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A Research Report for Westinghouse Hanford Company

Preliminary Assessment of Candidate Immobilization Technologies for Retrieved Single-Shell Tank Wastes

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January 1992

Prepared for the U.S. Department of Energy
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Pacific Northwest Laboratory
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PRELIMINARY ASSESSMENT OF CANDIDATE
IMMOBILIZATION TECHNOLOGIES FOR
RETRIEVED SINGLE-SHELL TANK WASTES

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Richland, Washington 99352

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SUMMARY

This report describes the initial work that has been performed to select technologies for immobilization of wastes that may be retrieved from Hanford single-shell tanks (SSTs). Two classes of waste will require immobilization. One is the combined high-level waste/transuranic (HLW/TRU) fraction, the other the low-level waste (LLW) fraction. A number of potential immobilization technologies are identified for each class of waste. Immobilization technologies that are candidates for future development were initially selected based on a number of considerations, including 1) the waste loading that could likely be achieved within the constraint of producing acceptable waste forms, 2) process flexibility (primarily compatibility with anticipated waste variability), 3) process complexity, and 4) state of development.

Based on these criteria, a number of promising immobilization technologies were selected for further development in initial scoping studies to be initiated in FY 1991. These include the following:

- for HLW/TRU waste - borosilicate glass, lead-iron phosphate glass, glass-calcine composites, glass-ceramics, and cement based forms
- for non-denitrated LLW - grout, latex-modified concrete, and polyethylene
- for denitrated LLW - silicate glass, phosphate glass, and clay calcination or tailored ceramic in various matrices.

The experimental work required to adequately assess the applicability of these candidate waste forms is discussed in this report. An approach to defining more realistic reference feed compositions is described. Potential chemical partitioning needs are also identified; such partitioning might allow greater waste loadings and thus result in a reduced volume of immobilized HLW/TRU waste.

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1.0 INTRODUCTION

From 1944 until the early 1970s, most of the reprocessing waste produced at the Hanford Site was stored in single-shell tanks (SSTs). Since 1970, double-shell tanks have also been used. The Department of Energy is currently examining a number of storage and disposal options for SSTs. The waste fractions may be regulated as dangerous and/or hazardous wastes as well as radioactive wastes. Certain of the SSTs may be remediated using in-place stabilization methods. Remediation of other SSTs may require that the wastes be retrieved. These retrieved wastes will need to be immobilized before disposal.

Retrieval and partitioning of SST waste will generate three fractions: HLW, TRU, and LLW. The immobilized LLW will likely be disposed of onsite at Hanford. Immobilized HLW and TRU will require offsite disposal. The volume of the TRU fraction will be very small compared to the HLW fraction, and combining the two streams would have a negligible impact on the composition of the HLW. Thus a decision was made that, at least during the initial stages of immobilization technology development, two rather than three waste types would be considered. These are the combined HLW plus TRU and the LLW. However, if at some point it becomes necessary to consider the HLW and TRU separately, this will be done.

1.1 OBJECTIVES

Pacific Northwest Laboratory (PNL)^(a) is identifying technologies that may be used to prepare final waste forms and packages for the disposal of retrieved SST wastes. This work is sponsored by the Westinghouse Hanford Company (WHC) as part of the environmental restoration effort at Hanford. Waste form development for HLW/TRU and LLW fractions of retrieved SST waste will be conducted in four stages: literature review, laboratory scoping studies, in-depth laboratory studies, and pilot-scale demonstration. This report

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documents the results of the literature review, the focus of which was to identify waste form immobilization technologies that would be promising candidates for future development work.

A flow diagram showing the process used for selecting candidates for waste form development is presented in Figure 1.1. This process involved identification of 1) waste form acceptance criteria that must be considered during SST waste form development, 2) approaches to defining the reference HLW/TRU feed stream compositions that will be used in subsequent waste form development work, 3) the criteria by which different potential immobilization technologies have been selected and will be ranked after initial laboratory scoping studies, 4) available immobilization technologies including treatments to destroy or mitigate hazardous waste characteristics, 5) those immobilization technologies that may be applicable to SST wastes and that can be developed in the near future and 6) potential chemical partitioning needs

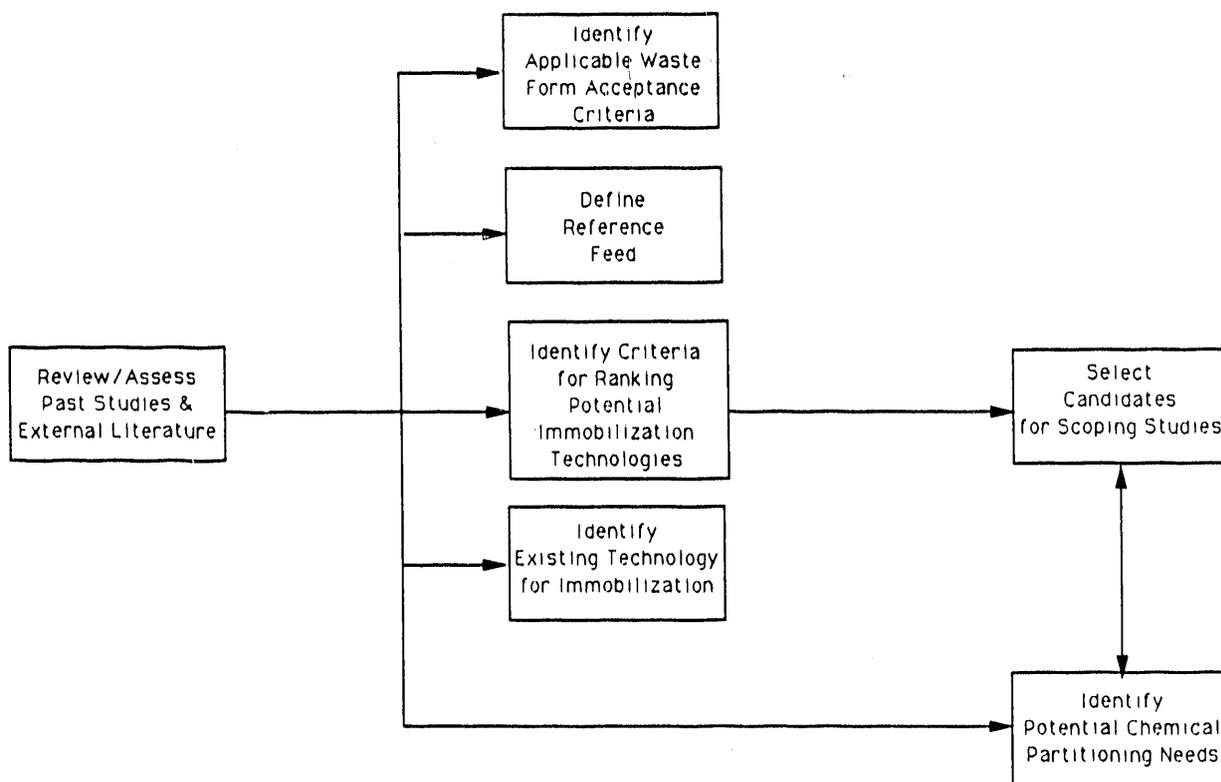


FIGURE 1.1. Process for Selecting Candidate Immobilization Technologies

(partitioning that might allow greater waste loadings in HLW/TRU waste forms and thus result in a reduced volume of immobilized HLW/TRU waste).

The report also proposes the scoping studies that must be performed to assess the applicability of the candidate immobilization technologies to retrieved SST wastes. In addition to supporting the selection process, these studies will provide input on achievable waste loadings to the WHC SST systems analysis activity (described by Boomer et al. 1990).

1.2 REPORT OVERVIEW

The remainder of this report is organized into three major sections. In Section 2.0, existing acceptance specifications and criteria for HLW, TRU, and LLW are discussed and those that are applicable during waste form development are identified. Section 3.0 describes the reference feed compositions that will be used (at least initially) in subsequent immobilization technology development efforts.

Section 4.0 describes the potential immobilization technologies that were considered for the HLW/TRU and LLW fractions of retrieved SST wastes. This section also describes the considerations that lead to the selection of particular immobilization technologies for future development. Section 4.0 also outlines the initial work that should be performed to demonstrate the applicability of these candidate technologies to the immobilization of retrieved SST wastes.

2.0 WASTE FORM ACCEPTANCE CRITERIA

Acceptance criteria have been developed for high-level wastes (HLW), transuranic (TRU) wastes, and low-level wastes (LLW). These criteria are designed to ensure the appropriate disposal behavior of these wastes, to ensure that certain prohibited materials are not disposed of without treatment, and to provide the basis for disposal facility design. Candidate waste forms that may be used to immobilize retrieved SST waste will need to comply with these requirements.

While consideration of these criteria must be an integral part of the process of waste form selection and development, not all of the criteria that will apply to these waste forms must be considered during waste form development. Certain of the criteria deal with information that must be supplied with the waste form. Others deal with the packaging of the waste forms. That the producer can comply with these types of criteria will be assumed. Only that subset of acceptance criteria that identifies requirements that waste form itself will be considered in waste form development, in other words, the criteria that specify waste form performance or characteristics.

These acceptance criteria can be used in the process of selecting and developing candidate immobilization technologies in several ways. Initially, the criteria can help to determine whether a potential immobilization technology would be likely to produce waste forms acceptable for disposal. During waste form development, the criteria also provide a valid, quantitative measure of waste form quality. The criteria can, therefore, guide the process of optimizing a particular waste form type. The criteria should not, however, be used as the basis for choosing the "best" waste form from a number of acceptable candidates. The selection process will need to consider the behavior of the waste form as one part of the disposal system, but potential trade-offs between processing complexity and waste form durability must be factored in.

During the initial development of candidate immobilization technologies, it will be assumed that the HLW and TRU fractions will be combined into a single waste stream and that separate HLW and TRU waste forms will not be

required. Thus, a single set of acceptance criteria for potential HLW/TRU waste forms needs to be identified, as does a set for LLW forms.

2.1 CRITERIA FOR HIGH-LEVEL AND TRANSURANIC WASTE FORMS

Two sets of criteria are potentially applicable to the forms that will be developed for the HLW/TRU fraction of retrieved SST wastes. These are the Waste Acceptance Specifications being developed for HLW to be disposed of in a Nuclear Regulatory Commission-licensed mined geologic repository, and the Waste Acceptance Criteria that will apply to defense TRU wastes disposed of at the Waste Isolation Pilot Plant.

2.1.1 Waste Acceptance Specifications for HLW

Preliminary Waste Acceptance Specifications have been developed for two types of HLW destined for disposal at a mined geologic repository. These are the HLW to be vitrified by the Defense Waste Processing Facility (DWPF) at Savannah River and the West Valley Demonstration Project (WVDP) at West Valley, New York. These two sets of specifications are essentially identical. Similar acceptance specifications are under development for the Hanford Waste Vitrification Plant (HWVP) waste form. These specifications have been developed for glass waste forms and thus should be directly applicable to potential glass waste forms for immobilization of SST HLW. However, they should also provide a guide as to what will be required of non-glass HLW forms.

The "Waste Acceptance Preliminary Specifications for the West Valley Demonstration Project High-Level Waste Form" (U.S. DOE 1990) identifies a total of 25 specifications with which the waste form producer must comply. These are divided into Waste Form Specifications, Canister Specifications, Canistered Waste Form Specifications, and Quality Assurance Specifications; see Table 2.1.

The Waste Form Specifications deal with the composition, chemical durability, and stability of the waste form. The durability (Spec. 1.3) and stability (Spec. 1.4) specifications are the primary specifications of concern during HLW form development. Specification 1.3 identifies the minimum chemical durability (resistance to attack by water) that HLW forms must exhibit.

TABLE 2.1. Waste Acceptance Specifications for High-Level Waste Forms

- 1.0 WASTE FORM SPECIFICATIONS
 - 1.1 Chemical Specification
 - 1.2 Radionuclide Inventory Specification
 - 1.3 Specification for Radionuclide Release Properties
 - 1.4 Specification for Chemical and Phase Stability
- 2.0 CANISTER SPECIFICATIONS
 - 2.1 Material Specification
 - 2.2 Fabrication and Closure Specification
 - 2.3 Identification and Labeling Specification
- 3.0 CANISTERED WASTE FORM SPECIFICATIONS
 - 3.1 Free-Liquid Specification
 - 3.2 Gas Specification
 - 3.3 Specification for Explosives, Pyrophoricity, and Combustibility
 - 3.4 Organic Materials Specification
 - 3.5 Free-Volume Specification
 - 3.6 Specification for Removable Radioactive Contamination on External Surfaces
 - 3.7 Heat Generation Specification
 - 3.8 Specification for Dose Rate
 - 3.9 Chemical Compatibility Specification
 - 3.10 Subcriticality Specification
 - 3.11 Specifications for Weight, Length, Diameter, and Overall Dimensions
 - 3.12 Drop Test Specification
 - 3.13 Handling Features Specification
- 4.0 QUALITY ASSURANCE SPECIFICATION
 - 4.1 Strategy
 - 4.2 Implementation
 - 4.3 Selective Application of the Quality Assurance Requirements
 - 4.4 Previous Work
 - 4.5 Documentation

In the current version of the specifications the method of determining this durability is the MCC-1 Static Leach Test Method (MCC 1983), developed by the Materials Characterization Center (MCC). Waste forms are required to exhibit a normalized elemental mass loss of less than $1 \text{ g/m}^2\text{-d}$ for certain waste form constituents. A proposed change to the specifications would substitute the Product Consistency Test (PCT) (Jantzen and Bibler 1987). The proposed change would also require that the waste form be tested in parallel with, and be more durable than, a specified standard glass. Specification 1.4 is designed to ensure that, under normal storage and handling at the producer's facility, the

waste form will not be significantly altered (e.g., by exposure to high temperatures) before delivery to the repository.

The Canister Specifications (which deal with the container that holds the waste form) and Quality Assurance Specifications are not applicable to waste form development. Certain of the Canistered Waste Form Specifications have a minor impact on waste form development. These are the specifications (3.1 - 3.4) that identify materials that must not be present in the canistered wastes.

2.1.2 Waste Isolation Pilot Plant Waste Acceptance Criteria for TRU

Waste acceptance criteria (WAC) have been developed for the defense TRU wastes to be disposed of at the Waste Isolation Pilot Plant (WIPP) (U.S. DOE 1989). These acceptance criteria cover both contact-handled and remote-handled TRU wastes. A total of 19 acceptance criteria are identified; see Table 2.2. They include acceptance criteria that deal with the container, the radionuclides contained in the waste, the waste matrix itself, surface contamination and documentation.

None of the WIPP-WAC will have a major impact on waste form development. However, certain of the waste matrix-related criteria will have a minor impact on waste form development. These are criteria (similar to those for HLW) that identify materials such as liquids, pyrophorics, and explosives that must not be present in the canistered wastes.

