High-Level Waste Melter Review Report

July 2001

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High-Level Waste
Melter Review Report

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High-Level Waste Melter Review Report

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Summary

The U.S. Department of Energy (DOE) has programs to treat and dispose of high-level waste at several sites. At the Hanford Site in Richland, Washington, a program has been established to vitrify wastes that have been stored in tanks. The first phase of this program will use borosilicate glass and a Joule-heated melter.

The DOE Tanks Focus Area (TFA) contracted a Study Team to develop information that could be used to consider whether other waste forms and melter technologies could lead to substantial cost savings. The TFA also established a Review Team to use the information developed by the Study Team and the knowledge of the Review Team's members to provide conclusions and recommendations.

This report provides the Review Team's conclusions and recommendations on waste form, melter technology, as well as on general issues. Chapters cover the detailed material on which the conclusions and recommendations are based.

Acronyms

ACCM	Advanced Cold Crucible Melter
DOE	U.S. Department of Energy
DOE-EM	DOE Office of Environmental Management
DOE-RW	DOE Office of Civilian Radioactive Waste Management
DWPF	Defense Waste Processing Facility
EVOP	EVolutionary OPerations
HLW	high-level waste
INEEL	Idaho National Engineering and Environmental Laboratory
MT/d	metric tons/day
ORP	Office of River Protection
PCT	product consistency test
SBW	sodium-bearing waste
SNF	spent nuclear fuel
SRS	Savannah River Site
TFA	Tanks Focus Area
TOE	total operating experience
TRUEX	transuranic extraction
UNEX	universal solvent extraction
WAPS	Waste Acceptance Product Specification
WA-SRD	Waste Acceptance System Requirements Document
WTP	Waste Treatment Plant
WVDP	West Valley Demonstration Project

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1.0 Introduction

1.1 Statement of Concern

The U.S. Department of Energy (DOE) has a massive cleanup task to resolve the legacy of environmental problems from years of manufacturing nuclear weapons. One of the major activities related to this task is to treat and dispose of the extremely large amount of high-level radioactive waste at the Hanford Site in Richland, Washington.

The method of choice for accomplishing this task is to vitrify this waste for disposal in a geologic repository. After several years of shifting financial approaches, DOE settled on a contract with Bechtel and the Washington Group to build a waste treatment facility that would process approximately 10% in volume and 25 % in radioactivity of the Hanford high-level waste (HLW) in Phase 1. The design is one chosen by the previous contractor, BNFL, Inc., and will use borosilicate glass. The remaining waste will be treated in Phase 2, which may require higher throughput than the initial Phase 1 program. This facility may not necessarily use the same waste form and melter technology as the initial facility.

Consequently, DOE is examining alternatives, which led to requesting the Tanks Focus Area (TFA) "to conduct a technical review of alternatives for solidification of Hanford HLW that could achieve major cost reductions within reasonable long-term risks...The potential for improved cost performance lies largely with increased waste loading (fewer HLW canisters for disposal), higher throughput, or decreased vitrification facility size."[1]

The approach used to implement this task was to establish two teams, a Study Team and a Review Team. The Study Team was the major funded effort and was asked to develop the information upon which the Review Team could reach conclusions and recommendations, although recognizing that by selecting a group of experts for the Review Team, it would use its own judgment as well as experience to guide its conclusions and recommendations.

1.2 Charter

The Review Team selected by the TFA is as follows:

- John Ahearne, Leader, JFRA, Inc.
- Joe Gentilucci, JAG Technical Services, Inc., TFA Technical Advisory Group
- David Pye, Alfred University, New York State College of Ceramics
- Thomas Weber, TFA Technical Advisory Group
- Frank Woolley, TFA Technical Advisory Group.

After reviewing the task statements for both itself and the Study Team, the Review Team developed the following charter, with notification to TFA:

> "The TFA has been requested by DOE-Headquarters to conduct a technical review of alternatives for solidification of Hanford HLW that could achieve major cost reductions within reasonable long-term program risks. An independent Review Team has been chartered by TFA to lead and guide the technical review; to review the products from a Study Team that will collect and analyze data and perform specific

[1] TTP: Advanced High-Level Wage (HLW) Melter and Waste Products Review, 25 August 2000.

analyses; and to recommend a research and development program, as warranted for future waste form and melter advancements.

The work will focus on Hanford waste, but will comment upon wider applicability to Savannah River (Savannah River Site [SRS]) and Idaho (Idaho National Engineering and Environmental Laboratory [INEEL]) wastes. Using work performed by the Study Team, under a separate contract, the Review Team will address the following:

- Are there other glasses or glass-ceramics compositions, including borosilicate glass, which could handle segments of DOE HLW with greater efficiency, cost savings, or lower program risk?

