\ NaNO_3 - 0.68\ H_2O$). Also, wastes that have been added to the tanks are often highly stratified with lateral and vertical inhomogeneities that make the sampling process especially difficult.

5.2 WASTE COMPOSITION ESTIMATES

Overall radionuclide inventories are predicted from reactor codes (e.g., ORIGEN2) (Hedengren 1985), which predict spent fuel exposure history in the production reactors. Overall chemical inventories are estimated from purchase records and process flowsheets. Process flowsheets, process sampling, transfer records, recorded waste volumes, and waste tank sampling

data have all been used as bases for estimating the contents of individual tanks.

5.2.1 Track Radioactive Component Model

The TRAC model was originally developed during the mid-1980's to estimate the distribution of radionuclides in the SSTs (Jungfleish 1984). The ORIGEN2 code provided the initial radionuclide inventory estimates for TRAC based on spent fuel exposure history in the production reactors. ORIGEN2 data were then processed through TRAC to distribute the waste to the tanks, based on (1) recorded transfers from process facilities to the tank farms and (2) estimated chemical solubilities (Boomer et al. 1993).

For various reasons (incomplete or faulty data, incorrect assumptions concerning solubilities), TRAC predictions are quite uncertain (Kupfer et al. 1994); however, TRAC was used as the basis for distributing chemical inventories in the Hanford Defense Waste Environmental Impact Statement (HDW-EIS) (DOE 1987) to different SSTs. Thus, TRAC was normalized to the HDW-EIS on a component-by-component basis.

5.2.2 Los Alamos National Laboratory Tank Layer Model

Until recently, TRAC was the only model available for estimating the composition of SST wastes. A more sophisticated model is presently under development at the Los Alamos National Laboratory (LANL) (Agnew 1994). This model, commonly referred to as the LANL Tank Layer Model (TLM), estimates the tank waste composition in each tank, based on tank transaction records, chemical and physical properties of the waste, and estimated compositions for about 50 of the most important waste streams produced at the Hanford Site (chemicals used and wastes produced). Preliminary estimates are currently available for all SST tank farms.

5.2.3 Sampling and Waste Analysis

Core samples are often used as a basis for estimating the composition of waste in the tanks. Tests performed on core samples have demonstrated that tank sludge composition and properties are quite variable. The nonhomogeneous nature of the wastes can seriously affect the accuracy of any sampling program. Core sample recovery problems have occurred as well. Tank waste compositions, therefore, should not be judged solely on the basis of one or two core samples nor necessarily from uncalibrated tank waste composition models (TRAC and TLM). It is anticipated that detailed, reliable characterization information will not be available until the wastes are retrieved and homogenized.

Since core samples are likely to provide only a limited perspective as to the composition in the tanks, a different approach to tank characterization has recently been adopted. Rather than attempt to characterize each tank individually, core sampling and analysis will focus on characterizing types of waste in a tank in an attempt to establish that the LANL TLM and other waste type models reasonably estimate waste compositions in the SSTs (Kupfer et al. 1994).

5.2.4 Double-Shell Tank Inventory

The DST inventory is divided into five waste types: NCRW, waste from dissolving fuel jackets in PUREX; neutralized current acid waste (NCAW), first cycle solvent extraction waste from PUREX; complexant concentrate, which contains complexed metals, including strontium and TRU; waste from the Plutonium Finishing Plant (PFP); and double-shell slurry feed (DSSF), a concentrated mixture of effluents from various process plants, along with saltwell liquids pumped from SSTs. The DST inventory is derived from core sample data and liquid sample data.

5.2.5 Tank Waste Remediation System Flowsheet Inventory

TWRS Process Technology has developed a "flowsheet inventory" for use in flowsheet calculations and other studies. Although not under change control at this time, the flowsheet inventory provides the best and most complete estimate of tank inventories. The flowsheet inventory will be included in the next revision of the TWRS flowsheet (Orme 1994). The TWRS flowsheet inventory uses parts of the TRAC data, LANL model, the HDW-EIS overall inventory predictions, and analytical data. The LANL model is the primary basis used for distributing wastes in the SSTs. Minor components not tracked by the LANL model are extracted from TRAC. Certain components are normalized to the HDW-EIS inventory estimates while inventories for other components are being individually assessed. Overall site inventories of aluminum, chromium, iron, and chloride are being reevaluated. The current estimates for chromium may have to be increased by a factor of three to account for the chromium in high-level redox waste. The DST waste composition estimates are based mainly on analyses of core samples and liquid wastes in the DSTs.

A final modification to balance ion charges in each tank is performed by TWRS Process Modeling. If the ion charge balance is positive, OH^- is added to make up the difference. If the balance is negative, OH^-, CO_3^{2-}, NO_3^-, and NO_2^- are removed in the order listed, the Na is added if needed. The charge balanced inventory also includes the dilution water necessary to bring the sodium concentration in the soluble phase to 5 *M* or less and the undissolved solids to less than 10 wt% (flowsheet parameters for retrieving waste) (Certa 1995a)

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6.0 PROCESS FLOWSHEET INFORMATION

The following sections describe the planned retrieval and processing activities that will impact the composition of the LLW stream sent to the vitrification facility. Process flowsheet information is derived from the TWRS Process Flowsheet (Orme 1994).

6.1 WASTE RETRIEVAL

Sluicing is the preferred method for mobilizing the sludge, salt cake, and mineralized waste in the tanks. After sluicing, slurry will be transferred by pipeline to a retrieval annex or DST. Long-reach arms may be used in tanks that are "assumed leakers," to avoid additional tank leakage as a result of sluicing operations. The long-reach arms would retrieve and condition the waste for transfer by pipeline to the retrieval annex or DST. 200 West Area wastes will accumulate in the 241-SY Tank Farm for transfer to the 241-AW Tank Farm for decanting and sludge treatment. 200 East Area wastes will be retrieved into the 241-AN Tank Farm for decanting and sludge treatment.