Certain of the radionuclide content-related criteria might restrict the amount of waste contained in a waste form, depending on the amounts and specific mixture of radionuclides present in the waste. These are the criteria dealing with specific activity, surface dose rate, and activity density. However, these criteria will not be considered during waste form development activities unless it is determined that waste forms containing TRU will likely be disposed of at the WIPP, and some or all of the wastes to be immobilized would cause these criteria to be violated unless waste loading were restricted.

TABLE 2.2. Waste Isolation Pilot Plant Waste Acceptance Criteria

- 1.0 CONTAINER CRITERIA
 - 1.1 Waste Container Types
 - 1.2 Waste Container Size
 - 1.3 Waste Container Handling
 - 1.4 Waste Container Weight
 - 1.5 Labeling

- 2.0 RADIONUCLIDE CONTENT-RELATED CRITERIA
 - 2.1 Specific Activity of Waste
 - 2.2 Nuclear Criticality
 - 2.3 Pu-239 Equivalent Activity
 - 2.4 Surface Dose Rate
 - 2.5 Thermal Power
 - 2.6 Activity Density

- 3.0 WASTE MATRIX-RELATED CRITERIA
 - 3.1 Gas Generation
 - 3.2 Immobilization
 - 3.3 Liquid Wastes
 - 3.4 Pyrophoric Materials
 - 3.5 Explosives and Compressed Gases
 - 3.6 Radioactive Mixed Waste

- 4.0 ADDITIONAL CRITERIA
 - 4.1 Surface Contamination
 - 4.2 Data Package

2.1.3 Acceptance Criteria to be Used During HLW/TRU Waste Form Development

Based on the above assessments of the HLW acceptance specifications and the WIPP-WAC, a limited number of criteria need to be considered during the development of waste forms for the HLW/TRU fraction of retrieved SST wastes. First, the waste forms must not contain certain materials such as free liquids, gases, organics, explosives, pyrophorics and combustibles. Second, a minimum chemical durability must be achieved. This durability is based on the performance in the MCC-1 and PCT leach tests. Third, the waste forms must be stable under anticipated storage conditions at the producer's facility.

2.2 CRITERIA FOR LOW-LEVEL WASTE FORMS

Single-shell tank wastes will be managed under the Resource Conservation and Recovery Act (RCRA) (Keller et al. 1989). For the purpose of this work it

is assumed that the LLW fraction of any retrieved SST wastes will be immobilized and disposed of at Hanford. The portions of RCRA that are applicable to waste form development are contained in 40 CFR Part 261: Identification and Listing of Hazardous Wastes, Subpart C - Characteristics of Hazardous Waste. As described in Subpart C, a material is considered to be hazardous if it exhibits the characteristics of ignitability, corrosivity, or reactivity. Such materials will not be considered for the immobilization of SST LLW. A waste may also be hazardous based on the application of the Toxicity Characteristic Leaching Procedure (TCLP). If the releases of certain species (including heavy metals, organics, etc) are greater than specified limits, the waste is considered to be hazardous.

Regulatory criteria derived from 10 CFR 61.56 "Waste Characteristics" will also apply to the immobilized SST LLW. These criteria are intended to ensure the stability of the waste forms. The waste forms must not exhibit any of the criteria listed in 10 CFR 61.56(a) (pyrophoric, explosive, reactive with water). As previously stated, such materials will not be considered for the immobilization of SST LLW. However, candidate waste forms will need to be tested to ensure that they exhibit an unconfined compressive strength of >50 psi using ASTM Test # C039 (2-inch-diameter, 4-inch-long cylinder). Alternate tests such as ASTM Test # C109-80 may be substituted if the acceptance criterion is adjusted appropriately.

An additional criterion that is imposed on grouted DST LLW (and is assumed to apply to candidates for SST LLW immobilization as well) is related to the Hanford site-specific performance assessment. An ANS 16.1 Leachability Index of ≥ 7 is required for the analytes Tc-99, I-129, U, total nitrogen ($\text{NO}_2^- + \text{NO}_3^-$), Se-79 and C-14.

2.2.1 Acceptance Criteria to be Used During LLW Form Development

Waste forms to be considered for the immobilization of SST LLW must not exhibit the characteristics of ignitability, corrosivity, or reactivity. Additional criteria to be considered during the development and evaluation of candidate waste forms for the immobilization of SST LLW will be the ability to

1) pass the TCLP, 2) exhibit an ANS 16.1 Leachability Index of ≥ 7 for the specified analytes, and 3) exhibit an unconfined compressive strength of >50 psi.

3.0 REFERENCE FEED COMPOSITION

Reference feed streams are required to provide a basis for the necessary development work that is part of evaluating the acceptability of the various waste forms. This section reviews recent considerations with respect to SST waste fraction compositions, proposes three scenarios that refine the approach to estimating feed stream compositions, and identifies tank groups that contain HLW/TRU waste fractions applicable to immobilization in borosilicate glass and groups that would require enhanced chemical partitioning, selective blending, and/or alternative waste form types. For this study the LLW fraction composition is considered to be primarily sodium nitrate; however, the impact of chemical partitioning and blending operations on LLW reference feed composition should be considered in the future.

3.1 BACKGROUND

The acceptability of an SST HLW/TRU waste fraction as feed for vitrification in a borosilicate matrix was addressed in prior PNL studies. These studies evaluated the compatibility of SST waste with borosilicate glass based on several composite compositions, including 1) the average of tank farm compositions based on the TRAC inventory, 2) an average for each of the four tanks farms for which samples have been analyzed, 3) a composite of the TRAC and measured values, 4) the Hanford Defense Waste Environmental Impact Statement (U.S. DOE 1987), and 5) other documented sources. It was concluded that the most significant concerns were phosphate, chromium, and bismuth loadings.

3.2 SCENARIOS FOR REFERENCE FEED COMPOSITION DEVELOPMENT

For this study, three scenarios focusing on borosilicate (BS) glass feed stream acceptance criteria and regulatory issues were developed to bound the potential reference feed compositions for waste form development. The focus on process criteria and regulatory issues is meant to provide more realistic

waste compositions for the HLW/TRU waste form development than does a composite feed representing blending of all the SSTs. The three scenarios are outlined below.

- Scenario a
 - consider all SSTs
 - group tanks by waste composition per BS feed stream acceptance criteria
 - treat waste per WHC option 3A (Boomer et al. 1990)
 - develop glass, alternative HLW/TRU forms and packages and/or identify potential chemical partitioning needs based on the blending of the largest fraction or largest problem fraction
- Scenario b
 - consider only "worst case" tanks as source of waste for retrieval
 - group tanks to be retrieved by waste composition per BS feed stream acceptance criteria
 - treat waste per WHC option 3A
 - develop glass and alternative HLW/TRU forms and packages and/or identify potential chemical partitioning needs based on blending of the largest fraction or largest problem fraction
- Scenario c
 - consider only "worst case" tanks as source of waste for retrieval
 - treat waste using enhanced separation technology (minimize inerts in HLW/TRU fraction)
 - develop glass and alternative HLW/TRU forms for "clean" HLW/TRU waste.

As prescribed by the three scenarios outlined above, the SSTs were grouped by database sorting of the TRAC inventory data (Jungfleisch 1984). The categorization was done for two data sets: 1) all of the SSTs and 2) SSTs whose estimated (TRAC) contents are in combinations that may preclude in-place

stabilization based on 10 CFR 61 limits for long- and short-lived radionuclides and Washington Department of Ecology (WDE) TEC (toxic chemicals) calculation limits. In addition, the selected retriever data set sorting criteria addressed the constituent constraints identified for the proposed vitrification process and BS glass formulation. Tanks waste which satisfied the BS concentration envelopes were identified. Those tanks excluded from this regime were considered as candidates for an alternative glass formulation, lead-iron phosphate (LIP), and/or additional chemical partitioning efforts.

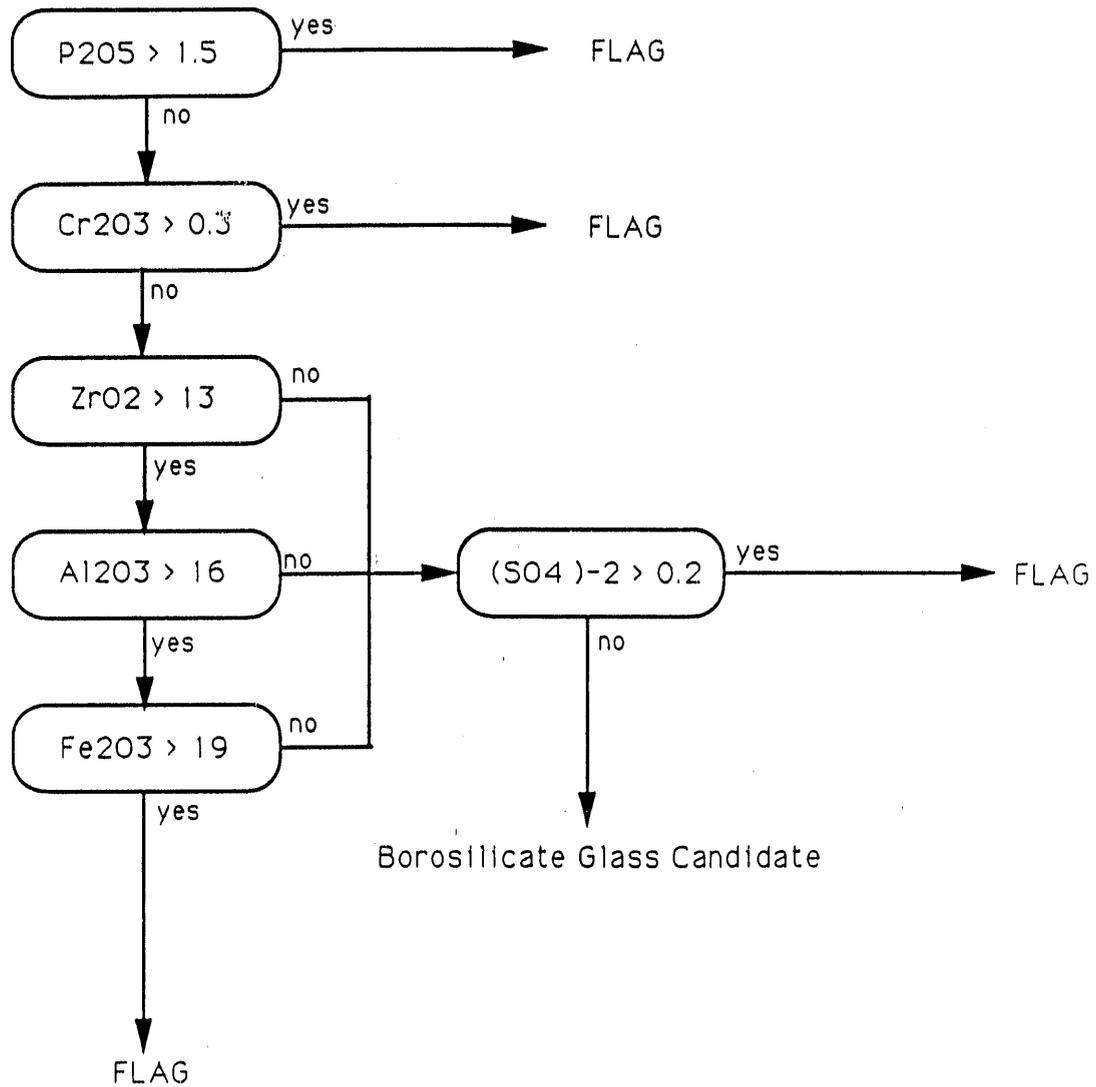
The composition of each tank group was averaged (representing blending) and subjected to a baseline chemical partitioning scenario, WHC Option 3A. The process steps for this scenario are described by Boomer et al. (1990) and summarized below.

- step 1 - sludge wash
- step 2 - >99% cesium removal by ion-exchange
- step 3 - nitric/oxalic acid dissolution of remaining solids
- step 4 - >99% transuranic removal by the TRUEX Process
- step 5 - >99% strontium removal by the SREX process
- step 6 - 25% technetium removal by ion-exchange from the uranium purification process step.

A second partitioning option will establish a HLW/TRU feed which is relatively free of inert materials. Inert materials refer to those constituents which are not classified as HLW or TRU waste. Such a feed might be provided via the "molecular recognition separation technology." Ongoing PNL studies to evaluate the volume and feed stream composition resulting from this technology will be referenced when available.

3.3 GLASS SELECTION CRITERIA FOR TANK SORT

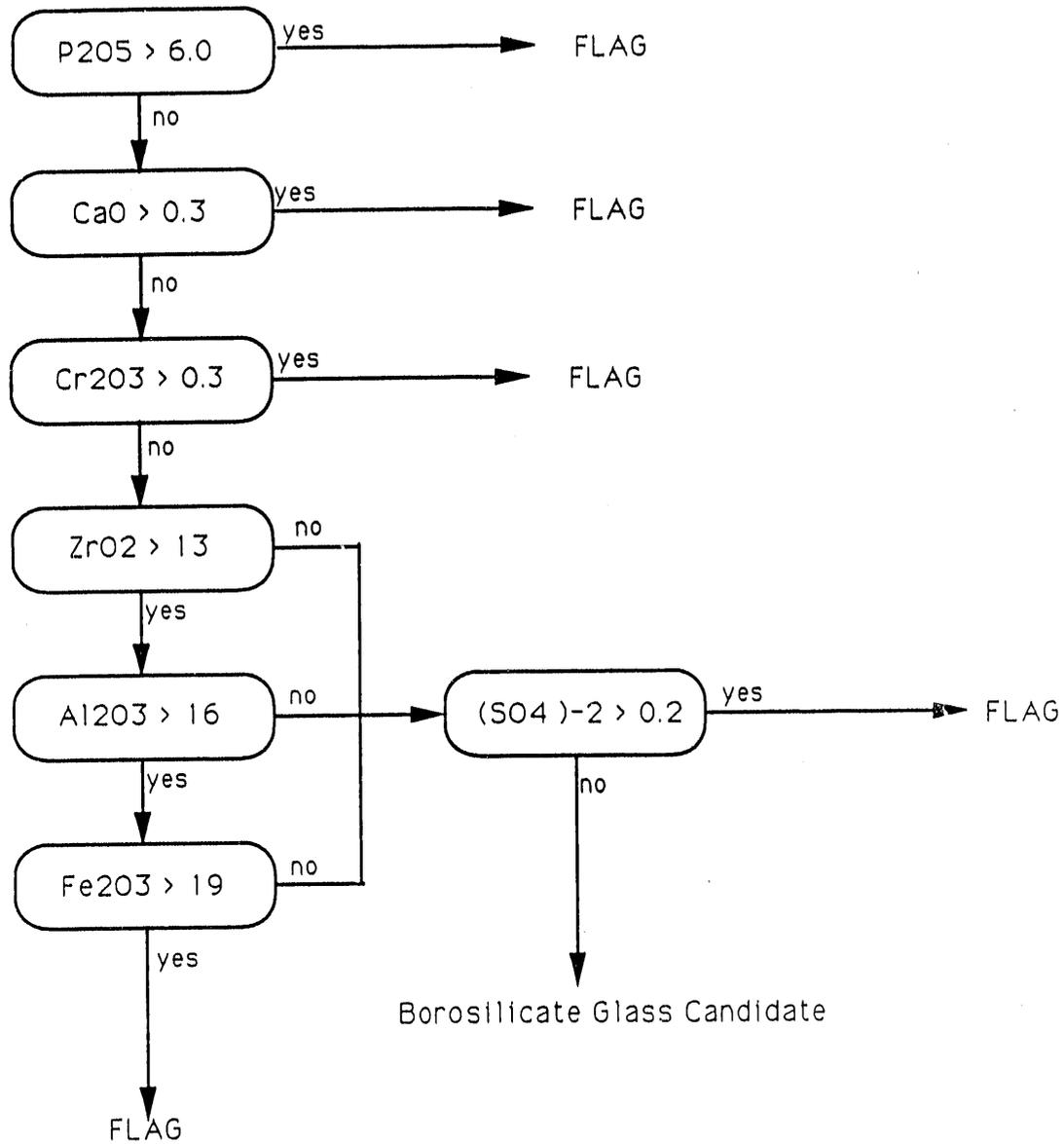
Two flowsheets were developed for sorting the SSTs (Figures 3.1 and 3.2). These sorts were designed to compare tank compositions based on TRAC inventory with existing criteria for producing an acceptable borosilicate glass. The two flowsheets differ in the maximum prescribed phosphate level



Notes

1. FLAG indicates individual tank waste concentration outside borosilicate glass concentration envelope (assumes no pretreatment); potential lead-iron phosphate glass feed candidate.
2. Assumed glass loading is 25 wt% waste oxide and 75 wt% frit.
3. Concentration limits are expressed in mole% in glass. Feed values would be four times higher.
4. Stated upper limits for elements in glass per Kalla 1991.