- Are there other vitrification technologies, including modifications of current DOE approaches, which could handle segments of DOE HLW with greater efficiency, cost savings, or lower program risk?

The study will address whether modifying current requirements, including those established by the DOE Office of Civilian Radioactive Waste Management (DOE-RW), could significantly reduce program costs. To develop a path forward for advanced melter and waste form material developments, the study will recommend "which studies should be done and on what."[2]

To guide the work of the Study Team, the Review Team will interact with the Study Team on a regular basis.

The Review Team's report shall be submitted one month following receipt of the final report of the study team."

1.3 Description of Review

The Study Team and Review Team met in November 2000 to develop a process of interaction. The Study Team was to develop an explicit set of five tasks set out in its contract. The Review Team role was to recommend changes to the approach identified by the Study Team to ensure that the final product would meet the needs of the Review Team. Subsequently, periodic conference calls were held among the Review Team and appropriate members of the Study Team. As the Study Team produced draft reports for each of its tasks, the Review Team provided comments and requests for additional material. The Study Team and Review Team met again in February 2001 to review in detail Study Team work and provide mid-course corrections to the work process.

After receiving the final draft report from the Study Team, the Review Team met in June 2001 to prepare its own report.

This report completes the Review Team task. The compiled Study Team (Perez, Jr. et al. 2001) provides supporting data and analysis.

[2] Letter of 12 October 2000 to Paul W. Kruger, Assistant Manager for Science and Technology, DOE Richland Operations Office, from EM DAS Mark Frei and EM DAS Gerald Boyd.

2.0 Conclusions and Recommendations

Using the extensive data collection and analysis by the Study Team, as well as the many years of experience of members of the Review Team, this section presents the principal conclusions and recommendations of the Review Team. These statements primarily refer to the Hanford Site, as this was the task given to the Review Team. A small section of this report does address INEEL; however, time precluded the Review Team from devoting much effort to SRS, where there is an operating melter, although in this report the Review Team does provide comment where statements appear to have particular relevance to that site. The Review Team also indicates those recommendations that are to be used for further studies, as was requested.

2.1 Principal Conclusions and Recommendations

1. The Review Team concludes that there are no other glasses or glass-ceramic compositions that are obviously better than borosilicate glass, although we do recommend a modest research program on other silicates and iron-phosphate glass, primarily as an insurance policy in case substantial problems arise in the use of borosilicate glass.

2. The Review Team concludes that the Joule-heated ceramic melter is the best approach for a vitrification technology, although we recommend substantial improvements in the current technology. We also recommend a short but intense research and technology program on the Advanced Cold Crucible Melter (ACCM), as an insurance policy.

3. The Review Team concludes that the biggest challenge to containing the overall life-cycle cost is to develop a total system plan that takes into account all aspects of the program, including retrieval, pretreatment, vitrification, storage, disposal, and decommissioning. Concentrating on technology improvement in only one segment, such as vitrification, can lead to a severely unbalanced program and elimination of the potential for cost savings.

2.2 Detailed Conclusions

2.2.1 Waste Forms

1. The borosilicate waste form has performed as predicted and is firmly entrenched in the nuclear waste remediation program. The vitrification process using this waste form has not been optimized.

2. Presence of crystals in cooled glass should be acceptable, under current waste acceptance requirements [Waste Acceptance System Requirements Document (WA-SRD) (DOE 1999a)], if the product consistency test (PCT) is not impacted and crystal formation is known and predictable.

3. Increasing the acceptable limits of crystallized phases in the waste glass offers the major opportunity to minimize the total volume of glass needed to immobilize all the Hanford HLW tank waste.

4. The current status of licensing of the HLW repository will require that any DOE HLW vitrification facilities to be constructed within the next five to ten years be designed to process good quality borosilicate glass.

5. Use of nonborosilicate waste forms will require modifications of the current WA-SRD and Waste

Acceptance Product Specification (WAPS) (DOE 1996) and other waste qualification procedures, including repository license amendments.

6. It is prudent engineering strategy to utilize an optimized borosilicate waste form and associated vitrification process whenever possible. However, given the wide compositional ranges of wastes stored at Hanford, INEEL, and other sites, other alternative glass waste forms can be considered, such as alkali-aluminosilicate glasses, iron-phosphate glasses, and their associated glass ceramic derivatives. These could be adopted when and if appropriate engineering and monetary justification can be demonstrated. A waste form that can accommodate large fractions of chrome oxide could be particularly valuable in view of the uncertainties in chrome leach factors and solubility.