6.2 SLUDGE WASHING

The purposed of sludge washing is to separate non-HLW components from the solids and process the supernate as LLW. Retrieved wastes will be consolidated in the 241-AN and 241-AW Tank Farms, and solids will be allowed to settle. Supernate will be decanted to a secondary settling tank. This operation will continue until a complete batch of settled sludge is obtained. Sludge batches will typically consist of 1.1 ML (300 kgal) of settled sludge at 20 wt% solids.

If the sludge contains significant amounts of chromium, phosphorous, and aluminum, a caustic leaching step will be conducted. Three-molar caustic is added to yield a final batch composition of 8 wt% solids. On average, 75% of the chromium, 70% of the phosphate, and 85% of the aluminum in the sludge are assumed to dissolve into the liquid phase in this step.

The sludge batch will be washed three times to separate the dissolved components from the sludge. Washing will be accomplished by dilution to 3.8 ML (1 Mgal) with dilute caustic (0.1 *M*), settling, and decanting the supernatant liquor. A flocculant may be added to promote settling. The washed sludge will be transferred to a storage tank as eventual feed to the HLW vitrification process. The decanted LLW will contain about 99% of the free (nonmineralized) sodium and 95 to 100% of the soluble chloride, fluoride, sulfate, and cesium.

6.3 LIQUID WASTE STORAGE AND TREATMENT

Decanted supernatant liquors from settling and washing operations will be accumulated in 241-AP Tank Farm. Seven tanks in the 241-AP Tank Farm should eventually be available for supernate storage and staging to the evaporator

and LLW pretreatment. The decanted liquid waste will be fed to an ion exchange process, where approximately 99% of the cesium will be removed. At nominal flowsheet rates, one tank of LLW must be fed through LLW pretreatment and vitrification processes every three weeks. The flowsheet assumes that LLW pretreatment and vitrification can be operated in an integrated, "close-coupled" fashion, with no DST storage required for LLW vitrification feed.

6.4 LOW-LEVEL WASTE VITRIFICATION AND DISPOSAL

The flowsheet assumes that a combustion-fired melter will be used to produce glass from the LLW feed. The flowsheet provides for mixing the cullet with molten sulfur and pumping the mixture to concrete vaults for onsite disposal. An extensive melter system testing and evaluation process is in progress (Wilson 1994) to select the optimum melter and related system components. Studies are currently underway to refine the disposal concept as well.

6.5 RETRIEVAL SEQUENCES AND BLENDING STRATEGIES

Specific strategies are being developed for optimizing the retrieval, blending, and vitrification of the HLW and LLW (Certa 1995b). This activity will ultimately recommend the order in which tanks are to be retrieved and processed through the prescribed pretreatment steps. Since many complicated and potentially conflicting issues are involved, compromises may be required. The approach being taken during the preliminary phase of this exercise is to identify how each strategy influences key measures such as attainment of Tri-Party Agreement milestones for retrieval, processing, and vitrification; predicted compositions of batches of HLW and LLW being fed to the respective melters; and HLW glass volume.

Development of retrieval sequences and blending strategies will continue over the next few years. In the near future, the sequences should prove useful for providing reasonable estimates of HLW and LLW feed variability.

The following list briefly describes some of the key strategies that are being used to develop retrieval sequences and blending strategies. This list is provided to illustrate the types of influences and competing constraints that must be considered.

- Process DST liquid wastes through LLW pretreatment and vitrification early. This option will free up tank space for receipt of SST wastes and sludge treatment.

- Retrieve salt cake in SSTs early. This will allow retrieval operations to proceed, yet avoid accumulating large amounts of sludge until the HLW vitrification plant is online.

- Minimize budget peaks by phasing in infrastructure upgrades and procurement of retrieval equipment. This strategy would lead to upgrading on a farm-by-farm basis, limiting the tanks available for retrieval at any point in time.

- Provide continuous feed to the LLW vitrification facility so that shutdowns can be avoided.
- Retrieve watch list tanks first to resolve the safety issues associated with them.
- Retrieve leaking tanks first to limit releases to the soil.
- Retrieve tanks with drainable liquid first to avoid risk of leaks to the soil.
- Minimize HLW glass volume. This is also an important consideration due to the anticipated high cost of HLW disposal. The HLW will be retrieved, pretreated, and blended to level the concentrations of constituents, such as chromium, phosphorus, aluminum, and zirconium, which adversely affect waste loading (and therefore, glass volume and repository costs). Conversely, problem wastes, such as high-zirconium or high-chromium wastes, may be segregated for special processing in a different melter (this would require qualification of a different HLW wasteform) (Lambert and Kim 1994).

There appears to be much less incentive to optimize the LLW feed stream because the variability of the LLW stream (which is dominated by sodium) will be much less than the variability of the HLW stream. Although the volume of LLW will be much larger than the volume of HLW, the repository costs for HLW greatly exceed the costs for LLW disposal. Further, optimization of the LLW stream composition is seriously constrained by the limited feed storage volume and the high throughput required to meet processing milestones. However, blending of the LLW stream should not be dismissed. LLW feed variability is discussed in Section 4.0.

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7.0 REGULATORY REQUIREMENTS

This section describes the various regulatory requirements for establishing LLW feed composition constraints to the LLW vitrification facility, but emphasizes the application of hazardous waste requirements and radioactive waste guidance (U.S. Department of Energy [DOE]/NRC) on the glass product. During operations, a LLW vitrification facility will be subject to extensive operational and environmental regulatory limitations that apply to the glass product, as well as to airborne emissions resulting from feed preparation of the LLW tank waste, along with solid and liquid waste byproducts resulting from vitrification. In addition, occupational and public exposure to the operations or their effluents must be considered.

The application of regulatory requirements to the glass product indirectly impacts LLW feed compositions through waste loading constraints. The assumption of near-surface disposal of LLW implies that NRC Class C limits are applicable as a minimum. Additional removal of certain constituents such as cesium to less than Class C may be achieved if economically feasible. This section summarizes both hazardous constituent limits and Class C limits and describes the procedure for determining waste classification. The application of these limits to high-sodium LLW glass is given in Section 2.0.