FIGURE 3.1. Flowsheet for Tank Sorting Based on Glass Selection Criteria: Nominal Phosphate Case



Notes

1. FLAG indicates individual tank waste concentration outside borosilicate glass concentration envelope (assumes no pretreatment); potential lead-iron phosphate glass feed candidate.
2. Assumed glass loading is 25 wt% waste oxide and 75 wt% frit.
3. Concentration limits are expressed in mole% in glass. Feed values would be four times higher.
4. Stated upper limits for elements in glass per Kalla 1991, Brouns 1986, and Jantzen 1986

FIGURE 3.2. Flowsheet for Tank Sorting Based on Glass Selection Criteria: High Phosphate Case

and consequential restriction on calcium concentration.^(a) Compositional constraints for borosilicate glass are defined in the Hanford Waste Vitrification Plant technical data package (Kalia 1991). Those SST constituents considered most sensitive and selected for the sort were phosphate, chromium, sulfur and combined zirconium, aluminum, and iron.

3.4 TANK SORT RESULTS

Reference feed stream compositions have been defined using the following approaches:

1. Consider the case in which wastes from all of the SSTs are blended together. This approach is considered a first approximation to defining the reference feed stream composition. The approach assumes that the regulatory environment will require all tanks to be retrieved and that technology will be available to accommodate blending of all waste during retrieval and partitioning stages. The assumption of large blending efforts also introduces the risk of artificially diluting components to which the vitrification is sensitive.
2. To the opposite extreme, comparison of individual tanks' waste composition with acceptable feed stream compositional ranges might be considered. This method would identify "worst-case" composition limits. However, these limits may be artificially high, as blending waste could dilute these impacts.
3. In between these two extremes lies an approach in which potential retrievers are identified based on regulatory guidelines and the potential for selective blending is evaluated. In addition, chemical partitioning is considered, as these processes may significantly impact the composition of the feed stream.

The reference feed development for this study was conducted per approach 3 above. The general logic was as follows:

- Tanks which on an individual basis contain constituents at a level unacceptable or not well defined for borosilicate glass were identified from both the total SST data set and from a data set of potential retrievers.

(a) High phosphate and calcium concentration can lead to a refractory calcium-rare earth-phosphate phase which has been shown to reduce processing rates (Brouns 1986).

- For the selected retriever data set, average concentrations for the "unacceptable" and borosilicate glass candidate tank groups were estimated based on no pretreatment, sludge wash, and TRUEX partitioning steps.

This approach tracked the constituents throughout the baseline chemical partitioning technology and provided worst-case needs for either enhanced chemical partitioning, glass concentration range expansion, blending strategies and/or alternative waste forms.

The results of the tank sort are presented by 1) identification of tanks categorized by sort groups and selected retrievers within each group (Table 3.1), and 2) a list of waste volumes for each tank group (Table 3.2). Tables 3.3, 3.4, and 3.5 list the chemical components of HLW/TRU feed streams as a function of the baseline chemical partitioning efforts applied to selected retrievers: no pretreatment, sludge wash, and sludge wash plus TRUEX, respectively. It was assumed that a minimal change in composition would result from downstream strontium, cesium and/or technetium partitioning. The six feed streams defined in these tables are averages for all the SSTs, the potential retrievers, selected retriever tanks whose waste is compatible with borosilicate glass, and selected retriever tanks whose waste is incompatible with borosilicate glass due to excessive levels of phosphate, chromium, or sulfur. Table 3.6 lists those waste constituents exceeding the upper limit for BS glass feed stream as a function of tank grouping and partitioning steps. If all potential retrievers could be blended and processed through the baseline pretreatment option, the borosilicate glass formulation would be acceptable if the concentration ranges for aluminum and silica could be accommodated via adjustment in frit composition. The feasibility of blending all potential retrievers (103 tanks, 39,000 kgal) requires further evaluation. Sorting of the tanks by sensitive elements identifies feed streams for selective chemical partitioning, selective blending and/or alternative HLW/TRU waste forms.

The waste containing unacceptable phosphate and chromium levels [4500 kgal (13 tanks) and 5400 kgal (15 tanks), respectively] remains so even

TABLE 3.1. Tank Groups Selected by Borosilicate Glass Process Criteria and Preliminary Regulatory Guidelines for Retrieval Criteria

Sort Groups ^(a)					
$P_2O_5 > 1.5$	$Cr_2O_3 > 0.3$	$SO_3 > 0.3$	Borosilicate Glass Candidates		
B-104 ^(b)	AX-101 ^(b)	A-102 ^(b)	A-101 ^(b)	C-104 ^(b)	A-105
B-105 ^(b)	AX-102 ^(b)	A-104 ^(b)	A-103 ^(b)	C-105 ^(b)	B-201
B-106 ^(b,c)	AX-104 ^(b)	AX-103	A-106 ^(b)	C-106 ^(b)	B-203
B-109 ^(c)	S-101 ^(b)	B-101 ^(b)	B-107 ^(b)	C-107 ^(b)	B-204
B-110 ^(b)	S-104 ^(b)	B-102 ^(b)	B-108 ^(b)	C-108 ^(b)	C-109
BX-112 ^(b,c)	S-107 ^(b)	B-103 ^(b)	B-112 ^(b)	C-111 ^(b,d)	C-111
C-110 ^(b,c)	S-110 ^(b)	B-111 ^(b)	B-202 ^(b)	C-112 ^(b,d)	C-112
T-105 ^(b)	SX-101 ^(b)	BX-104 ^(b)	BX-101 ^(b)	S-103 ^(b)	C-202
T-106 ^(b,c)	SX-104 ^(b)	BX-107	BX-102 ^(b)	S-109 ^(b)	C-203
T-107 ^(b,c)	SX-107 ^(b)	BX-109	BX-103 ^(b)	S-111	S-102
T-108	SX-108 ^(b)	BY-110 ^(b)	BX-105 ^(b)	S-112 ^(b)	S-105
T-110 ^(b)	SX-109 ^(b)	C-201	BX-106 ^(b)	SX-102 ^(b)	S-106
T-111 ^(b)	SX-111 ^(b)	C-204	BX-108 ^(b)	SX-103 ^(b)	S-108
T-112 ^(b)	SX-112 ^(b)	T-101 ^(b)	BX-110 ^(b)	SX-105 ^(b)	T-201
TX-113 ^(b)	U-110 ^(b)	T-102	BX-111 ^(b)	SX-106 ^(b)	T-202
TX-116 ^(c)		T-109	BY-101 ^(b)	SX-110 ^(b)	T-203
TX-117 ^(c)		TX-103	BY-102 ^(b)	SX-113 ^(b)	T-204
		TX-108 ^(b)	BY-103 ^(b)	SX-114 ^(b)	TX-102
		TX-109 ^(b)	BY-104 ^(b)	SX-115 ^(b)	TX-104
		TX-110 ^(b)	BY-105 ^(b)	T-103 ^(b)	TX-105
		TX-111	BY-106 ^(b)	T-104 ^(b)	TX-106
		TX-112	BY-107 ^(b)	TX-101 ^(b)	TX-107
		TX-114	BY-108 ^(b)	TY-101 ^(b)	TY-104
		TX-115	BY-109 ^(b)	TY-106 ^(b)	U-103
		TX-118 ^(b)	BY-111 ^(b)	U-101 ^(b)	U-104
		TY-102 ^(b)	B112 ^(b)	U-107 ^(b)	U-105
		TY-103 ^(b)	C-101 ^(b)	U-112 ^(b)	U-106
		TY-105	C-102 ^(b)	U-201 ^(b)	U-108
		U-102	C-103 ^(b)	U-202 ^(b)	U-109
				U-203 ^(b)	U-111
				U-204 ^(b)	

- (a) Refer to Figures 3.1 and 3.2. Assumes 25 wt% waste oxide loading of glass. Chemical partitioning not included.
- (b) Potential retriever.
- (c) Potential candidate for borosilicate glass if the phosphate loading upper limit was 6.0 mole% (in the glass).
- (d) Tank that contains calcium exceeding levels acceptable for the high phosphate loading flowsheet (Figure 3.2).

TABLE 3.2. Waste Volume Estimates for Tank Groups

	Sort Groups ^(a)			
	$P_2O_5 > 1.5$	$Cr_2O_3 > 0.3$	$SO_3 > 0.3$	Borosilicate Glass Candidates
<u>All SSTs (51,114 kgal)</u>				
number of tanks	17	15	29	88
volume, kgal	6,033	5,417	9,902	29,762
% total SSTs	12	11	19	58
<u>Potential retrievers (38,197 kgal)^(b)</u>				
number of tanks	13	15	15	59
volume, kgal	4,452	5,421	5,831	22,493
% total SSTs	9	11	11	45
% total retrievers	11	14	15	58

(a) Refer to Figures 3.1 and 3.2. Assumes 25 wt% waste oxide loading of glass.

(b) 25% of total SST waste volume (47 tanks) treated via in-place stabilization.

TABLE 3.3. Average Glass Feed Stream Composition with No Pretreatment, wt%

Oxide	All SSTs	Selective Retrieval ^(a)				Borosilicate Glass Candidates	Glass Limit
		All Retrievers	$P_2O_5 > 1.5$	$Cr_2O_3 > 0.3$	$SO_3 > 0.2$		
Na ₂ O	78.6	56.0	21.4	46.8	50.1	67.1	22.0
Al ₂ O ₃	5.6	17.1	0.7	15.8	7.8	23.2	26.0
SO ₃	1.5	1.8	1.4	0.2	5.5	1.5	2.0
P ₂ O ₅	7.3	8.3	20.3	0.1	3.1	1.6	4.0
SiO ₂	1.1	1.7	0.3	0.1	0.4	0.3	17.5
CeO ₂	0.3	<1	<1	<1	<1	<1	NA
Cr ₂ O ₃	0.2	1.6	0.1	8.3	<0.1	0.3	2.0
Fe ₂ O ₃	1.1	1.8	1.1	3.7	1.7	1.2	60.0
SrO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	NA
Bi ₂ O ₅	0.3	11.8	43.1	0.2	5.3	1.2	NA
CaO	0.2	0.1	<0.1	0.1	<0.1	0.1	20.0
MnO ₂	0.2	0.1	<0.1	0.3	<0.1	<0.1	20.0
NiO	0.3	0.1	<0.1	<0.1	<0.2	0.2	8.0
ZrO ₂	0.4	0.4	0.1	0.4	0.1	0.5	40.0
U ₃ O ₈	1.8	(b)	(b)	(b)	(b)	(b)	32.0

(a) Refer to Figures 3.1 and 3.2. Assumes 25 wt% waste oxide loading in glass.

(b) Not available through TRAC inventory. Assumed same as SST "master blend." Concentrations refer to wt% in the feed.

TABLE 3.4. Average Feed Stream Composition After Sludge Wash, wt%

Oxide	All SSTs	Selective Retrieval ^(a)			SO ₃ > 0.2	Borosilicate Glass Candidates	Glass Limit
		All Retrievers	P ₂ O ₅ > 1.5	Cr ₂ O ₃ > 0.3			
Na ₂ O	5.4	1.8	0.4	1.4	2.0	2.7	22.0
Al ₂ O ₃	29.2	40.2	0.9	34.2	23.7	69.9	26.0
SO ₃	0.2	0.1	0.1	<0.1	0.4 ^(b)	0.1	2.0
P ₂ O ₅	25.3	8.3	18.3	0.1	6.3	1.1	4.0
SiO ₂	7.3	5.3	0.6	0.2	1.6	4.1	17.5
CeO ₂	2.2	<1	<1	<1	<1	<1	NA
Cr ₂ O ₃	1.0	4.4	0.1	21.5	0.2	1.1	2.0
Fe ₂ O ₃	7.8	5.6	1.9	10.6	6.7	5.0	60.0
SrO	0.3	<0.1	<0.1	<0.1	0.1	0.1	NA
Bi ₂ O ₅	1.8	27.6	58.2	0.5	16.1	3.5	NA
CaO	1.3	0.2	<0.1	0.3	<0.1	0.3	20.0
MnO ₂	1.4	0.2	<0.1	0.8	0.1	0.1	20.0
NiO	1.6	0.3	<0.1	0.1	0.2	0.6	8.0
ZrO ₂	2.5	1.2	0.2	1.1	0.4	2.1	40.0
U ₃ O ₈	4.6	(c)	(c)	(c)	(c)	(c)	32.0

- (a) Refer to Figures 3.1 and 3.2. Assumes 25 wt% waste oxide loading in glass.
- (b) Note sulfur level reduced to acceptable levels via sludge washing step.
- (c) Not available through TRAC inventory. Assumed same as average for all SSTs.

after sludge washing and TRUEX processing. These tanks are candidates for enhanced partitioning steps, selective blending to dilute the concentrations to within acceptable BS limits, and/or alternative waste forms.