7. Chrome content of the waste feed, the leach factor for pretreatment, and the solubility in glass are the main determinants in the number of canisters that will be produced. However, the data supporting the current 0.77 leach factor and 1.0% glass solubility used by the Study Team are not strongly substantiated. Confirmation of these factors would result in a substantial cost savings with respect to the Hanford Office of River Protection (ORP) baseline.

8. Iron-phosphate waste forms may have the potential to provide increased waste loading for certain tank wastes, but there is currently insufficient information to define the trade-offs among development, waste form qualification, and facility conversion costs against the cost savings from incremental reductions in total immobilized HLW volumes.

9. Development of technical bases that would allow higher concentrations of phosphate phases, and possibly other secondary phases, in the glass could enhance waste loading for some specific waste streams.

10. Iron-phosphate glasses may provide higher waste loading than borosilicate for some streams, especially at INEEL if a calcine separations flowsheet is selected that results in vitrification feeds high in phosphate. Borosilicate formulations may be limited to unusually low waste loadings for such a waste stream.

2.2.2 Melter Technology

1. There appear to be only two practical options to meet Hanford's long-term vitrification needs:

   - The Joule-heated ceramic melter with Inconel™ electrodes, enhanced to handle suspended crystals, is the best overall technology for both short- and long-term Hanford HLW needs. Problem glasses would need to be handled by dilution. This technology is simple, reliable, well developed, and proven by considerable HLW experience. Aggressive development is warranted to optimize its performance. Further development of the baseline Joule-heated ceramic melter is more likely to produce large cost savings than changing to another basic melter technology.

   - The ACCM (cold-wall induction-heated) technology appears to be the most promising of the alternate melter technologies. The slightly higher temperatures available decrease the number of problem glasses. However, at present, its development for HLW is incomplete. Neither the melter nor the power supply has been proven at the scale needed for Hanford HLW, the number of people with any experience with this technology is extremely limited, and almost nothing is known about it in the United States from firsthand experience. This technology could provide an alternative if unforeseen problems arise in applying the Joule-heated ceramic melter to Hanford HLW. Therefore,

development is warranted to learn more about it.

2. No new technologies are currently being proposed or developed that offer an attractive alternative to HLW vitrification in resistance- or induction-heated melters.

3. Alternative melter technologies should be judged on their potential to replace the Joule-heated ceramic melter for the Hanford Balance of Mission. They should not be developed as additional technologies for specific troublesome wastes. The costs of developing and deploying any of the alternatives appear to be higher than any potential savings if only used for part of the wastes.

4. The current limitations to waste loading at Hanford are related primarily to processing constraints associated with the current Joule-heated ceramic melter, rather than requirements imposed by HLW repository waste acceptance requirements. Waste loading is predominantly dependent on both the melter operating temperature and ability to process precipitates (e.g., spinels and noble metals). Compositions that have a liquidus near or above the melter operating temperature will provide the maximum waste loading. Providing melter processing capabilities that can accommodate crystals in the melt and operate at higher temperatures offers the most promising approach to optimized waste loading at Hanford. Technology development directed to higher temperature melting capability could provide waste loading improvements for some streams, but these cases represent a relatively small fraction of the total waste.

5. Significant increases in waste loading, melting rate, and predictability of processing rate can be achieved through enhancements to the existing Joule-heated ceramic melter technology.

2.2.3 Other

1. Good detail design, good operating practices, and a focus on continuous improvement have a much larger influence on ultimate success of the HLW vitrification process than the initial choice of melter technology. Any of the technologies that have been seriously considered in the long history of HLW vitrification development could be made to work satisfactorily with enough effort and expense. The differentiation is much more an issue of costs than of fundamental technical feasibility.

2. Both the design and the operating practices of a melter technology need to receive equal attention during the development of the technology. A melter technology includes not only the design of the melter, its components, and support systems, but also its operating practices, including definition of targets for controllable parameters, and strategies for controlling these parameters, and for adapting operating conditions to changes in feed or production goals.

3. Greater use of lab tests and pilot melters, both reduced- and full-scale, in the development of new melter technology could significantly reduce program risks and long-term program costs.

4. It would be prudent to provide design features in new plants that allow conversion to a more advanced melter technology after startup.