7.1 LOW-LEVEL WASTE GLASSES

Regulatory requirements for the glass product include those dealing with hazardous waste and those dealing with radioactive material. The waste streams anticipated to be received from pretreatment will have both hazardous and radioactive components and are termed mixed wastes. Mixed wastes are regulated as hazardous wastes by federal and state environmental authorities while radioactive components of the waste are regulated by DOE.

7.1.1 Hazardous Waste Requirements

Hazardous wastes are regulated by the EPA and, as delegated, to Ecology. Federal legislation governing hazardous wastes exist under the *Resource Conservation and Recovery Act of 1976* (RCRA) and the *Hazardous and Solid Waste Amendments* to RCRA. Regulations for the federal control of hazardous wastes are published in 40 CFR 260. Washington Sate has received delegation of authority from the EPA for enforcement of federal hazardous waste regulations through the publication of comparable standards within the WAC. These regulations of hazardous wastes are published in WAC 173-303, *Dangerous Waste Regulations*.

Mixed waste is any solid waste that contains both a radioactive component and a hazardous (per RCRA) or dangerous (per WAC) component. Washington State also regulated characteristic waste based on WAC toxicity, persistence, and carcinogenicity. Regulations for identifying and listing hazardous/dangerous wastes are found in 40 CFR 261 (EPA 1989a) and WAC 173-303-070, respectively. Radionuclides in the waste are not regulated by RCRA or WAC.

7.1.2 Waste Types

There are two general categories of hazardous/dangerous waste, characteristic and listed. The LLW feed stream anticipated for the LLW vitrification facility is expected to contain both types. Characteristic wastes are categorized based on ignitability, corrosivity, reactivity, and toxicity. Regulations governing designation of characteristic hazardous/dangerous waste are found in Subpart C of 40 CFR 261/WAC 173-303-070.

7.1.3 Waste Product Limitation (Nonradioactive)

To qualify the glass product for disposal under these regulations, the primary characteristic of concern is toxicity. The toxicity characteristic is based on the maximum concentration of contaminants in the treated waste as determined by the Toxicity Characteristic Leach Procedure (TCLP). Toxicity addresses both organic and inorganic components, but the vitrification process is expected to either volatilize or destroy organic constituents so only hazardous metal constituents are considered here for the glass product. Table 7-1 contains the limiting values for metal components in leachates.

Table 7-1. Maximum Concentration of Metal Contaminants for TCLP.

Contaminant	Wastewater limit (mg/L)	Nonwastewaster limit (mg/L)
Arsenic	1.4	5.0
Barium	1.2	100
Cadmium	0.20	1.0
Chromium	0.37	5.0
Lead	0.28	5.0
Mercury	0.15	0.2
Selenium	0.82	1.0
Silver	0.29	5.0

7.2 RADIOACTIVE WASTE GUIDANCE

The disposal of radioactive waste is regulated by DOE. Primary guidance for such control is contained in DOE Order 5820.2A, *Radioactive Waste Management*. In general, this order classifies wastes into HLW, LLW, and TRU. Specific guidance includes controls on the near-surface disposal of LLW and deep geological disposal of TRU and HLW.

7.2.1 U.S. Department of Energy Requirements

DOE Order 5820.2A (DOE 1989) established policies, guidelines, and minimum requirements for management of radioactive or mixed waste facilities. Specific requirements include the following limits: (1) external exposure to waste and concentrations of radioactive material which may be released into surface water, groundwater, soil, plants or animals is limited to an effective

dose equivalent not to exceed 25 mrem/year to any member of the public, (2) atmospheric releases are required to comply with the limits specified in 40 CFR 61 (EPA 1989b), and (3) limits are also imposed on the committed effective dose received by an individual after loss of active institutional control, 100 years.

7.2.2 U.S. Nuclear Regulatory Commission Guidance

The NRC regulates and licenses the disposal of radioactive materials from non-DOE facilities. NRC guidance on waste classification is contained in 10 CFR 61. DOE disposal of LLW is not currently regulated by the NRC; however, considerations for treatment and waste feed limitations are discussed below.

7.2.2.1 Basis for Consideration. Section 202 of the *Energy Reorganization Act of 1974* provides for the NRC to exercise licensing and regulatory authority over "Facilities authorized for the express purpose of subsequent long-term storage of high-level Radioactive wastes generated by (DOE) which are not used for, or are part of Research and Development activities." Thus, it is important to determine which tank wastes are HLW and fall within NRC's jurisdiction.

Of particular interest is the discussion in 58 FR 12344 (58 Federal Register 12344, March 4, 1993, "States of Washington and Oregon: Denial of Petition for Rulemaking"), which provides insight to the NRC's principles which influence their position on the question of the proper classification of tank wastes at the Hanford Site. These principles are derived from the U.S. Atomic Energy Commission's overall regulatory objectives, which led to the promulgation of 10 CFR Part 50, Appendix F in 1970. These principles are

1. Achieve a high degree of decontamination capability. This implies that the facility should separate for disposal as much of the radioactivity as possible, using processes that are technically and economically practical

2. The residual radioactive contamination should be sufficiently low as not to endanger public health and safety.

The principles of achieving a high degree of decontamination must consider technical and economic practicality as it would not be prudent to expend potentially vast sums without a commensurate expectation of benefit to health and the environment.

Wastes that are not determined to be HLW are considered "incidental wastes" and thus not regulated by NRC. DOE terminology (DOE Order 5820.2A) for these incidental wastes is LLW.

7.2.2.2 Waste Classifications. In 58 FR 12344, the NRC found that DOE's plans for handling DST wastes were consistent with their principles of waste decontamination and protection of the public. As such, NRC ruled that the DST wastes would be incidental waste provided that DOE followed through with its announced intentions. In consonance with the waste classification standards of 10 CFR 61.55, disposal of DST wastes not exceeding the Class C standards would be the disposal of incidental wastes. The Class C waste limitations based upon feed concentrations are described in Table 7-2.