High-sulfate wastes are rendered acceptable for borosilicate glass after sludge washing. These wastes (6000 kgal, 15 tanks) would therefore contribute to the total amount of waste that could be immobilized via the borosilicate formulation after sludge wash or the WHC option 3A partitioning (23,000 kgal, 60 tanks).

The map in Figure 3.3 provides the location of potential retrievers by sort group and a preliminary indication of the logistics that could be considered for retrieval operations to support a sort/blending approach.

TABLE 3.5. Average Feed Stream Composition After Sludge Wash and TRUEX Pretreatment, wt%

Oxide	All SSTs	Selective Retrieval ^(a)			SO ₃ > 0.2	Borosilicate Glass Candidates	Glass Limit
		All Retrievers	P ₂ O ₅ > 1.5	Cr ₂ O ₃ > 0.3			
Na ₂ O	18.9	7.0	3.4	7.3	11.0	9.6	22.0
Al ₂ O ₃	32.5	49.1	2.5	56.2	39.2	76.0	26.0
SO ₂	0.1	<0.1	<0.1	<0.1	0.2 ^(b)	<0.1	2.0
P ₂ O ₅	9.0	3.4	16.5	0.1	3.5	1.1	4.0
SiO ₂	25.9	21.8	5.4	1.2	9.1	4.1	17.5
CeO ₂	<1	<1	<1	<1	<1	<1	NA
Cr ₂ O ₃	0.3	0.1	0.1	33.0	0.1	0.4	2.0
Fe ₂ O ₃	5.5	2.8	1.8	5.9	4.2	2.7	60.0
SrO	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	NA
Bi ₂ O ₃	0.6	11.3	52.6	0.3	8.9	1.3	NA
CaO	0.5	0.1	<0.1	0.2	<0.1	0.1	20.0
MnO ₂	0.5	0.1	<0.1	0.4	0.1	<0.1	20.0
NiO	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	8.0
ZrO ₂	0.9	0.5	0.2	0.6	0.2	0.8	40.0
U ₃ O ₈	4.3	(c)	(c)	(c)	(c)	(c)	32.0

- (a) Refer to Figures 3.1 and 3.2. Assumes 25 wt% waste oxide loading in glass.
 (b) Note sulfur level reduced to acceptable levels via sludge washing step.
 (c) Not available through TRAC inventory. Assumed same as average for all SSTs.

TABLE 3.6. SST Waste Constituents Exceeding the Upper Limit for Borosilicate Glass

Tank Group	Chemical Partitioning ^(a)		
	None	Sludge Wash (SW)	SW + TRUEX
SSTs	Na, P	Al, P	Al, P, Si
Retrievers	Na, S	Al, P, Cr	Al, Si
P ₂ O ₅ > 4.0	P	P	P
Cr ₂ O ₃ > 2.0	Na, Cr	Al, Cr	Al, Cr
SO ₃ > 2.0	Na, S	P	Al
glass candidates	Na	Al	Al

- (a) Based on average concentration (blends) of tanks in sort group from potential retriever data set (refer to Table 3.1).

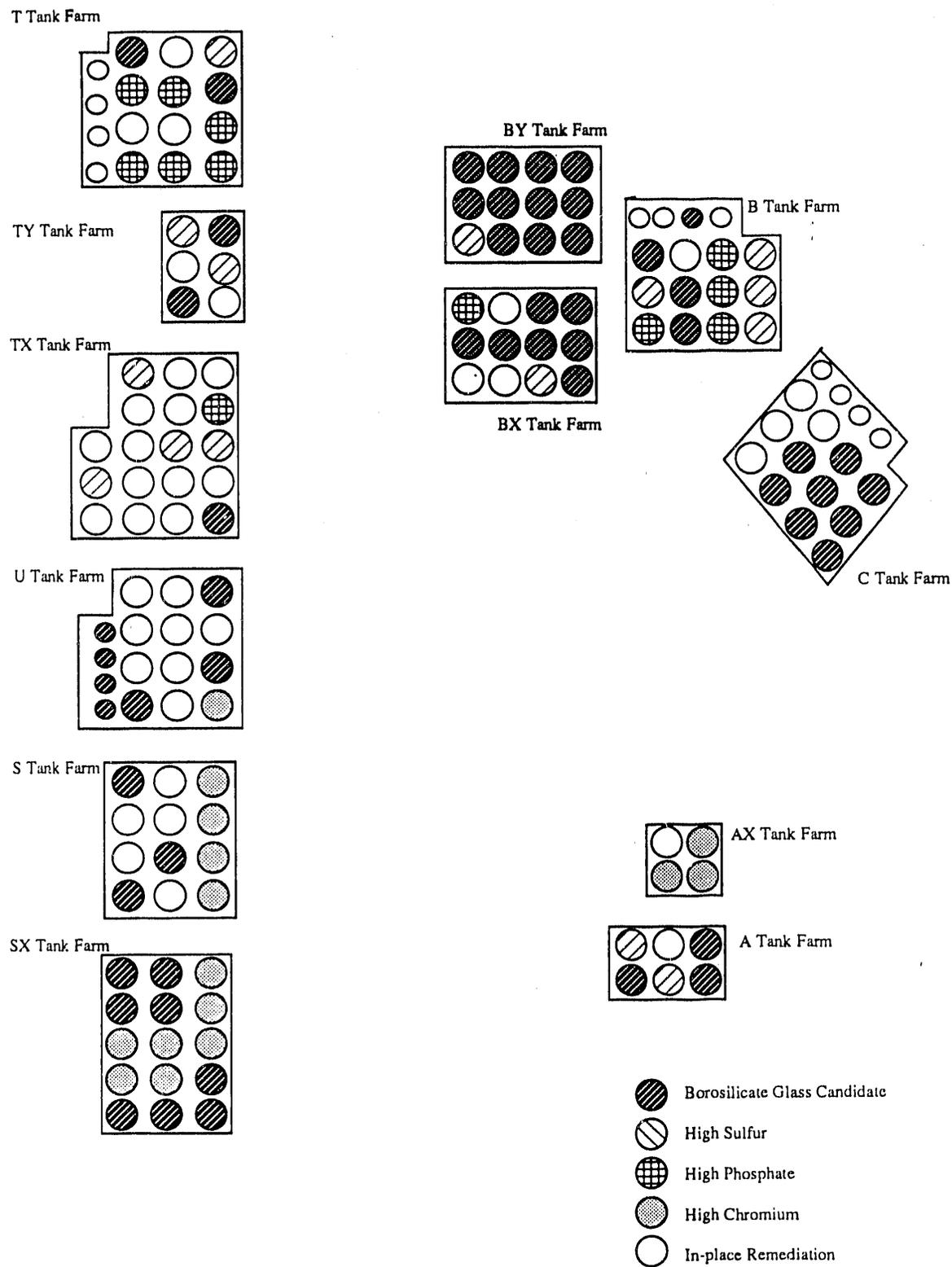


FIGURE 3.3. Location of Potential SST Retrievers by Groups

4.0 WASTE FORMS FOR IMMOBILIZATION OF HLW/TRU AND LLW

This section documents the literature review that was the basis for selecting the waste forms that will be the subject of initial laboratory scoping studies. The selection criteria for candidate waste forms include 1) the waste loading that could likely be achieved within the constraint of producing acceptable waste forms, 2) process flexibility (primarily compatibility with anticipated waste variability), 3) process complexity, and 4) state of development. Application of these criteria to specific waste forms is discussed below and recommendations for future development are offered.

The applicability of a particular waste form to SST waste immobilization is very dependent upon the composition and variability of the waste. At present, the compositions in the individual SSTs, how the wastes will be blended, and the partitioning processes all have yet to be defined in detail. Section 3.0 describes an approach to defining reference wastes which might be used to support waste form development activities in future years. As discussed in Section 2.0, it is assumed that the HLW/TRU waste form(s) will be disposed of offsite. Therefore, RCRA-related issues are not applicable. For the LLW fraction, passing the Toxicity Characteristic Leaching Procedure (TCLP) will be a major criterion.

4.1 BACKGROUND

The last 30 years have seen a major research and development effort to solidify radioactive wastes. First attempts to immobilize HLW in clays and minerals were made in the 1950s (Ginell 1952; Hatch 1953; Ginell et al. 1954; Warde and McVay 1957). The first reports of the preparation of nuclear waste glass (NWG) and synthetic micas were made in 1958 (Bonniaud et al. 1958).

Borosilicate (BS) glasses have become generally accepted for HLW vitrification (Jantzen 1986) because of their satisfactory processability, good durability, and ability to incorporate a wide variety of chemical components in large concentrations. The application of borosilicate glass and a potential alternative formulation, lead-iron phosphate, to retrieved SST HLW/TRU fraction is discussed in Section 4.2. During the development of borosilicate

glass as an HLW form, several alternative materials were studied, some of them quite extensively (Lutze and Ewing 1988). Alternatives to vitrification of the retrieved HLW/TRU fraction are discussed in Section 4.3.

Following pretreatment to partition the HLW and LLW fractions of the retrieved SST waste, the LLW fraction will constitute the major part of the waste. Grout, a portland cement-based waste form, is being used to immobilize the LLW fraction from DSTs at Hanford, and also the LLW fractions at Savannah River and West Valley. Grout may also be a satisfactory waste form for the LLW fraction from SSTs. However, because SST LLW is more voluminous, and more heterogeneous, than the other wastes for which grout is being utilized, and because SST LLW immobilization will not begin for approximately 20 years, an investigation will be conducted to determine if there are alternative waste forms that should be considered. Alternative waste forms for SST LLW are discussed in Section 4.4.

4.2 VITRIFICATION OF HLW/TRU

4.2.1 Factors to Be Considered in Selection of Potential Glass Waste Forms

Glasses developed for waste vitrification must meet rigorous chemical and physical requirements. Such glasses must possess: 1) acceptable processing properties (viscosity, electrical conductivity, liquidus temperature, rate of crystallization during cooling, and absence of volatilization of the melt components); 2) acceptable resistance to leaching in aqueous environments; 3) the highest possible waste loading; 4) relative ease of manufacture in a remotely controlled facility; and 5) an absence of degradation from self-irradiation (Lutze and Schubert 1989).

An important factor that was considered in the selection of potential glass waste forms was compatibility with the Hanford Waste Vitrification Project (HWVP). Baseline physical properties for HWVP glass are listed in Table 4.1. In addition to the listed properties, phase separation during vitrification (e.g., of sulfate salts) must be avoided, as it can lead to decreased melter lifetime, production rates, and durability.

TABLE 4.1. Baseline Physical Property Requirements for HWVP
(Goles and Nakaoka 1990)

<u>Property</u>	<u>Limit</u>
Viscosity	100 Poise between 1070 - 1150°C
Electrical Conductivity	0.18 to 0.5 (ohm-cm) ⁻¹ at 1150°C
Waste Loading	25 wt% waste oxide
Melting Temperature	<1200°C ^(a)
Durability	<1 g/m ² -day ^(b)

(a) Above 1200°C, volatilization of radioactive and chemical components such as cesium, mercury, ruthenium, technetium, selenium, sulfur and fluorine is nearly quantitative.

(b) Value corresponds to a 28-day MCC-1 test at 90°C in deionized water.

4.2.2 Potential Glass Waste Form Candidates

Five potential glass families have been considered for vitrification of retrieved SST HLW/TRU waste. Halide and chalcogenide (e.g., copper-tellurium arsenic-sulfide) glasses were dismissed due to the relatively high volatility of melt components. Organic (and acetate) glasses were dismissed on the basis of low durability. Borosilicate (BS) and lead-iron phosphate (LIP) remain as the two viable candidates. The pertinent thermal, physical, and chemical properties of BS and LIP nuclear waste glass are summarized in Table 4.2. The BS and LIP formulations, as they apply to the retrieved SST HLW/TRU waste fraction, are discussed below.

4.2.2.1 Borosilicate Glass

Borosilicate glass has been chosen as the waste form for the immobilization of HLW at Savannah River, Hanford, and West Valley. Apart from possessing excellent processing properties and durability, BS glasses have also been systematically studied over a wide range of compositions. Also, melters and other processing facilities have been designed and tested for BS glass waste forms. Although BS glasses have been studied extensively, their limits for accommodation of some of the SST constituents (e.g., phosphate and bismuth) have not been determined.

TABLE 4.2. Summary of Thermal, Physical, and Chemical Properties of Borosilicate and Lead-Iron Phosphate Glasses Loaded with Simulated Defense Waste

<u>Property</u>	<u>Borosilicate</u>	<u>Lead-Iron Phosphate^(a)</u>
Glass melting temperature	1150°C	1050°C
Glass pouring temperature	1025°C	900°C
Glass density	2.7 ±0.2 g/cm ³ (25°C)	4.7 ±0.1 g/cm ³ (25°C)
Waste loading	0.76 g/cm ³ (25°C)	0.73 g/cm ³ (25°C)
Corrosion rate in water ^(b)	< 1 g/(m ² -d)	0.001 g/m ² -d ^(c)
Temperature of maximum rate of crystallization	650 ±25°C	680 ±25°C
Annealing temperature	500°C	470°C
Softening temperature	710°C	518°C
Thermal expansion	9.1 x 10 ⁻⁶ /°C (40-450°C)	11.0 x 10 ⁻⁶ /°C (40-450°C)
Heat capacity	0.24 cal/(g°C) (1100°C)	0.1-0.16 cal/(g°C) (50-350°C)
Thermal conductivity	0.012 W/(cm°C) (100°C)	0.006 ±0.001 W/(cm°C) (30-90°C)

(a) Sales and Boatner (1988).

(b) Refers to 28-day MCC-1 test at 90°C in deionized water.

(c) Durability observed for samples that were quenched from the melt temperature to prevent devitrification.

The waste loading of BS glasses is unlikely to be higher than 25-30 wt% (Mitchell and Nelson 1988). The waste loading that can be achieved will depend upon the composition of the waste to be immobilized.

The high concentration of phosphate in the SST waste is not compatible with BS glasses (Vogel 1971). An additional complication is the sensitivity to the content of calcium oxide and rare earth oxides (Brouns 1986). Depending upon the calcium concentrations, BS glasses may accommodate no more than 1 to 6 wt% P_2O_5 (Jantzen 1986) due to the formation of a calcium-rare earth-phosphate phase that is insoluble in the glass. Although a single glass containing 4.3 wt% of P_2O_5 and 0.25 wt% CaO was successfully processed in a pilot-scale melter, the waste loading of SST waste is likely to be limited by the phosphate concentration. The high phosphate loading may be better accommodated by LIP glasses; therefore, these are being considered as an alternative formulation.

4.2.2.2 Lead-Iron Phosphate Glasses

Whereas borosilicate glasses have been extensively studied as a form for HLW immobilization, the lead-iron phosphate glasses have received less attention. As iron and phosphorus are significant components of SST waste material, this ternary phosphate is a natural candidate for a nuclear waste glass.