5. Useful changes in melter design and operation, such as increased temperature capability, bottom drains, and melt agitation by mechanical stirring or bubblers, would be of great help in obtaining increased flexibility in developing waste form modifications.

6. Hanford life-cycle costs are dominated by the facility operating cost. The operating time period principally determines that the facility operating cost and total cost can be significantly reduced by

increased throughput. Construction costs, although important, are not major determinants in life-cycle cost.

7. High-level waste operating cost savings from increased waste loading or throughput may not be attainable without corresponding throughput improvements (or additional facilities) in retrieval, pretreatment, and low-level waste vitrification.

8. Cost implications of melter throughput capacity, plant operating efficiency, and melter disposal appear to be in the same range as the implications of potential waste-loading enhancements, indicating that there are incentives for process development activity to assure a balanced system optimization.

2.3 Detailed Recommendations

2.3.1 Waste Forms

1. We recommend that the DOE-Office of Environmental Management (DOE-EM) establish a program to determine if glass formulations that result in high levels of crystal formation are predictable in either the melter or canister, can meet repository requirements, and can be modeled. This will require demonstrating the predictability of crystal compositions at various waste loading and Hanford glass compositions. Programs to determine liquidus, crystal formation, leach mechanisms, and radionuclide partitioning for the various glasses containing crystals are required to provide this predictability.

2. We recommend that the program to determine reliable chrome leach factors and glass solubility values should be one of the top priority items for the Hanford Waste Treatment Plant (WTP) because of its high impact on glass volume.

3. We recommend a modest research program to develop alkali-aluminosilicate glasses and iron-phosphate glasses as alternative waste forms, including crystallization in cooling to produce a glass ceramic, primarily as an insurance policy in case substantial problems arise in the use of borosilicate glass.

2.3.2 Melter Technology

1. We recommend a major program to develop enhancements to the existing Joule-heated ceramic melter technology. We believe that significant increases in waste loading, melting rate, and predictability of processing can be achieved through further development in the following areas:

   - Forced convection will increase tolerance for crystals in the melter, melt rate, and predictability of processing rate. Mechanical stirring, bubbling, and hot spots should be investigated.

   - Aggressive cooling of electrodes and other immersed metal components to permit operating temperatures up to 1350°C will allow higher waste loadings and higher and more predictable processing rate. Means to limit volatilization will be needed.

   - Bottom drains and melter bottom redesign could increase tolerance for crystals in the melter.

   - Reduction of the thickness of refractories by substituting shell cooling and provision for emergency draining of the melter could substantially reduce the high disposal cost of failed melters.

   - Very intensive mixing just under the cold cap has the potential to markedly increase melting rate and

hence decrease melter size, but the technology is quite immature.

- Secondary heating to evaporate water could improve predictability of processing rate for both Joule- and induction-heated melters.

2. We recommend a short but intense research and technology program on the ACCM, focused on establishing within a reasonable period (e.g., five years) whether this technology could replace an enhanced Joule-heated ceramic melter for the Hanford Balance of Mission.

3. We recommend that an expanded program of melter testing be undertaken, including these elements:

   - Lab melters and computational models to investigate specific processes within melters (e.g., cold cap reactions, foaming, and noble metal accumulation).

   - Lab and pilot melters to test components (e.g., stirrers and bubblers, secondary heaters, feed distributors, and delivery systems).

   - Simulants that have melting behavior sufficiently close to actual wastes to permit advanced development of melting processes in nonradioactive facilities.

   - Nonradioactive development melters, both reduced- and full-scale, used extensively throughout design and construction, commissioning, and well into the production periods of Hanford vitrification to assure continuous improvement and evolution of melter design and operating practices, and to train personnel. (These facilities will have much greater value if they are located onsite.)

4. We recommend that an expanded program of production optimization be undertaken, including these elements:

   - Lab methods for pretesting of melter feed during production to permit fine-tuning of waste loading in each batch. Additional storage capacity for pretreated feed may by required.

   - Procedures for safe but efficient testing during hot production to permit continuous optimization of melter operations throughout the production period.

   - Procedures to continually reassess and reset production targets to reflect the process capability, as demonstrated by the best-sustained process performance.

2.3.3 Other

1. We recommend that DOE-EM develop a total system plan that takes into account all aspects of the program, including retrieval, pretreatment, vitrification, storage, disposal, and decommissioning.

2. We recommend that the current design effort should not preclude the ability to install an improved Joule-heated ceramic melter or ACCM or the ability to install additional or larger melters to provide assurance of adequate throughput capacity. This assumes that only one Hanford HLW processing facility will be constructed, and the melter throughput required will be doubled.