Table 7-2. Radionuclide Waste Feed Limitations (Ci/mol sodium) Based on NRC Guidance (10 CFR 61.55).

Isotope	NRC Class		
	A	B	C
Na_2O loading in glass	--	25%	25%
Long-lived isotopes			
^{14}C	3.97 E-05	3.97 E-05	3.97 E-04
^{99}Tc	1.49 E-05	1.49 E-05	1.49 E-04
^{129}I	3.97 E-07	3.97 E-07	3.97 E-06
TRU	1.24 E-06	1.24 E-06	1.24 E-05
Short-lived isotopes			
^{3}H	1.98 E-03	--	--
^{60}Co	3.47 E-02	--	--
^{63}Ni	1.74 E-04	3.47 E-03	3.47 E-02
^{90}Sr	1.98 E-06	7.44 E-03	3.47 E-01
^{137}Cs	4.96 E-05	2.18 E-03	2.28 E-01

IMPLEMENTATION NOTES:

[1]Long-lived isotope analysis required first, short-lived isotope analysis second. Each analysis requires sum of fraction of limits for each isotope of consideration.

[2]Vitrification operations will drive off hydrogen, carbon, and potentially iodine and technetium. Class analysis should not account for these analytes as determined by glass retention capability.

[3]Limitations based upon other waste loadings should be scaled by the tabled value times the ratio of the tabled Na_2O and target Na_2O. Example: Class C ^{137}Cs for 20% Na_2O = 0.228*(0.25/0.2)= 0.285.

[4]Table calculated assuming glass product density of 2.5 Mg/m^3. Application of other densities may be scaled by 2.5/target density.

In 58 FR 12344, the NRC explicitly did not rule upon the waste classification of SST wastes. NRC indicated that "the appropriate classification of some Hanford wastes remains to be determined -- specifically, any single shell tank wastes.... a case-by-case determination of the appropriate waste classification might be necessary." As such, some consideration may be required for the regulation of SST wastes by the NRC.

Precedence indicates that SST waste handling consistent with DST waste handling (not greater than Class C waste disposal in near-surface disposal units) would yield NRC interpretation of these wastes as being incidental wastes and not regulated by the NRC. If the wastes are deemed to be HLW, the NRC would regulate the wastes under 10 CFR 60.

As economic considerations are directly applicable to the principle of decontamination capability, some further treatment by DOE to remove radionuclides could result in compliance with NRC guidance for Class A or Class B wastes (see Table 7-2). These considerations should remain tempered with the fact that if LLW, these materials will not be regulated by NRC.

7.2.3 Radionuclide Deposition Limits

NRC regulations applicable to licensed facilities require that no waste exceeding the Class C limits may be disposed in near-surface disposal units. Wastes with radionuclide concentrations exceeding Class C limits would require an NRC disposal license. Class C limits are given in Tables 7-3 and 7-4. The rule for determining whether a waste is Class C or below using the tables is as follows:

- If the waste contains only long-lived radionuclides, then the waste is Class C or lower if the concentrations do not exceed the limits listed in Table 7-3. The concentration basis is determined as the sum of fractions for contributions within Table 7-3 with a limiting sum of unity.

- If the waste does not contain any radionuclides listed in Table 7-3, then the waste is Class C or lower if the concentrations do not exceed the limits listed in Table 7-4. Again, the concentration basis is determined as the sum of fractions for contributions within Table 7-4 with a limiting sum of unity.

- If the waste contains a mixture of radionuclides, some of which are listed in Table 7-3 and some of which are listed in Table 7-4, then classification will be determined as follows:

  - If the concentration of a nuclide listed in Table 7-3 does not exceed 0.1 times the value listed in Table 7-3, the class shall be determined by the concentration of the nuclides listed in Table 7-4.

  - If the concentration of a nuclide listed in Table 7-3 exceeds 0.1 times the value listed in Table 7-3, but does not exceed the value in Table 7-3, the waste shall be Class C, provided the concentrations of the nuclides listed in Table 7-4 do not exceed the corresponding limits.

  - If the sum of fractions of a waste is determined to be less than 1, using Table 7-3 and using Table 7-4 (separate evaluations), then the waste is Class C or lower.

Table 7-3. Long-Lived Radioactive Materials.

Analyte	Concentration limits
^{14}C	8 Ci/m^3
^{14}C	80 Ci/m^3
^{59}Ni	220 Ci/m^3
^{94}Nb	0.2 Ci/m^3
^{99}Tc	3 Ci/m^3
^{129}I	0.08 Ci/m^3
^{63}Ni	700 Ci/m^3
^{241}Am	100 nCi/g total
^{237}Np	
^{238}Pu	
$^{239/240}Pu$	
^{242}Cm	20,000 nCi/g
^{241}Pu	3,500 nCi/g

Table 7-4. Short-Lived Radioactive Materials.

Analyte	Concentration limits (Ci/m^3)
^{63}Ni	700
^{63}Ni	7,000
^{90}Sr	7,000
^{137}Cs	4,600

7.2.4 Comparison with Double-Shell Tank Wastes

Current estimates of long-lived radionuclides in some DST waste indicate that the TRU content in complexant concentrate wastes exceeds Class C limits, but the volume of complexant concentrate wastes is small in comparison with other DST wastes. By comparison, using estimates of short-lived radionuclides in DST wastes indicates that ^{137}Cs content in NCAW exceeds Class C limits. However, current pretreatment plans to remove ^{137}Cs to approximately 1 Ci/m^3 in all wastes will preclude the application of Class C limits for ^{137}Cs to LLW wastes. In addition, current estimates of all waste designated as DSSF that are among the first LLW to be vitrified have compositions that comply with Class C limits.