Early studies on the application of phosphate glasses involved a process developed at Brookhaven National Laboratory (Tuthill et al. 1966) and applied at Pacific Northwest Laboratory (Barton 1965). Subsequently, it was found that the addition of iron oxide, while increasing the softening point by approximately 150°C, also increased the chemical durability of the glass (Sales and Boatner 1984a, 1984b). In fact, some lead-iron phosphate glasses have aqueous corrosion rates that are approximately 10^3 times lower than the BS nuclear waste glasses (Lutze and Schubert 1989).

Fabrication of durable LIP glasses, however, requires that they be cooled fairly rapidly from the melt temperature. If this is not done, these glasses have a tendency to devitrify. This devitrification results in a substantial degradation of their aqueous corrosion rates (Chick et al. 1986). Due to the need for rapid cooling, an alternative to the current process of casting large canisters would be required.

The waste loading of LIP glasses is typically 16 wt%. However, given the high density of these glasses (4.7 g/cm^3), this waste concentration gives

essentially the same waste-per-volume loading as the BS glasses. The compatibility of high aluminum, calcium, and silica concentrations in SST waste with the LIP formulation is uncertain. The effect of these constituents on waste glass loading and durability will be evaluated during the initial scoping studies.

4.2.3 Development Needs

The testing and development of borosilicate glass and lead-iron phosphate glass as media for the immobilizing SST HLW/TRU waste fraction will begin with development of reference formulations for each glass, followed by the scoping tests and composition variability study, after which time-temperature transition (TTT) diagrams and the effect of heat treatment on durability will be established. Eventually, radioactive glasses will be investigated. This program is similar to the DST waste glass development and will utilize DST results as far as practicable.

The main focus will be on the waste components, such as phosphorus and bismuth, that have not been addressed by the HWVP glass development program. Since the behavior of phosphates in BS glasses is affected by calcium and rare earth elements, attention will also be given to these components. In the development of the LIP glass, the SST waste components of primary interest will be the aluminum, calcium, and silicon. The detailed studies will use reference HLW/TRU compositions which will be continually refined as more reliable data become available.

In parallel with the glass development work described above, melting chemistry will also be addressed. Once reference glasses have been defined, melting chemistry studies will focus on determining the optimum form of the melter feed to allow smooth operation of the melter. One aspect of melting chemistry to be studied will be the form in which the glass former components are added to the feed (e.g., frit or as nitrates, carbonates, hydroxides, or formates). Other aspects of melting chemistry will also be addressed, such as the need for reducing agents.

4.3 ALTERNATIVES TO VITRIFICATION FOR IMMOBILIZATION OF HLW/TRU

4.3.1 Factors to Be Considered in Selection of Alternatives to Vitrification

In order to identify three waste form candidates for further evaluation, several assumptions were made; first, in order to be considered as an alternative to glass, a candidate waste form should be capable of being processed in a modified HWVP after its initial mission is complete. Second, the waste loading should be at least as high as current glass compositions. Finally, the form must meet durability requirements. Although combination of HLW and TRU fractions is not specifically addressed below, the nature of the viable processes is such that combination would not be precluded.

Processes considered as viable were regarded as capable of accommodating the SST waste composition variability.

4.3.2 Potential Waste Form Alternatives to Vitrification

This section addresses the alternatives to vitrification considered for the SST HLW/TRU fractions. The goal is to identify the strengths and weaknesses of each waste type, in order that future developmental work might better be defined. Alternatives considered to date are discussed below.

4.3.2.1 Synroc

This waste form was conceived in Australia (Ringwood 1980) and is based on the concept that crystalline titanates can provide a durable host phase to contain many of the radionuclides of most concern, and that other durable compounds can handle the rest. During research on the material, several different Synroc recipes were conceived to act as host phases to various high-level wastes. Synroc waste forms are among the most durable ever made, but are prepared by a complex route (hot pressing of a specially prepared fine powder) which is much different from glass melting.

Screening Assessment: Because Synroc is not a glass, most of the existing HWVP process equipment could be incompatible with this waste form. Although waste loadings can be higher than possible in borosilicate glasses,

long-term radiation damage, especially from alpha particles, is not nearly so well tolerated in any dense, crystalline solid as it is in glass. The above disadvantages were sufficient to reject Synroc as an option.

4.3.2.2 Tailored Ceramics

This waste form is based on the idea that radionuclides can be reacted with inert materials to form a series of durable crystalline phases (Harker and Flintoff 1984). The concept is much like Synroc except that a greater range of compounds would be involved. For best efficiency, the crystalline phases must be tailored to the specific waste stream, and the ability to do this was demonstrated several times during work on this option. The chemical variability in the Hanford SSTs would greatly complicate the tailoring process. Very high waste loadings (approximately 60 wt%) are possible using the tailored ceramics approach. Leaching performance is complex because of the assortment of crystalline phases, but appears to be at least equal to that of borosilicate glass.

Screening Assessment: As with Synroc, long-term radiation damage by alpha particles and recoils is an open question at present. The processing method involves preparation of powders containing the wastes and subsequent densification by hot isostatic pressing, necessary to achieve a pore-free state. This processing scheme is unlikely to be accommodated within the HWVP without almost complete redesign, so this option was rejected.

4.3.2.3 Coated Waste Forms

If one is willing to accept lower overall waste loadings and substantially increased process complexity, several coatings exist which could enhance the leaching performance of either glass or crystalline waste forms. Foremost among these is graphite, which has the lowest reaction rate with water that has ever been measured (Gray 1980). Application of high-density graphite, however, requires temperatures high enough to cause the most volatile radionuclides such as cesium to migrate into the coating and thus degrade leaching performance.

Screening Assessment: Process complexity and loss in volume efficiency are disadvantages of coated forms, and a primary waste form which needs a

coating to meet durability requirements is unlikely to be given serious consideration. Coated particles were thus rejected.

4.3.2.4 Cement-Based Forms Such as FUETAP

Concrete which is Formed Under Elevated Temperature And Pressure has a potential to be very durable in an aqueous environment, and the process is extremely simple (Moore et al. 1977). In essence, portland cement is mixed with sand, flyash, and calcined waste, then hydrated at temperatures up to 200°C under an overpressure sufficient to prevent vaporization of the water. The radionuclides are either chemically combined with the various complex cement phases or are physically immobilized in a solid mass. Calcination of the waste stream before combination with cement would preclude most chemical interactions with the cement, making this waste form extremely flexible as regards waste stream variations.

Screening Assessment: Although this process would require somewhat different equipment than in the present HWVP, the equipment is much simpler than in any of the other processes considered above. Although not one of the two main choices, the FUETAP process will be retained as an additional option, and dropped if any flaws emerge which preclude its use. In addition to a simple application of the developed FUETAP technology, other variations on the concept are possible. For instance, the weak point of all cement-based waste forms is the porosity necessitated by the excess water used for mixing and placement of the material. There may be methods which would permit attainment of pore-free concrete, short of the hot-pressed concrete studied previously (Roy 1978). Hot pressing would sacrifice most of the fundamental simplicity of a cement-based process. Early in the planned work, a small effort will address whether pore-free concrete can be made by a simple process.

4.3.2.5 Glass-Calcine Composite Made by Warm-Pressing Glass and Calcine

This material has the advantage of not requiring dissolution of the HLW/TRU, assumed to be in the form of mixed oxides (calcine). The waste form is made by warm-pressing at a temperature dependent on the glass matrix composition, in a sealed canister which would be subsequently shipped to the HLW repository. According to work done in Germany (Galhert and Ondrack 1988), the

pressing temperature can be as much as 500°C lower than the melt-processing temperature of a typical glass. The process is thus relatively simple. Advantages include production of a crack-free monolith that is tougher than glass. Disadvantages include a durability that may be less than that of conventional HLW glass compositions, at comparable waste loadings.

Screening Assessment: Freed from the necessity to actually dissolve waste stream constituents, matrix glasses could be chosen with regard only for processing ease and durability. German studies showed that more durable matrix glasses of the general borosilicate type could be used, the main processing impact being a higher pressing temperature. It is also possible that LIP glass would be a good matrix, and if so could substantially lower processing temperatures. Glass development efforts would be well-rewarded if the same glass could be used for all of the HLW and TRU from all of the single-shell tanks. Also, a processing innovation originated by the Australian Synroc program may provide a more efficient way to make this kind of waste form. If a canister is provided with flutes along the cylindrical surfaces, it can compress like a bellows during pressing to accommodate shrinkage on densification. Since the fluted surface provides support in the radial direction of the canister, a relatively simple uniaxial press may be used, precluding any requirement for hot isostatic pressing. Use of this idea will be explored in early development and evaluation.

4.3.2.6 Glass-Ceramics Made by Controlled Devitrification of a Cast Melted Glass

Several compositions have been studied in Canada, Germany, and the United States (Hayward 1988; Guber et al. 1979; Rusin et al. 1980). These are true glass-ceramics, as the term is properly used to designate devitrified glasses. Since such waste forms are originally formed as glasses, it is fairly probable that the HWVP could be used as is, or after only slight modifications, to produce the glass. The glasses are of different compositions than borosilicate types, so that precipitation of crystalline solids containing most of the radioactive material is encouraged. Another difference is that glasses are heat-treated after pouring into canisters in order to form many nuclei which are then grown into microcrystals. The resulting

crystalline phases are thermodynamically more stable, hence more durable than vitreous materials, and when made properly are incorporated in a glass which is itself nearly as durable as borosilicate waste glasses. The heat treatment varies with the composition but is no more than a few hours' duration and so does not constitute a significant change from normal operation. Moreover, the resulting devitrified solid is stronger and has a lower expansion rate than its vitreous predecessor, and so cracking of the glass during cooldown is less likely than with borosilicate compositions.

Screening Assessment: Leach testing has shown the resulting glass-ceramics to be at least as durable as borosilicate glasses (Hayward 1988). Disadvantages of producing glass-ceramics involve additional processing steps, although these are minor. Issues such as radiation damage effects have been addressed in the Canadian effort, and suggest no undesirable results, particularly as long as the crystals are kept small, as is always the aim. One question not addressed to date is how the controlled-temperature heat treatment is to be accomplished in the case of a waste form producing substantial amounts of heat; this should be addressed early in feasibility studies of this option. Variability of the Hanford waste stream is another issue requiring early resolution, because the glass must be designed to provide the other constituents to form durable crystal phases during devitrification.

4.3.2.7 Summary Evaluation of Candidate Alternatives to Glass for SST HLW/TRU

The desirability that single-shell tank HLW/TRU wastes be processed in the HWVP narrows the choices to either waste forms which are glass-based, such as glass-calcine composites or glass-ceramics, or which are comparatively simple and cheap, such as cementitious materials. Two distinctly different methods can be used to produce the glass-based materials, but both are quite compatible with the HWVP as envisioned, with modifications. The present state of development of the candidate waste forms is summarized below, as are the issues to be addressed by the planned work. The advantages and disadvantages of the candidate alternatives to glass are summarized in Table 4.3.

TABLE 4.3. Advantages and Disadvantages of Candidate Alternatives to Glass for Immobilization of HLW/TRU

Advantages	Disadvantages
<u>Glass-Calcine Composites</u>	
Glass composition almost independent of waste composition	Batch process
Process produces crack-free monolith	HLW must be calcined, probably in separate operation
	Largest demonstrated scale approx. 12" diameter
<u>Devitrified Glass-Ceramics</u>	
Utilizes HWVP hardware most extensively, only requiring addition of a heat treatment furnace	Composition must be carefully designed to obtain desired crystalline phases
Many HLW elements partitioned into discontinuous phases separated by durable glass which acts as a metering device to impede release	Probably much less tolerant of waste stream composition variations than other two alternatives
Heat treatment simple in principle, but see Disadvantage caveat	Heat-producing HLW may dictate small canister sizes in order to do heat treatment
Crystalline waste materials thermodynamically more stable than glasses	Crystals possibly more subject to radiation damage
Crack-free monoliths are realistically attainable	Possible uncontrolled devitrification any time melter is cooled from glass melting temperature
Devitrification products common in many igneous rocks have demonstrated durability over geologic time periods	Pouring rate of glass must be slow enough to prevent premature devitrification
Generally higher glass melt temperature, 1400-1500°C; some compositions limited to lower waste loadings, approximately 15 wt%	
<u>Cementitious Waste Forms</u>	
Cheapest process	Batch process
Very low-temperature process	HLW would have to be calcined in separate process
Cement phases inherently stable in water, waste only leachable by pore access	Good mixing required, minimum-water option might require good mixing of dry powders

4.3.3 Initial Study of Selected HLW/TRU Waste Forms

For both of the glass-based forms, release rate of radionuclides is expected to be a function of waste loading. Data on leach rate as a function of waste loading is needed, and will permit choice of the highest waste loading consistent with current durability requirements. Second, heat-generation rates for the SST wastes should be used to calculate the maximum canister size consistent with temperature control during devitrification. The ability of devitrified glass-ceramics to tolerate Hanford waste-stream variability should be addressed soon, because the viability of that concept depends largely on this factor. In regard to the FUETAP option, past data will be examined to evaluate the viability of the concept, paying particular attention to processing parameters and effect of waste loading on durability. A brief description of the initial developmental work to be performed for each of the candidate waste forms is given below.

4.3.3.1 Warm-Pressed Glass-Ceramics

These waste forms will be fabricated while evaluating the pleated-canister, using a borosilicate glass matrix phase and varying the waste calcine loading over a credible range. Leach testing will then be used to define the waste loading limit.

4.3.3.2 Devitrified Glass-Ceramics

The fabrication of these waste forms will require some experience and expertise in their design. It is anticipated that an expert in the field will be consulted. This individual will be supplied information on waste compositions and will recommend trial glass compositions that will be fabricated into evaluation samples. Leaching studies will focus on defining waste loading limits.

4.3.3.3 FUETAP

Two approaches will be taken: 1) fabrication of evaluation specimens by the published FUETAP methods and 2) working to decrease the water in the concrete to reduce its permeability. Both of these approaches will seek to produce specimens containing a wide range of waste compositions and loadings, which can then be evaluated by standard leach testing.

4.4 WASTE FORMS FOR IMMOBILIZATION OF LLW

4.4.1 Factors to Be Considered in Selection of Potential Waste Forms for LLW

Grout can almost certainly be used for the immobilization of SST LLW as well as DST LLW. However, because grout has some drawbacks (e.g., relatively high leachability and low waste loading) and because there is time before a decision on the technology has to be made, other potential methods of immobilizing SST LLW will be examined.