7.3 AIRBORNE EMISSIONS

Airborne emissions are expected from facilities involving waste storage, waste evaporation, waste vitrification, and glass storage. Federal, state, and local regulations control the release of airborne pollutants of three general categories: radionuclides, priority air pollutants (conventional), and toxic air pollutants. The offgases from these operations must be treated to meet the appropriate and applicable emission standards. Offgas systems and air emissions abatement equipment design has not been selected for the LLW vitrification facility. Airborne emission standards will be applied as part of the design considerations for these offgas systems and are not expected to constrain feed compositions or volumes at this time.

7.4 LIQUID AND SOLID SECONDARY WASTES

Secondary liquid and solid wastes that cannot be recycled back into the feed stream will be generated during vitrification operations. The amount and characteristics of these wastes will depend in part on the type of facility selected and specific design choices of effluent treatment. Appropriate regulations applicable to the disposal of these wastes will be considered in future revisions of this document.

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8.0 PERFORMANCE ASSESSMENT GUIDANCE

Evaluations of the long-term performance of LLW glass disposal system options are in progress to identify technical issues, uncertainties, and provide program guidance for disposal system facility design options as part of an effort to prepare a future site-specific performance assessment as required by DOE Order 5820.2A. Some of this guidance, along with experience gained from the *Performance Assessment of Grouted Double-Shell Tank Waste Disposal at Hanford* (WHC 1993) can be used as a basis for estimating preliminary durability requirements for LLW glass. This section summarizes the function, scope, and limitations of performance assessment methodology and discusses some of the significant parameters in performance assessment analyses with emphasis on waste-form and waste-package durability. Approaches to contaminant release models and applications of system performance objectives are summarized. An approach to the application of performance assessment methodology to establishing waste-form performance requirements and subsequently waste-form composition and associated waste feed composition limitations is suggested.

8.1 PRELIMINARY WASTE-FORM DURABILITY REQUIREMENTS

Preliminary evaluation of LLW glass disposal system performance using numerous simplifying assumptions and several design options have indicated that for the intruder scenario, ^{90}Sr and ^{137}Cs are the dominant dose contributors for the first 200 years, while after 300 years the dose is dominated by ^{241}Am. For the drinking water scenario, dose is dominated by ^{99}Tc for about the first 20,000 years with a small contribution from ^{129}I. For future years, uranium group isotopes followed by ^{237}Np are major contributors. These results are generally consistent with observations from the Grout Performance Assessment results with LLW inventories from DSTs (WHC 1993).

Sensitivities of several orders of magnitude of constant corrosion rates were evaluated in these preliminary calculations along with several assumed glass surface areas. For a first approximation, decreased surface area for a given inventory results in lower dose contributions as does lower corrosion rates. Decreased glass surface area per unit inventory can be achieved by fabricating larger glass monoliths, but there are production considerations such as annealing time and devitrification problems that impose practical limits to this approach. Because a number of LLW glass disposal system and glass production issues have not yet been determined, it seems best at this time to assume that the LLW glass durability will have leach test characteristics at least as good as those of the more durable glass compositions considered in the LLW glass formulation activities. Based on 7-day PCTs conducted at 90 °C, these glasses yield mass losses on the order of 0.1 $g/m^2/day$. Alternatively, recent workshop discussions involving experts from several DOE sites suggested that a forward release rate of 1×10^{-5} $g/m^2/day$ based on a flow-through test at 20 °C may eventually be a better LLW glass durability specification, but data for this test are limited at present. The PCT limit is offered here as a preliminary figure of merit for LLW glass durability to provide at least an initial target for the quality of glass required. As performance assessment activities continue, it is anticipated that these durability definitions will be updated.

The following discussion concern more detailed explanations of performance assessment methodology that directly or indirectly influence glass durability requirements.

8.2 PERFORMANCE ASSESSMENT FUNCTIONS AND SCOPE

A performance assessment evaluates a complete engineered disposal system to determine if the contaminant release rate from the waste package system under a set of reasonable but conservative parameters, both site specific and design specific, results in sufficiently low contaminant transport such that performance objectives established for the system are achieved. The performance objectives, which include regulatory requirements to the extent possible, are selected as a definition of reasonable assurance of long-term public protection.

Since LLW glass is expected to be disposed in near-surface engineered systems at the Hanford Site, the performance objectives used by the Grout Performance Assessment will probably be applicable to LLW glass as well. These performance objectives focussed on protection of the general public, inadvertent intruder protection, and protection of groundwater resources. The general public protection based on DOE, Richland Operations Office (RL) Order 5820.2A indicated that maximum exposure to any member of the general public does not exceed 25 mrem/year for at least 1,000 years after disposal. After 1,000 years, as low as reasonably achievable guidance applies, but the maximum population exposure is 500 person rem/year. A performance objective of 25 mrem/year for 10,000 years was adopted by the Grout Program and may also be adopted by revised DOE orders. DOE Order 5820.2A provides a limit of 100 mrem/year for continuous exposure and 500 mrem/year for single acute exposure for intruder protection after institutional control (100 years). DOE Order 5820.2A requires groundwater protection consistent with federal, state, and local requirements, but RL Order 5820.2A clarifies that the dose from radionuclides in drinking water should not exceed an effective dose equivalent of 4 mrem/year to an individual who drinks 2 L/day from the contaminated aquifer. These objectives must be met for 1,000 years, but the grout program adopted 10,000 years. Additional regulatory details are given in Section 7.0.

A performance assessment includes developing a site-specific conceptual model of a disposal system, based on the actual system design. The model includes appropriate physical environmental conditions. Computer simulations of contaminant release and transport are performed based on the model. The waste form is part of the source term for such a model. The conceptual model is necessarily a simplistic representation of the actual system and attempts to be realistically conservative. For LLW glass disposal, either glass alone or glass in a matrix may be considered the source term. While several system components, such as barriers or climate, in addition to the waste form can affect system performance, performance assessments indicate, other things being equal, that the better the durability of the glass, the better the system performance. The performance assessment evaluates the gradual release of the waste inventory with the release rate controlled by the waste form and the engineered system properties, and identifies the most significant waste components that impact performance objectives. Thus, the performance

assessment provides indirect guidance and feedback for waste-form durability requirements but does not directly specify durability limits except in the context of the assumed performance model.

8.3 SYSTEM PARAMETERS AFFECTING PERFORMANCE ASSESSMENT

The surface area of the waste form exposed to water is a major factor in controlling contaminant release rate. Therefore, the waste package geometry and the engineered system design including waste package distribution types and sizes of matrices or barriers must be considered as enabling assumptions. Eventual dose calculations are based on the fractional release of the waste inventory, which is a fundamental parameter. Waste loading and glass formulation parameters influence the total amount of glass required, which can, in turn, influence the amount of disposal space required.

Hydraulic parameters of the system determine the net, unsaturated flow of water past the waste-form surface. Climate and net recharge rate are the primary site-related parameters of interest. The net recharge is the net amount of total precipitation that infiltrates through the unsaturated zone to the water table. Net recharge is influenced by sediment texture, vegetation, temperature, and engineered systems such as capillary breaks consisting of adjacent materials with large differences in porosity/permeability characteristics. Hydraulic parameters that must be measured or assumed for both engineered and natural materials are porosity/permeability, saturated hydraulic conductivity, and moisture retention properties as a function of pore water content. These parameters are used to calculate unsaturated hydraulic conductivities that determine the flow rate of water past the waste-form surface.

Chemical properties of water reaching the waste-form surface influence the contaminant release rate and can also influence contaminant transport away from the surface or the formation of secondary mineralization products at the waste form surface or in adjacent barriers. Water properties of interest include chemical composition and related characteristics such as redox state and pH. In a near-surface, arid environment such as the Hanford Site, net water movement occurs as a surface film over sediment/soil grains, so water chemistry is dominated by reaction with local sediment material and constituents such as carbon dioxide from air. Because of these types of interactions, water that might reach near-surface disposal systems would tend to be oxidizing, nearly saturated with carbon dioxide, saturated in dissolved silica with respect to minerals such as quartz, and have pH values slightly alkaline. Water chemistry will be locally dominated by the glass waste-form at the waste form surface, probably resulting in increased pH and silica dissolution due to alkali leaching from the glass. As the water again moves back into the surrounding sediment material and away from the glass, the chemistry is again dominated by water sediment interactions that can result in precipitation or sorption of contaminants that retard contaminant transport. These are some of the considerations used to develop a reaction path source term, but because of chemical complexity of the system a practical, preliminary approach that is often taken is to adopt a release rate model and include transport retardation factors from either measured or estimated sorption (Kd) properties of natural or engineered materials.

8.4 WASTE FORM RELEASE MODELS AND DURABILITY

Considerable literature exists on mechanistic and theoretical studies of glass corrosion including chemically complex waste glasses. While details of these studies are complex, in a simplistic sense glass-water interactions can be thought of as follows: water reacts with network ions through hydrolysis with both bridging and nonbridging oxygen atoms, for example

$$-Si-O-Si- + H_2O = -Si-OH + HO-Si-$$

so that a corrosion layer, often called a "gel layer" of partially hydrolyzed silica and alumina, develops at the glass surface region. The more mobile network formers, such as sodium, are leached from the gel layer into the aqueous solution where they also hydrolyze and can gradually result in an increase in pH in a closed system. Some silica and alumina from the gel layer dissolves so that particularly in an open system a steady state can occur such that the gel layer thickness becomes nearly constant with time.

A number of leach tests have been developed to compare glass durability and define a "figure of merit" for acceptability. For waste glasses, two of the more common tests are MCC-1, which specifies a monolithic sample and fixed solution volume; and MCC-3/PCT, which specify crushed samples with high glass surface to solution volume ratios. Both of these types of tests emphasize comparing different glass formulations and waste loadings and are short-term, closed-system, static tests compared to performance assessment needs of long-term, site-specific durability behavior. Other tests have adopted flow-through systems, leachate replacement, refluxing, two-phase (water plus steam) systems or variations of these.

Corrosion reactions of glass follow a reaction path that is analogous to processes of rock weathering to form soil minerals. Short-term leach tests alone are not sufficient to predict long-term behavior, so reaction path modeling is often used to develop performance assessment source term models. However, some general relationships concerning glass corrosion can be made from leach test data. Contaminant concentrations in solution versus time can be described by first order kinetic functions and leach rates tend to decrease with time. In special cases rapid formation of corrosion products may result in an increased rate after apparent steady state, but there is some controversy if this is likely to occur in a disposal system or is only test-type related. For performance assessment purposes, first order kinetic functions sometimes modified by solubility products and retardation factors or related transport terms, are often adopted. For preliminary evaluations, constant leach rates based on short term leach tests are often used and may be conservative in many cases.

9.0 ACCOMMODATION OF CHANGES AND OPTIONS

The purpose of this section is to discuss major options, decisions, and changes that are being considered that may modify the LLW feed guidance. Some of the major options are being developed through engineering trade studies, but the final decision is not known. Other options may need to be negotiated with Ecology, DOE, and/or the EPA. The result of these negotiations may affect the total amount of radionuclides allowed in the LLW product, or the concentration of a specific radionuclide allowed in the product. This section accumulates most of the major decisions and options that will affect the process. Specific items such as waste variability have been covered in other sections to allow more coherent and timely discussion of the options. Major items that could change are noted below, along with the impact of the change on the feed guidance. The items are arranged in the order they might be found in the flowsheet.