The fundamental problem for waste forms used to immobilize SST LLW is the aqueous solubility of the principal waste constituent, NaNO_3 , and its radiolytic product, NaNO_2 . Because the water-soluble NaNO_3 and NaNO_2 are present in such large quantities in SST LLW, their leach behavior tends to dominate and control the leach behavior of other important waste constituents, such as the radionuclides Se-79, Tc-99, and I-129. In other words, because their properties are so dominant, if NaNO_3 and NaNO_2 can be retained in the waste form it is very probable that all other waste constituents will also be retained. The $\text{NaNO}_3^{(a)}$ in the waste must be shielded from contact with the ground water, whether by the use of external barriers as is done for the DST LLW in grout, or by waste form properties that prevent water ingress. Thus, the optimum waste form should be as nonporous and hydrophobic as possible. As described in Section 4.4.2, there are potential waste forms that have these characteristics to a perhaps sufficient degree.

An attractive alternative approach for waste form development is to remove or destroy the NaNO_3 so that there will be no water soluble NaNO_3 in the SST LLW disposal system. Partitioning of NaNO_3 from SST LLW is being considered in another task and is outside the scope of this report. However, destruction of NaNO_3 can be done during the immobilization processing and will be considered as a major option in this report. Destruction of the nitrate in the SST LLW fractions has significant potential benefits and merits a thorough evaluation:

(a) For simplicity, in the remainder of this discussion the term NaNO_3 will be understood to also include any NaNO_2 that is present. This is legitimate because in the context of waste form behavior, NaNO_2 and NaNO_3 are chemically analogous.

- Nitrate is the major RCRA hazardous chemical in the SST LLW fractions. Destruction of the nitrate (conversion to elemental nitrogen) would eliminate this hazard completely.
- Thermal nitrate destruction would also ensure the decomposition of any organics in the wastes.
- The volume of immobilized SST LLW could be reduced significantly. The Na_2O remaining after nitrate destruction can be stabilized readily, either in a glass matrix or by "mineralization," e.g., converting to an aluminosilicate or other crystalline form. But even when this is done, the higher waste loading that can be achieved without the nitrate should result in a lower volume. Certainly glass could reduce the volume, possibly by as much as a factor of four.
- The quality of the waste form, i.e., its ability to retain radionuclides and toxic chemicals, would be improved. The quality of the baseline grout is "acceptable" in the context of the total disposal system, but only when the system includes a series of barriers emplaced in and around the grout vaults. The improved properties of non-nitrate-containing waste forms should reduce the need for barriers in the disposal system.

Strictly from the standpoint of waste form quality, which is the thrust of this report, nitrate destruction appears to offer the potential for significant advantage. Ultimately, however, a detailed systems engineering analysis will be required to assess the relative merits of nitrate destruction. Data on waste form quality will be only one of many considerations that are factored into that analysis. The potential advantages of nitrate destruction will have to be balanced against potential disadvantages that include added complexity and extra steps in the disposal system; increased energy requirements for a high-temperature process; and the need for a complicated, possibly very large, off-gas system.

Several processes for nitrate destruction are discussed below.

4.4.1.1 Destruction of Nitrates in LLW

Low-temperature NO_3 destruction techniques, such as microbial destruction, are deemed too slow and cumbersome (dilution to 200 ppm initial nitrate is required) to be applicable to the immense quantities of SST LLW that must be processed. Reactions with organic compounds (e.g., sugar denitration)

could perhaps also be considered after a thorough safety analysis, but these reactions are generally unsatisfactory in that they do not go to completion. All of the nitrate could not be destroyed.

The high temperatures of well-developed vitrification and calcination processes readily destroy NaNO_3 . Additives are required, however, in order for the processes to operate properly. In vitrification with a joule-heated melter, the additives are required to make glass (the sodium concentration must be low enough to maintain proper resistance in the melt). In calcination, the additives must act as both diluents and sodium mineralizers. Diluents are needed to prevent molten NaNO_3 from interfering with proper calciner operation; mineralizers are needed to maintain Na_2O in a stable form in the calcine after NaNO_3 decomposition.

To date, most of the waste vitrification and calcination experience is in the processing of HLW. There, much of the NO_x produced from nitrate destruction is collected in the condensate and off-gas scrubber solution to form an LLW stream. However, catalytic NO_x destruction techniques are available using reactions with natural gas or ammonia (Adlhart et al. 1971):



When using natural gas the first reaction is quite easily accomplished by addition of fuel in excess of the stoichiometric amount. However, to obtain complete destruction of nitrogen oxides, sufficient fuel must be added

to react with all of the oxygen; i.e., the second reaction must proceed before the third. Ammonia, however, reacts primarily with the nitrogen oxides--the fourth and fifth reactions dominate over the sixth reaction--and only a slight excess of ammonia over the stoichiometric amount for the reaction with nitrogen oxides is required.

There are plans to destroy the residual NO_x in the off gas from the West Valley HLW vitrification process using a commercial catalyzed ammonia reaction process. The Waste Calcining Facility at INEL utilizes in-bed combustion and is operated in an oxygen-deficient manner to abate NO_x in the off gas. For LLW processing by vitrification or calcination, the off-gas treatment should be designed for maximum gaseous discharge of decontaminated water vapor and nitrogen and minimum generation of streams that have to be recycled.

4.4.1.2 Sodium Mineralization (Tailored Ceramic)/Clay Calcination

As described above, the nitrate destruction process must also contain provisions for tying up the Na_2O that remains after the NaNO_3 is destroyed. No special provisions are required. During vitrification, the Na_2O is incorporated in the glass matrix. Special provisions are required, however, if the nitrate is to be destroyed by calcination. At least two related sodium mineralization techniques can be considered for use with calcination: formation of tailored ceramics (tailored to tie up sodium) and reaction with clay to form compounds containing sodium.

In the conceptual tailored ceramic process, sodium would be incorporated into the crystalline structure of one or more compounds that are similar to naturally occurring minerals. The fact that the minerals survive in nature would give confidence that the sodium mineralized waste form should also be durable. There are several naturally occurring aluminosilicate minerals that have relatively high sodium contents and could potentially form the basis for a tailored ceramic waste form for SST LLW. For example, naturally occurring sodalite, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_24]\text{Cl}_2$, contains 24.8 wt% Na_2O ; nosean, $\text{Na}_8[\text{Al}_6\text{Si}_6\text{O}_24]\text{SO}_4$, contains 23.9 wt% Na_2O ; and nephelene, $\text{Na}_3(\text{Na},\text{K})[\text{Al}_4\text{Si}_4\text{O}_{16}]$, contains 17.2 wt% Na_2O (Deer et al. 1966). Various hydrothermal or sol gel techniques may be applicable to fabrication of the synthetic minerals. Conceptually, they could even be formed during the calcination step. The work of Bjorklund (1977) may

be cited as evidence for the feasibility of using fluidized-bed calcination for the calcination of NaNO_3 . Bjorklund was not attempting to maximize the concentration of NaNO_3 in the calciner feed solution nor the amount of sodium in the calcine, but he did demonstrate the calcination of waste containing up to 1M NaNO_3 using a bed of SiO_2 particles and obtained a waste loading of 10 to 15 wt% in the calcine. By tailoring the aluminum and silicon concentrations in the feed solution and the bed it may be possible to produce sodalite, nosean, nephelene, or other sodium minerals in a fluidized-bed calciner.

Another approach to mineralization of the Na_2O in denitrated LLW is to utilize various reactions with clay. A mixture of several sodium-containing reaction products may result. A conceptual process using clay reactions before and after calcination is described in Boomer et al. (1990).

From the foregoing, it can be concluded that there is a good probability that SST LLW can be converted to a sodium mineral(s) suitable for incorporation in any of several candidate waste form binder materials, or for consolidation without a binder, i.e., by hot pressing or hot isostatic pressing.

4.4.2 Potential Waste Forms for LLW

The purpose of the literature review that follows is to do a preliminary screening of waste forms. Those that survive the screening will become candidates for more detailed study, as described in Section 4.4.3. Reviews or meeting proceedings that were especially applicable for this literature review include Kibbey and Godbee (1980); Rockwell International (1980); Schulz et al. (1980); Treat et al. (1980); Neilson and Dole (1985); Jolley et al. (1986); Arnold et al. (1983); Roggenthen (1989); ANS (1984); ASTM (1990); and the proceedings of the various periodic nuclear-waste-oriented meetings, such as Scientific Basis for Nuclear Waste Management (annually), Waste Management (annually in Tucson, Arizona), Spectrum (biannually, sponsored by American Nuclear Society), Nuclear Waste Management (biannually, sponsored by American Ceramic Society), and Annual DOE LLW Management Conference (coordinated by EG&G, Idaho, 12th annual meeting being held in 1990). It should be noted that much of the LLW literature deals with reactor wastes (i.e., ion exchange resins and boric acid solutions) which are so different from SST LLW that the information is of little relevance.

The waste forms that have been utilized or at least proposed for various kinds of LLW are listed in Figure 4.1. Each of these waste forms is discussed briefly here and evaluated for its potential application to non-denitrated and denitrated SST LLW fractions.

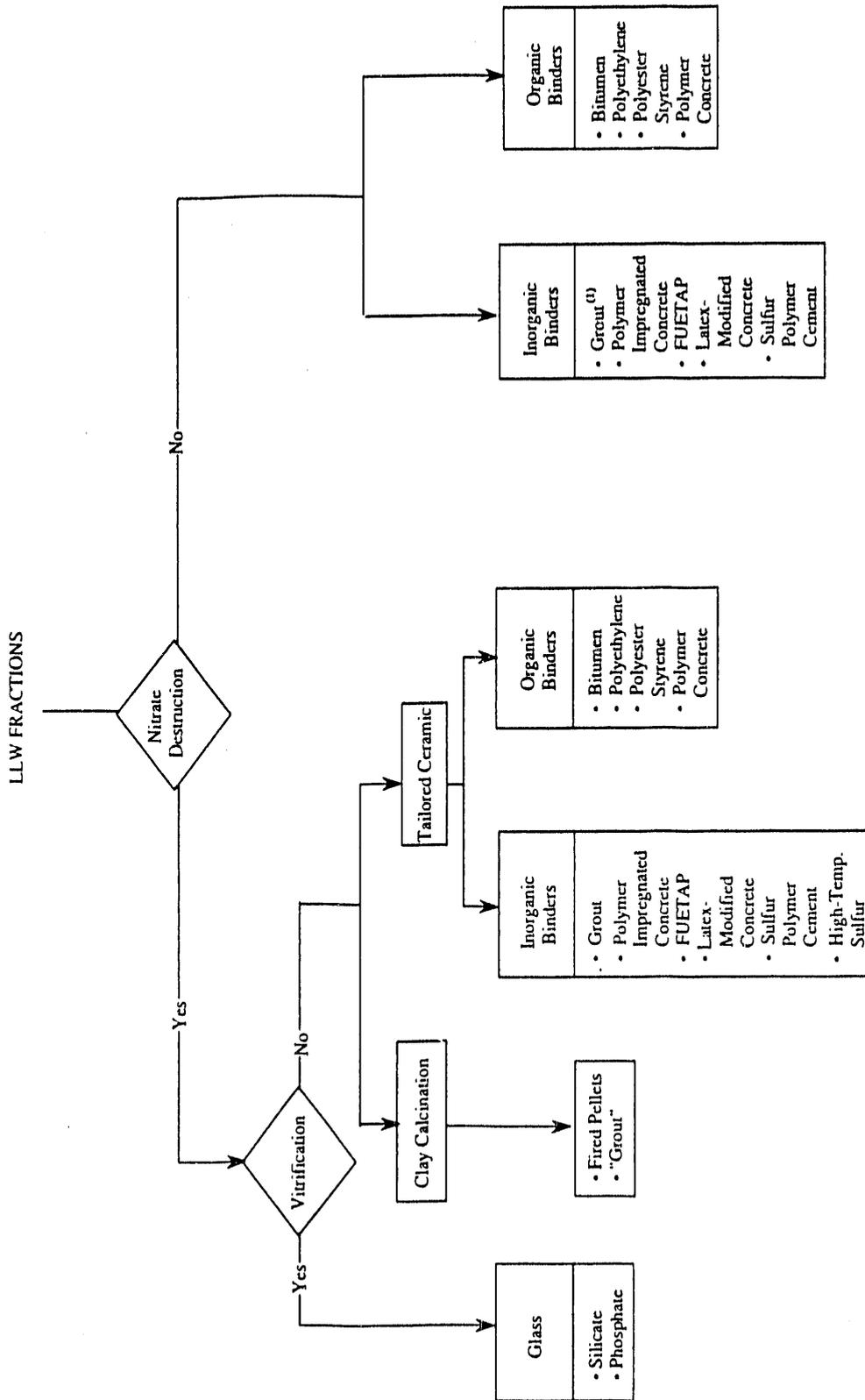
Some of the potential waste forms for immobilizing SST LLW have already been discussed as alternatives for the immobilization of SST HLW. This raises the interesting potential of using one of these waste forms for the immobilization of the SST wastes in toto (entirely) without separation into HLW and LLW fractions. Such in toto processing of SST wastes would probably require disposal of the resulting waste forms onsite; the large volumes would make offsite transportation and disposal costs very high. Onsite disposal of the immobilized in toto SST wastes would necessitate new regulatory decisions, but no more so than would in situ vitrification of the SST tanks and contents, which is presently being given serious consideration.

In toto solidification is beyond the immediate scope of this report, but in the cases where the same kinds of concrete or glass waste forms are being studied for both SST LLW and SST HLW, the data will be also be applicable, with little additional input, to an evaluation of in toto solidification of SST wastes.

Candidate waste forms for SST LLW may be divided into six categories: portland cement-based materials; clay-based materials; tailored ceramics; sulfur-based materials; organic matrix materials; and glasses. These are discussed in turn below.

4.4.2.1 Portland Cement-Based Materials

Five major types of cements that have been considered for LLW immobilization are: 1) portland, 2) gypsum, 3) pozzolanic, 4) aluminous, and 5) masonry (Jolley et al. 1986). Of these, portland cement is most widely used, but it is usually used as part of a pozzolanic blend. Pozzolanic cements are somewhat ill-defined but are essentially blends of portland cement with natural materials, such as diatomaceous earths and volcanic ashes, or



(1) Baseline Reference Case

FIGURE 4.1. Immobilization Options for SST LLW Fractions

industrial by-products, such as fly-ashes, blast furnace slag, and silica fume. As described below, the grout used for immobilization of the DST LLW is also a portland cement/pozzolan blend.

Portland cement is a hydraulic cement (i.e., it sets, hardens, and does not disintegrate in water). Portland cement consists mainly of tricalcium silicate and dicalcium silicate. Other phases are tricalcium aluminate, a ferrite phase, and calcium sulfate. In the United States, portland cement is classified into five general types designated by ASTM Specification C150-76 as follows: Type I, when special properties are not required; Type II, for general use, and especially when moderate sulfate resistance or moderate heat of reaction is desired; Type III, for high early strength; Type IV, for low heat of hydration, and Type V, for high sulfate resistance.

Throughout the world, most LLW is being immobilized in portland cement-based waste forms. The NRC accepts concrete as a waste form for LLW (Tokar et al. 1989). For reactor LLWs, the waste form is generally formed in individual containers up to 200 ft³ in capacity. This is convenient because of the relatively small waste volumes involved and because the immobilized waste must be shipped some distance for final disposal.