9.1 WASTE FEED TO PROCESS

9.1.1 Waste Inventory Data Chemical Composition

The current inventory data from many tanks are suspected to be incomplete. The total waste inventory drives process capacity requirements, glass composition, and final glass volume. To better manage this variable an investigation of waste inventories for both SSTs and DSTs is being conducted at LANL and Hanford. Sampling of the SSTs is being conducted that will finalize inventory data. If the new data is different than currently used it could affect the processing limits by changing anticipated compositions of feed to LLW vitrification. The most significant effect of changing waste composition is anticipated to be variations of compositional extremes in some tanks; larger variations could drive glass compositions to their limits of acceptability or have other effects. These effects can be made manageable by engineering modifications noted at the end of this chapter and actions noted in Section 4.0.

9.1.2 Solubility of Individual Chemicals and Radionuclides

The enhanced sludge washing solubilities currently in use for tank waste are based on experience with a limited number of tank samples, in some cases the data were unpublished. Solubilities of key components can have a significant impact on the TWRS Process Flowsheet, which could result in more or less waste to LLW vitrification, and cause compositional variations between families of feeds.

Core samples are planned to be taken and leached to determine solubility limits of key components. This will be incorporated into the flowsheet and help determine composition of the waste feed. If there is a significant amount of feed of greatly differing compositions than projected, it may be necessary to develop alternate glass formulations that would have different chemical compositions than those given in the present recommendations. This might increase costs of the program by producing more glass than anticipated

or cause increased testing and qualification of different glass formulations. This deviation is anticipated to be manageable with the modifications noted above.

9.1.3 Feed Composition to Process

The feed used in the TWRS flowsheet (Orme 1994) is a homogeneous mixture of the SST wastes and DST wastes. Actual feed compositions and characteristics need to be defined, as noted above. These compositions may be modified by modification of retrieval and blending scenarios, and by addition of glass modifiers in the melter feed.

9.2 RETRIEVAL SCENARIOS

The order in which waste is retrieved will tend to define process composition bounds and process upsets, which will determine the volume of HLW produced. Retrieval should be laid out in a way as to minimize the variation to the LLW and HLW melter feeds while simultaneously minimizing the volume of glass produced. Realistically HLW retrieval and blending will be a priority due to its higher costs. Tank waste safety issues may have a controlling voice in retrieval and blending scenarios. Specific waste from tanks may be required to be retrieved first, and in specific ways that require more chemical addition than currently anticipated.

If additional water and sodium are required to retrieve waste this may require that more glass be made to deal with the larger sodium mass, thus lowering the concentrations of other waste components. Water addition for retrieval is based on a nominal 5 molar sodium content in the evaporator/ vitrification feed; a higher water concentration will require more evaporation, or higher capacity equipment. Suggested changes for this sodium concentration have ranged from 7 to 0.5 molar.

The impact to the LLW vitrification may be in equipment sizing, lag storage requirements, chemical composition of the feed, and total volume of glass produced. Westinghouse Hanford Company (WHC) computer modeling of retrieval scenarios is ongoing and will help minimize the affect of this variable on the process.

9.3 TANK FARM PROCESSING

9.3.1 Effectiveness of Enhanced Sludge Washing

The effectiveness of enhanced sludge washing will determine what composition of feed goes to LLW and HLW vitrification, and will have all the effects noted in Section 9.1. In addition, items such as addition of flocculant and extra leaching steps may be required. Flocculant addition may mean that there are more organics to destroy and remove at the melter level. This may require a limit on total organic carbon, or the type of organic used as a flocculent. Additional caustic leaching may require additional sodium additions and/or other chemicals. These additional chemicals may increase the

volume or change the composition of the glass produced. Ongoing pretreatment studies with tank waste will determine the type and necessity of further treatment.

9.3.2 Reactions Between Tank Wastes

Precipitation reactions can occur when tank wastes are combined. These reactions may occur when the waste is evaporated and combined, or any time two different compositions of waste interact. Because LLW has significant tank-by-tank variations in composition, some amount of precipitation is probable when the waste is moved. Precipitation could change the composition of the waste going to LLW vitrification without the operators being aware of it. If wastes react, both LLW and HLW melters and product performance may suffer, due to precipitation of the reactants and resulting unanticipated allocation of the waste components. Literature studies and process feed compositional testing may be workable options to reduce this risk.

9.4 RADIONUCLIDE REMOVAL

In the TWRS flowsheet only ^{137}Cs is anticipated to be removed. This section covers other radionuclides that may require removal and their affect on the LLW process.

9.4.1 Strontium and Transuranic Removal

Strontium removal is not planned but may be selectively required to reduce the LLW to Class C limits. Complexant concentrate wastes currently exceed the LLW limit of 100 nCi/g for TRU (Boomer et al. 1993, Appendix D). It is expected that organic destruction will be required to drop the TRU level of this waste stream to less than 100 nCi/g in glass. If TRU removal is required, then other chemical compositional changes to the feed may be inevitable.

Further development of the heat and digest process for removal of strontium and TRU from solutions may be warranted. This treatment may be appropriate for only a few waste tanks or specific waste types. Application of the process may introduce other chemicals into the process. If other chemicals are introduced they should be carefully screened to assure that they will not adversely affect the process.

It is estimated that 16 tanks (8 SSTs and 8 DSTs) exceed the TRU limit. Organic destruction, if required, would most likely be performed by heating the waste to allow degradation reactions to proceed more rapidly. This heat/digest treatment would probably be carried out in aging waste tanks which have heating coils.

9.4.2 Technetium Removal

Technetium removal is not planned but may be required to meet regulatory requirements resulting from the LLW performance assessment. The performance assessment is performed to determine if radiation doses will affect future occupants of the site. If technetium removal is required then other chemical compositional changes to the feed may be inevitable. Further development of the technetium removal process is planned, and the possibility of an ion exchange treatment for removal of technetium may be warranted. This treatment may be appropriate for only a few waste tanks or specific waste types.

Depending on melter design and operating parameters, technetium might also be separated by volatilization in the melter, captured, and either fed to the HLW melter or immobilized in a secondary waste form. Work is in progress on immobilization in secondary waste forms (Young 1994).