Grout. A cement-based grout is preferred for defense facilities where the LLW can be disposed of onsite. Grout is more convenient and economical at these sites because it can be handled in bulk rather than in individual drums. The waste-cement-additive grout mixture is pumped to the final disposal location before it solidifies into a concrete-like material.

Grout was first used as a radioactive waste form in the Hydrofracture process at the Oak Ridge National Laboratory (ORNL) (Weeren and McDaniel 1983). Now it is also being used for immobilization of LLW in the Saltstone process at the Savannah River Site (Wilhite et al. 1988) and the DSTs at Hanford (Van Beek and Wodrich 1990); thus the technology may be considered well developed.

The Hanford DST grout will be put in near-surface concrete vaults (123.5 ft long, 50.5 ft wide, and 34 ft deep), each holding up to 1.4 million gallons of grout. Auxiliary barriers include an asphalt-based sealant applied

to the interior walls and floor of the vault, and a nonradioactive "grout cap" placed over the grout mass after it has set and cured for 30 days. The exterior walls of the vault are surrounded by a high-density polyethylene membrane that drains to a catch basin beneath the vaults. A 3-ft-thick diffusion barrier of solid asphalt pavement (but with less than 4% voids, rather than the 8 to 10% voids typical of road surfacing asphalt) will completely surround the vault. Finally, the vaults will be covered with caps that are designed to reduce or prevent wind erosion, plant, animal, or human intrusion, and to deflect water away from the vaults. The grout will be a minimum of 18 ft below grade. Preliminary performance assessments indicate that this grout disposal system will meet all disposal requirements.

Grout is nominally considered a portland cement-based waste form; however, portland cement may actually be a relatively minor component. For example, the first grout formulation for the DST LLW calls for mixing one gallon of waste with nine pounds of "grout former." The grout former consists of 40 parts CaCO_3 , 28 parts fly ash, 28 parts blast furnace slag, and [only] 4 parts portland cement. This may not be a typical DST LLW grout formulation (i.e., the grout formulation may change as more experience is gained).

Although grout, and cement-based waste forms in general, can be considered well-developed based on their wide usage, improvements are still being sought in many areas, including increased waste loading, better control of setup time (particularly for organic containing wastes), better control of the temperature rise caused by heat of hydration (the CaCO_3 in the above DST LLW formulation is added solely for that purpose), better control of the amount of free-standing water after setup, and a better understanding of how to tailor grout formulations to specific waste formulations.

Efforts at waste form improvement center around attempts to improve retention of waste constituents, including organics, and to improve long-term grout matrix durability. Because many of the waste constituents are dissolved in the pore water (grout waste forms are over 25 wt% water) rather than being chemically bound to the grout matrix, one approach is to decrease the porosity and ensure that it is discontinuous. "Water vapor return," a phenomenon in

which grout absorbs water from the surrounding environment because of a vapor pressure differential, could also be minimized by decreased and discontinuous porosity.

The other main approach for improving retention of waste constituents in grout is to use additives that sorb or chemically bond waste constituents within the matrix. This approach cannot be used for nitrate, a major component of SST LLW, but it is applicable to some radionuclides, and perhaps organics. For example, the leaching of technetium is reduced several orders of magnitude by the presence of ground blast furnace slag in grout (Spence et al. 1989), and various clays have long been known to reduce the leaching of cesium from grout (Moore 1976).

Screening Assessment: Regular grout (i.e., grout formulated according to the well-developed technology being used for the similar DST LLW) should be an acceptable waste form for SST LLW. As such, "regular" grout, of an optimal formulation for non-denitrated waste (which remains to be developed), will be considered the reference form for SST LLW. Alternative waste forms must hold promise of marked cost reductions or safety enhancement to be considered as a replacement for "regular" grout.

FUETAP Concretes. Concretes formed under elevated temperatures and pressures were studied in the late 1970s and early 1980s at Oak Ridge National Laboratory (Dole et al. 1982). The formulations resemble those used for grout, utilizing portland cements, fly ash, sand, clays, and waste. Batch processing is used; the curing of individual batches is accelerated under mild autoclave conditions (100°C, 1 atm gauge), followed by dewatering at 250°C for 24 hours. The product is strong (40-100 MPa compressive strength) and radiolytically stable. The available data indicate that the leaching of FUETAP concretes is similar to grout. Apparently the dewatering step leaves open porosity that resaturates quickly upon contact with leachant. No studies of the immobilization of NaNO_3 wastes in FUETAP have been conducted; there is no reason to expect that higher NaNO_3 loadings could be achieved in FUETAP concretes than in grout.

Screening Assessment: The minor benefits in strength and resistance to radiolysis of the product do not outweigh the disadvantage of FUETAP's batch-wise processing for the large volume of LLW.

Organic-Modified Concrete. In recent years there has been increased industrial application of organic additives to portland cements. The use of these additives can best be summarized by a direct quotation (Encyclopedia 1985a):

Many of the undesirable properties of products made of portland cement result from the porosity of the cement matrix, which may be as high as 25% in total; pore diameters may range from 1-10 nm (gel pores) and 10-100 nm (capillary pores) to macroscopic pores (>100 nm) arising from entrapped air and poor particle packing. Thus, an interconnecting pore system within the cement matrix allows the ingress of water or aqueous solutions containing sulfate and chloride ions. Such penetration promotes attack on the cement matrix itself or on the bond between the cement matrix and the aggregate, and the mechanical properties of the composite structure deteriorate. The addition of polymers seals the pore system and reduces the permeability of the structure. Polymeric materials may be used in three ways to modify the properties of cement and concrete products:

1. A preformed concrete object is impregnated with a liquid monomer which is polymerized in situ, giving polymer-impregnated concrete (PIC).
2. A monomer, prepolymer, or polymer latex is incorporated into the mix of cement, aggregate, and water, forming an intimate part of the hardened structure called Polymer Portland Cement Concrete (PPCC). [Note: In this report we will use the more descriptive term, latex-modified concrete, which is in common usage (Ohama 1987).]
3. A water-soluble polymer is incorporated in a cement-water mix to give a rheology eliminating macroscopic defects owing to poor particle packing and entrained air. This recently developed technology is still experimental; the products are termed macrodefect-free (MDF) cement.

The first two of these organic-modified concretes are discussed below. The third, MFD cement, has been found to swell, lose strength, and be generally unstable in the presence of water (Poon et al. 1987).

Polymer-Impregnated Concrete. This is the only kind of organic-modified portland concrete that has been studied as a nuclear waste form (Donato 1976;

(Colombo and Neilson 1977). The steps in the manufacture of PIC include preparation of the precast concrete specimen incorporating the waste, drying (to remove free water, since impregnation is sensitive to residual water), saturation with monomer (preferably after removal of air by evacuation), and in situ polymerization of the monomer thermocatalytically or by radiation. Radiation-induced polymerization is preferred and would of course be augmented by contained radioactive waste. PIC exhibits improved fracture toughness (Encyclopedia 1985a). The leach rates of cesium and strontium are decreased by at least two orders of magnitude (Colombo and Neilson 1977).

Screening Assessment: PIC does not merit further consideration as a waste form for SST LLW at this time. Conceptually, blocks of grout containing SST LLW could be impregnated with polymer and stacked in the disposal vault with little loss of volumetric efficiency over the bulk grout process. The possible incremental improvement in waste form quality does not appear to justify the additional processing steps that would be required.

Latex-Modified Concrete. Little information is presently available on this kind of organic-modified concrete. The following is taken from Encyclopedia (1985a):

To form latex-modified concrete 10-15% (dry basis) of a polymer (usually as a latex) is added to the cement-water-aggregate mix. The polymer forms an intimate part of the structure of the hardened material, modifying the porosity and, hence, the permeability, and increasing fracture toughness. The most widely used materials are latex systems based on styrene-butadiene copolymers or on vinylidene chloride or acrylics. The latex covers the cement grains and aggregate particles in a thin film and the polymer is integrated in the concrete structure. Initially, the latex increases the mix fluidity and thus allows reduction of water.

The resistance of latex-modified concrete to cracking is greater than that of ordinary concrete, possibly because of crack bridging by the polymer network. Latex addition reduces permeability to water and aqueous solutions. This enhances durability in extreme environments.

Screening Assessment: Latex-modified concrete has never been studied as a nuclear waste form, but from the description available it appears to have

the potential to significantly improve grout properties without much additional cost. Conceptually, it may be possible to add latex to grout formulations and improve the solidified grout properties with little or no perturbation in operation of the existing Grout Treatment Facility.

4.4.2.2 Clay-Based Materials

Immobilization processes utilizing clay-based materials are described by Rockwell International (1980) and Boomer et al. (1990). The genesis of these processes is earlier work conducted by Scott Barney at Hanford. The Rockwell International version is actually a type of "brick plant," except that pellets rather than bricks are produced. The waste is mixed with kaolin clay to form a thick paste, which is extruded, chopped into pellets, dried, and calcined at 1200°C. A somewhat similar process is described by Lehto et al. (1983), who used 80% clay as a binder and fired the bricks at 1020 to 1060°C. The Boomer et al. process mixes clay with the waste and calcines the mixture at temperatures just sufficient to destroy nitrate. The calcine is then rehydrated with water and more clay and other components are added to form a "grout" that can be pumped to disposal vaults. Most of the mineral formation is expected to occur as the grout solidifies in the disposal vaults.

Screening Assessment: Some type of clay calcination process merits scouting laboratory work that is directed specifically toward SST LLW because the potential exists for producing a significantly improved waste form. The product can potentially be transferred in bulk to the disposal sites, either as fired pellets, transferred in sulfur polymer cement, for example, or as the "grout" envisioned by Boomer et al. (1990). The first property that needs to be experimentally defined is waste loading, because low waste loading is probably the biggest potential drawback to clay-based waste forms.

4.4.2.3 Tailored Ceramics

Tailored ceramics and Synroc are similar waste forms. The Synroc waste form was first proposed by Dr. A. E. Ringwood of Australia (Ringwood 1978). The concept is to incorporate the waste components in the crystalline structure of compounds that are similar to naturally occurring minerals known to survive in nature. The difference between Synroc and tailored ceramics (which

have been studied most extensively at Pennsylvania State University and Rockwell Science Center) is generally considered to be that Synroc emphasizes titanium-containing minerals, whereas tailored ceramics emphasize silicon-containing minerals, but the distinction is somewhat fuzzy. For simplicity the designation "tailored ceramics" will be used in this report. As described in Section 4.4.1.2, there are sodium-containing minerals that could potentially be adapted to a tailored ceramic process for SST LLW.

Tailored ceramics can conceptually be combined with many different matrix materials for final disposal (see Figure 4.1). The other option, which has usually been considered for disposal of tailored ceramics, is hot isostatic pressing (HIPing). But questions concerning the feasibility of HIPing in a large-scale radioactive plant have led the Australian developmental work away from HIPing. A recently developed Australian process for the consolidation of Synroc powder could potentially be applied to the processing of an LLW-tailored ceramic. A batch process is used in which the waste is mixed and dried with the Synroc precursor materials and transferred to bellows-shaped containers for calcination. The containers are then hot-pressed into final waste form (Ramm and Vance 1990).

Screening Assessment: Although the bellows concept that has now been developed for Synroc in Australia substitutes a somewhat simpler uniaxial hot pressing for HIPing, it remains a batch process and there is probably a definite limitation on the size of individual containers that can be hot-pressed. Therefore, direct consolidation of an SST LLW-tailored ceramic is not considered a viable option because of the large number of containers that would be required. As shown in Figure 4.1, tailored ceramics would best be considered as promising methods for stabilizing the Na_2O in LLW when the waste is incorporated in other matrix materials for final disposal.

4.4.2.4 Sulfur-Based Materials

Sulfur is a relatively stable, readily available raw material that has been investigated as a nuclear waste form in two applications, described chronologically below.

High-Temperature Sulfur Matrix. W. E. Winsche and co-workers at the Savannah River Laboratory (SRL) investigated the "calcination" of nuclear wastes in molten sulfur to produce an insoluble product (Winsche et al. 1963; Winsche and Davis 1964). In the laboratory testing done at SRL, aqueous acidic wastes were reacted with molten sulfur at 150°C so that the water and volatile acids are driven off and the chemical compounds present in the waste were calcined and/or chemically reduced. The resulting sulfur-waste slurry was then heated at 400-444°C for 1 to 5 hours and cast. The waste constituents were thus dispersed in a matrix of solid sulfur in the form of sulfides and oxides.

The experimental apparatus was a stirred stainless steel vessel. Three acidic wastes high in iron, aluminum, and zirconium were solidified successfully. "Treatment of Purex waste containing sodium nitrate has not yet been as successful as treatment of the preceding wastes" (Winsche et al. 1963, p. 199). Leach rates of the sulfur waste forms were reported in the range of 10 to 20 mil/yr (roughly 1 to 2 g/m²-day in the units commonly used today). In some tests, however, the specimens cracked after a few weeks' exposure in water, with a resultant increase in leaching.

Screening Assessment: The brief testing that was done at SRL is sufficient to show that this innovative process, which in a sense is analogous to a low-temperature slurry-fed vitrification process, has little potential for application to SST LLW. Sodium nitrate is more difficult to calcine than most other nitrates, requiring a temperature of 600 to 700°C, well above the maximum temperature of this process.

Sulfur Polymer Cement. Since 1976, commercial production and installation of corrosion-resistant sulfur concrete has been increasing continually. The development of sulfur polymer cements (SPCs), first in Canada and then at the U.S. Bureau of Mines, Albany, Oregon, has made commercial use of sulfur concrete practical. A good review of the development of SPCs is given in the report by ACI Committee 548 (1988). Advantages of sulfur concrete include impermeability, resistance to acids and corrosive chemicals and high strength.

Early sulfur concrete products, prepared with unmodified sulfur as the binder, were plagued with durability problems. This problem was solved by

reacting the sulfur with organics, such as olefinic hydrocarbon polymers or cyclopentadiene, to form SPCs. The carbon content of SPCs ranges from 5 to 18%. Commercial sulfur concrete generally contains about 15% SPC and 85% aggregate. The concrete is formed by heating to 140°C. The mix may be maintained at this temperature for indefinite periods in a closed system. Vibration does not cause mix separation, as it can with portland cement concretes. There is no curing time after sulfur concrete sets upon cooling; it has its full strength immediately.

SPC has been evaluated for the immobilization of low-level nuclear waste (Colombo et al. 1983; Kalb and Colombo 1985). Optimal waste loading of simulated sodium sulfate, boric acid, and incinerator ash wastes was determined to be 40, 40, and 43 wt%, respectively. Leachability indexes, obtained by the ANS 16.1 leach test, ranged from 9.7 to 11.1 for cesium and from 10.7 to 14.6 for cobalt.

Screening Assessment: SPC merits investigation as a matrix material for denitrated SST LLW (glass particles, fired clay pellets, or tailored ceramic powder). Conceptually, the SPC waste form could be pumped to vaults through heated lines achieving the same kind of bulk disposal that is used for standard grout. In fact, the process could be more trouble-free because, if for any reason the waste form set up in the line, it could be easily reliquified by heat. Recovery from a similar blocked line event with standard grout would be much more difficult. The potentially much lower diffusion of waste components in SPC (as evidenced by the leachability indexes reported above) could offer substantial cost benefits: 1) by reducing the barrier requirements of the vault design, or 2) by permitting the empty SSTs and DSTs to be used as disposal "vaults" without external barriers.

4.4.2.5 Organic Matrix Materials

Bitumen and several kinds of plastics have been used for the immobilization of LLW, usually reactor wastes.

Bitumen (Asphalt). Bitumen is being used for immobilization of low and intermediate radioactive wastes in about 12 countries, but is very little utilized in the United States (Schneider et al. 1988). In all cases, the

waste-bitumen mixture is poured/extruded into drums, or other types of containers, where it hardens to an elastic solid.

Screening Assessment: Bitumen is not applicable to non-denitrated SST LLW. Scientists at ORNL have investigated bitumen extensively. They recommend that it not be used for the fixation of high-nitrate wastes because of their oxidation potential (Neilson and Dole 1985). However, bitumen could be a viable waste form for denitrated SST LLW. A feature in favor of bitumen as a waste form is the proven stability of naturally occurring bitumen (Hellmuth 1989). Conceptually, a rail-mounted bitumen facility that could be moved from vault to vault would permit bulk disposal of a bitumen waste form (if it is not possible to pump the bitumen to the disposal vaults from a central facility through heated lines).

Polyethylene. Polyethylene is a thermoplastic material that softens between 86 and 127°C; hence, it can be processed in the same manner as bitumen. However, because polyethylene is more expensive it has been less utilized for waste disposal. In the United States, development of polyethylene as a waste form was initiated at ORNL, but the more recent work has been done at Brookhaven National Laboratory (BNL). In particular, Colombo and co-workers have been evaluating polyethylene as a waste form for high- NaNO_3 wastes (Kalb and Colombo 1984; Franz and Colombo 1985, 1986; Franz et al. 1988).

Single-screw extruders (originally 1 1/4-inch, more recently 4 1/2-inch diameter) operating at 130°C have been used in the BNL studies. Polyethylene and dry simulated NaNO_3 wastes are fed to the extruder by proportional feeders. A demonstration of immobilization of high-nitrate wastes in polyethylene is planned at Rocky Flats during 1991. The Rocky Flats wastes will be dried before introduction into the extruder. Many bitumen processes using an extruder evaporator operate with liquid feed (see for example Miyao et al. 1984), but predrying is apparently a process necessity for polyethylene because of the lower processing temperature, 130°C for polyethylene vs >200°C for bitumen.

In the BNL program, polyethylene waste form specimens were prepared containing 30, 50, 60, and 70 wt% NaNO_3 and leached by the ANS 16.1 leach test method. The resulting leaching indexes were (Franz et al. 1987):

<u>Waste Loading NaNO₃ (wt%)</u>	<u>Leaching Index</u>
30	11.1
50	9.7
60	9.1
70	7.8

Differential scanning calorimetry tests were also performed on the samples. The absence of peaks representing exothermic reactions indicated the stability of the polyethylene-NaNO₃ materials over a range of temperatures to 400°C.

Screening Assessment: Polyethylene should be considered for evaluation as a waste form for non-denitrated SST LLW. Potential advantages over regular grout are increased waste loading and superior durability. Conceptually, the process would produce large blocks of polyethylene which would be stacked in the disposal vaults. Many questions concerning thermal, radiation, and chemical stability would have to be resolved.

Polyester-Styrene. A diversity of plastics belonging in this general class, some proprietary, have been applied to the solidification of LLW. The essential ingredients are a linear polyester resin, a cross-linked monomer, such as styrene, and inhibitors to retard cross-linking until the resin is ready to use. The process of converting polyester resins from the liquid to the solid involves a catalyst-promoted chemical reaction between the polyester resin and the monomer in which the polyester is dissolved, to form a cross-linked, thermoset polymer. High-shear mixing to form an emulsion is required when polyester-styrenes are used for liquid wastes, but not for solid wastes (Jolley et al. 1986).

Apparently the only investigation of the use of polyester-styrene for immobilization of NaNO₃ is that of Franz et al. (1987). When they incorporated 33 wt% NaNO₃ in polyester-styrene, the resulting product had a leaching index of 9.2.

Screening Assessment: There is no incentive to investigate the use of polyester-styrene for the immobilization of SST LLW. As a plastic waste form, it appears to be inferior to polyethylene.

Polymer Concrete. Polymer concrete is a composite material consisting of selectively graded aggregates with an organic resin binder. Polymer concretes have been used in Europe and Japan for more than 20 years and are now being accepted in the United States as viable substitutes in many architectural, construction, electrical, and industrial applications (Encyclopedia 1985b). The amount of organic binder used is in the range of 5-15 wt%. BNL was active in the development of polymer concretes as a structural material, and this led to testing of polymer concretes as nuclear waste forms at that Laboratory (Colombo et al. 1974). Polymer concrete was reconsidered in 1983 when BNL reviewed potential LLW forms to select those meriting further development (Colombo et al. 1983). It was rejected in favor of polyethylene and sulfur polymer concrete.

Screening Assessment: Polymer concrete should not be considered for further evaluation for non-denitrated SST LLW. Neither should it be considered for the immobilization of denitrated SST LLW. Although a polymer concrete process for denitrated SST LLW is conceivable, a large amount of development would be required. Polymer concrete has no apparent advantages that merit such a development effort.

Glass. Glass is an accepted waste form for HLW, and it has been considered as a waste form for TRU wastes (Peterson and Johnson 1989; Roggenthen 1989). It may also be applicable to SST LLW. Several scenarios for immobilization of SST LLW in glass can be envisioned:

1. In situ vitrification of the SSTs (which is being investigated in another program, and is outside the scope of this report)
2. Vitrification of SST LLW and SST HLW together. A new larger-capacity vitrification facility would be required. This scenario would seem to be feasible only if the glass containing the HLW could be disposed of onsite; offsite disposal costs would be extremely high because of the extra glass volume needed to incorporate the SST LLW (see the "geologic disposal" option in U.S. DOE 1987)
3. Vitrification of SST LLW alone. A new vitrification facility would be required.

Scenario 3 will be assumed for this literature review.

Silicate Glass. Sodium is a major component of most commercial silicate glasses. Window glass contains 12-15 wt% Na₂O (Shand 1958). The processing temperature of window glass is about 1500°C. Such high temperatures would cause considerable volatility of SST LLW components, such as cesium, which would have to be accommodated in design of the off-gas system. Alternatively, lower melting glass compositions could be developed (e.g., analogous to the borosilicate compositions used for HLW, which can be processed at 1150°C). In fact, sodium can be used to lower the processing temperature; it may be possible to develop low-melting formulations containing 20 wt% Na₂O, or more, without greatly degrading leachability of the glass.

Screening Assessment: Silicate glass merits further evaluation as an immobilization medium for SST LLW. The potential exists to decrease the volume of solidified SST LLW by a factor of four, and to produce an improved waste form, free of organics, that could do away with the need for all of the extra barriers that are required in the disposal system for regular grout. Conceptually, a large tank-melter of the type used industrially can have sufficient capacity to process the SST LLW. Several options for glass product configuration and disposal methodology can be envisioned; for example, large rectangular castings stacked in underground bunkers for disposal. Alternatively, techniques are available for the remote fabrication of glass marbles (or at least semispherical glass "blobs"), or for simply quenching the molten glass very rapidly to produce glass particles, or frit. Glass marbles could possibly be transferred pneumatically; glass marbles or particles could be transferred in molten sulfur polymer concrete (Boomer et al. 1990). The glass marbles or particles could be disposed of in underground caissons, or used to fill and prevent collapse of the empty Hanford tanks (probably in conjunction with a sorbent material that would "getter" any radionuclides released from the residual contents of the tanks).

Phosphate Glass. Phosphate glass is described extensively in Section 4.2 of this report. As described there, phosphate glasses are very flexible in their ability to incorporate varying amounts of different elements. This flexibility includes sodium. Phosphate glasses incorporating 26 wt% Na₂O are described by Brezneva et al. (1979). There are limitations on the size of

phosphate glass products; large castings are probably not practicable because they cannot be cooled quickly enough to avoid devitrification, which degrades the quality of the phosphate glass.

Screening Assessment: Although silicate glass is probably to be favored, because of the much larger experience base and fewer processing limitations, phosphate glass also merits an in-depth examination as a potential SST LLW form.

4.4.2.6 Summary Evaluation of Candidate Waste Forms for SST LLW

The preceding literature review shows that there are several candidate SST LLW waste forms with the potential for cost savings and improved safety, when compared with regular grout. The literature review also clearly demonstrates that more data are needed before informed decisions can be made concerning the candidate forms. This section utilizes the results of the literature review to identify the waste forms (see Table 4.4) that will be the subject of the initial data acquisition, which is described in Section 4.4.3.

TABLE 4.4. Candidate SST LLW Forms Selected for Initial Laboratory Evaluation

Candidates for Non-Denitrated SST LLW

- Grout^(a)
- Latex-modified cement
- Polyethylene

Candidates for Denitrated SST LLW

- Silicate glass
- Phosphate glass
- Clay calcine in "grout" or pelletized
- Tailored ceramic in grout
- Tailored ceramic in sulfur polymer cement
- Tailored ceramic in polyethylene
- Tailored ceramic in bitumen

(a) Regular grout that has been specially formulated for the immobilization of non-denitrated SST LLW will be used as the reference waste form.

Improved Waste Forms for Non-Denitrated LLW As shown in Table 4.4, two candidate waste forms offer a potential for improvement over regular grout for the disposal of non-denitrated SST LLW. One of these, latex-modified concrete, can potentially be incorporated into the existing Hanford Grout Treatment Facility. It offers the potential of substantially improving the leachability of the grout, which could provide cost reductions through a relaxation of vault barrier requirements. The other, polyethylene, also offers potential cost savings due to a significantly higher waste loading plus improved waste form properties. However, an entirely new processing facility would be required.

Waste Forms for Denitrated LLW. Denitration of SST LLW, whether done by vitrification, clay calcination, or a tailored ceramic process, will require new facilities but will ensure a much improved and considerably lower-volume waste form. The initial data acquisition should emphasize defining maximum waste loading (in terms of a tradeoff with product quality) for the seven candidate waste forms shown in Table 4.4. When these data are available, preliminary cost estimates can be made that will determine the direction of subsequent development.

4.4.3 Initial Study of Selected LLW Forms

A laboratory evaluation of the waste forms identified in Table 4.4 was begun in FY 1991. The goal of these laboratory studies is to obtain data on maximum waste loading and waste form characteristics that can be used to make a decision on which waste form(s) should be developed further.

4.4.3.1 Reference SST LLW Compositions

The first step in the laboratory studies is to define reference SST LLW compositions to be used in fabrication of test specimens of the candidate waste forms. SST LLW is composed of the "leftovers" after pretreatment and HLW processing; thus these processes will affect SST LLW composition. It is likely, however, that because of the dominance of NaNO_3 in SST LLW, only two compositions will be required for the initial laboratory studies, a reference non-denitrated SST LLW and a reference tailored ceramic SST LLW. Later, when additional information on pretreatment and HLW processing is available, it

will be possible to define the potential range of the non- NaNO_3 SST LLW components more accurately, and to factor these ranges into the laboratory testing.

The reference non-denitrated SST LLW will be used for formulating test specimens of the reference SST LLW grout, the two candidate waste forms for non-denitrated SST LLW shown in Table 4.4, the two candidate glasses and the clay calcine in "grout"; the reference tailored ceramic SST LLW will be used for formulating test specimens of the remaining four candidate waste forms shown in Table 4.4. The reference tailored ceramic SST LLW will be conceptual in nature (i.e., sodium mineralization will be assumed), as described in Sections 4.4.1.2 and 4.4.2.3, but demonstration of the mineralization process will not be part of the initial laboratory studies.

4.4.3.2 Development of Reference SST LLW Grout

A reference SST LLW grout is being developed as a "baseline" against which the candidate alternative waste forms will be compared. The reference SST LLW will be "regular" grout (i.e., grout containing the same grout-forming constituents that are used for DST LLW grout), but in amounts that are optimized for non-denitrated SST LLW. Considerable effort will be expended to optimize the composition of the reference SST LLW grout. It is important that the "baseline" defined by the reference grout set the highest possible standards against which to judge the candidate waste forms. Actually, there will be a series of reference SST LLW grouts formulated with waste loadings from 15% to the highest waste loading possible in 5% increments.

4.4.3.3 Evaluation of Candidate Alternative Waste Forms for SST LLW

The candidate waste test specimens will be prepared to have waste loadings in the same 5% increments as the reference SST LLW grouts to facilitate comparison as far as possible. Measurements of bulk density, physical strength, and leachability (of selected radionuclides and hazardous constituents) will be performed on the test specimens and compared with results of similar measurements on the reference grouts as a function of waste loading. (Note: The maximum waste loading in some of the candidate waste forms may

extend considerably beyond that achievable in regular grout.) The bulk density measurements will be used to calculate waste loading on a volumetric basis. Physical strength in excess of the minimum requirement is not considered an important factor; thus evaluations of the laboratory results will be based mainly on waste loading and leachability. To merit further investigation there should be marked improvements when compared with the reference grout (i.e., a factor of X improvement in waste loading or a factor of Y improvement in leachability). (The exact criteria will be developed in conjunction with Westinghouse Hanford Company.)

If improvements meeting or exceeding the criteria cannot be shown in the early testing, then further study can probably be abandoned because any of the alternative waste forms will require substantial amounts of research and development before they can be utilized for immobilization of SST LLW. Such a commitment will not be warranted for a marginal improvement; it will only be justified if the initial laboratory tests, and follow-on evaluations, show potential for truly large benefits.

Although the initial laboratory testing will be limited to the waste forms identified in Table 4.4, there will be a small effort to continue examining the literature on the alternatives identified in Section 4.4.2, and to consider other potential waste forms that may come to light. The testing program will be flexible; after consultation with Westinghouse Hanford Company, waste form candidates may be added or removed from the testing program as new information warrants.

4.4.3.4 Advanced Development

The laboratory testing described in Section 4.4.3 will provide sufficient data so that preliminary engineering assessments of the most promising alternative waste forms can be made by PNL and Westinghouse Hanford Company using conceptual flowsheets. The preliminary engineering assessments will be used to select one or more alternative waste forms for detailed testing and process development. The final goal is implementation of a practical, improved method for disposal of SST LLW at Hanford.

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