9.5 LAG STORAGE VOLUME FOR VITRIFICATION

Currently the TWRS flowsheet (Orme 1994) shows limited (close coupled <1 million gallons) lag storage for LLW melter feed. Increased lag storage volume for mixing prior to the LLW melter may be advantageous to ensure that large step changes in feed composition do not occur too fast to process. Another alternative would be to sacrifice optimum HLW blending to blend critical LLW feeds to lower concentrations to allow processing within recommended feed ranges. See Section 4.0 for more information.

9.6 LOW-LEVEL WASTE MELTER

9.6.1 Melter Selection

Currently a combustion melter design is modeled in the LLW flowsheet. There are seven different melter investigations being conducted by WHC for vitrification of LLW. Some of the melters have more stringent feed requirements that others. Therefore it is very possible that changes to the feed guidance will have to be made to accommodate the final selection. The final selection is anticipated to be completed by June 1996.

Prior to that time it is advisable to keep the LLW feed guidance more conservative than absolutely necessary to ensure that any of the melters can be inserted into the application without radical changes in pretreatment or the waste recovery process. After the melter selection process is complete and the alternate melter chosen it may be possible to relax the feed guidance to suit the reference melter.

9.6.2 Process Control

Two different process control schemes are being contemplated for LLW which could affect the waste feed guidance. The two control schemes are feed forward or feed back with recycle.

Feed back control is defined as certifying the product by direct analysis of the product sample, with product recycle capability. Process control is used to minimize off-specification product.

Feed forward control is defined as precertifying the vitrification process and equipment with only initial or infrequent product sampling. After the process and equipment are certified, process control data is the primary gauge used to qualify the product.

The feed forward control system is most likely to cause increased compositional limits in the incoming feed. The system relies on process performance and does not extensively test or recycle the product after the equipment and process have been certified. Therefore the incoming glass formers and waste have to be within an acceptable quality assurance area to assure that the product will be as designed. In the feed forward control a more conservative product envelope would have to be established that would allow only acceptable vitrified product to be produced. This acceptable product window would not be as large as that of the feedback control formulation.

In feedback control the edges of the waste and product acceptability envelope could be approached in order to increase waste loading, or throughput. The testing and recycle of off-specification product would allow the flexibility to make some marginal product and to better determine where the boundaries were. It would also provide flexibility to compensate for plant upsets and relatively rapid changes in feed composition without the time consuming detailed testing required with feed forward control.

The results of a LLW process control study are due June 1, 1995. The decision concerning which system to use will come after that time.

9.5.3 Offgas Recycle Streams

Some volatile and semivolatile components recovered from the offgas will be recycled to the LLW melter. If retention of these components in the glass is very poor, the quantities of these species in the recycle stream could build up over time, resulting in significantly higher concentrations in the melter. Significantly higher concentrations of sodium and potassium in the melter will enhance corrosion of the melter lining and other equipment. High concentrations of chlorine and fluorine may cause the formation of a secondary phase (molten salt layer) in the melter, along with excessive corrosion of offgas system components. This ultimately will force the waste loading to be reduced, increasing the volume of glass produced.

Other semivolatile metals (e.g., nickel, mercury, lead, arsenic) could also accumulate in the recycle stream. Most of these metals are largely insoluble and, therefore, should be present in very low concentrations in the LLW stream.

Radionuclides such as ^{137}Cs, ^{129}I, and ^{99}Tc could accumulate in the recycle stream as well, causing higher concentrations in the melter feed than would be predicted from the nominal feedstream. As a secondary treatment step, technetium may be precipitated as a sulfide and diverted to the HLW stream.

If certain components cannot be forced into the glass in sufficient quantities, a portion of the recycle stream may have to be purged off and disposed of as a secondary waste. It is anticipated that most of the compounds will be able to be recycled to the melter. Vitrification formulation development will continue to give a better idea of the chemical limits in the product. Melter testing is planned to advance the knowledge base on volatile and semivolatile behavior. Studies on appropriate secondary waste forms are also proceeding as noted in Young (1994).

9.7 NUMBER OF MELTERS

By increasing the number of melters it may be possible to run different streams at the same time, in parallel, with different formulations. The number of melters is expected to influence the number of chemically different waste streams that could be run at one time. Multiple melters could shorten the length of time it takes to change from one waste stream to another. A more complex feed system than now envisioned may be required to effectively distribute the feed to the melters. Determination of the number of melters needed is expected to be performed during the conceptual design effort.

9.8 VITRIFICATION PRODUCT

The quality of the vitrification product will be influenced by the incoming waste, the melting, cooling and crushing/pouring process. The final product and disposal system must be acceptable to the performance assessment. These items are interrelated, and are being evaluated by the performance assessment, see Section 8.0.

The disposal method shown in the flowsheet (Orme 1994) uses a sulfur cement process which contains LLW cullet in a sulfur matrix. The cullet is mixed with molten sulfur and oligomers (dicyclopentadiene and cyclopentadiene); the final product has a 60/40 glass/sulfur cement volume ratio.

A leading option to the sulfur cement process is a canister product in which the glass would be poured into a large container. Variations on this scenario include making marbles, or other objects which might be easily heat treated to increase product quality. If the LLW vitrified product is to have treating and forming requirements then the formulation of the product could be impacted by having additional requirements added, including modification of the LLW feed guidance. These options are being evaluated in ongoing studies.

9.9 IMPACTS OF FEEDS WHICH EXCEED RECOMMENDATIONS

Analytical verification of waste feed for LLW vitrification may show that some feed components extend beyond the currently known acceptable ranges identified in Section 2.0. Feed with component concentrations outside of the

preliminary guidance ranges may still be rendered acceptable for vitrification following an engineering evaluation of the relative impacts of the following alternatives:

- Blending with other acceptable pretreated feeds
- Reduction of the waste loading in the glass
- Modification of the glass formers
- Modification of the glass formulation
- Modification of the pretreatment process
- Modification of the melter system design
- Modification of the disposal system design.

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