3. We recommend that a funding scenario should be developed to minimize overall program cost because the savings from HLW vitrification improvements are dependent on the ability for retrieval, pretreatment,

and low-level waste vitrification also to increase throughput. The savings from optimizing these other three areas of the facility could substantially exceed the savings from the HLW vitrification improvements.

2.4 INEEL

1. Improvements in waste form flexibility and melter capabilities targeted primarily at Hanford also have potential to enhance waste loading and process efficiencies at INEEL, depending on the flowsheet selected for calcine at that site.

2. Technical advances that have the effect of allowing more crystallization in the glass should be beneficial to waste loading in some INEEL process options. Melters with features that allow processing of high volume fractions of crystals in the glass, along with justification for repository acceptance, could open formulation ranges or nonborosilicate waste form options advantageous to waste loading.

3. Performing detailed waste loading assessments for projected waste feed compositions, analogous to the cluster analysis performed on Hanford HLW in this study, should be considered as soon as INEEL flowsheets stabilize and retrieval and blending plans have matured.

4. Vitrification of sodium-bearing waste (SBW) at INEEL can be accomplished with reasonable waste loadings using the existing Joule-heated ceramic melter technology. For calcine wastes, there is some chance that the ACCM could have sufficient advantages over the Joule-heated ceramic melter to justify its development for that application alone.

3.0 Importance of Waste Loading

The process of preparing a waste form for the repository is dependent on meeting certain criteria to demonstrate that an acceptable product has been produced. These requirements are defined in the WA-SRD and WAPS documents prepared by DOE-RW and DOE-EM, respectively. The overall cost of disposing of the waste form is a combination of capital and operating costs at both the producing sites and the repository. However, this assumes that the operating cost of the sites does not increase significantly, negating the repository savings and thereby increasing the overall program cost. One potential way to reduce the number of canistered waste forms is to increase the waste loading in the waste form (glass). If this is accomplished at the same throughput rate as the lower waste loading, then the total operating time will be reduced, resulting in incremental savings at both the site and the repository. The following discussion relates the impact of various requirements on the ability to produce glass at a higher waste loading.

3.1 Description and Definitions Regarding Waste Loading

The nuclear waste at the various sites consists of both soluble and insoluble components that can be separated for processing as either low-level waste or HLW. These streams may also contain some materials that are considered glass formers (boron, silica, etc.) but are generally not in high concentrations. Waste loading is generally defined (in percent) as the weight of cation elements in the waste feed expressed as their predominant oxides, divided by the total weight of the glass produced. For the purpose of this Waste Form and Melter Technology review, waste loading is defined as follows:

- **Non-volatile metals**: Includes all HLW sludge components converted to their oxides, including oxides also added as glass formers. For the purpose of estimating waste loading, the most abundant single metal oxide form in equilibrium in glass under air at 1150°C will be assumed for multivalent elements (even for higher temperature melting). Examples of those multivalent oxides in their most abundant state include Fe_2O_3, Ce_2O_3, Cr_2O_3, U_3O_8, CoO, TcO_2, P_2O_5, SO_3 and MnO.

- **Volatile metals**: Excludes mercury and iodine, as these have essentially no retention in glass during vitrification.

- **Semi-volatile metals**: Components such as cesium, chloride and fluoride will only be partially incorporated into the glass. Semi-volatile materials captured in the off-gas condensate, as soluble species, may also not be recycled to the HLW process. However, to remain on the conservative side, waste loading will account for 100% of these species. Halogens that are retained in the glass will be reported in elemental form (e.g., fluorine and chlorine). The over-counting of anions is not expected to significantly impact waste loading estimates.

3.2 Factors Affecting Waste Loading for HLW Processing

3.2.1 Regulatory Requirements

The DOE-RW is responsible for defining the requirement for accepting waste for the repository. These requirements are documented in the WA-SRD, Revision 3. Section 4.2.2 of the WA-SRD pertains to acceptance criteria imposed by the Codes of Federal Regulation, and relates to both spent nuclear fuel (SNF) and HLW. Although these requirements do not directly impact the amount of waste loading in the waste form, knowledge of certain characteristics are necessary to understand potential alternatives to the current waste form. The most significant of these are as follows:

- The waste form must be in a solid form and placed in a sealed canister.
- The waste form is consolidated, if in a particulate form, to limit the availability and generation of particulates.
- The canistered waste form must not contain any combustibles relative to the repository environment unless it can be demonstrated that a fire involving the waste packages containing combustibles will not adversely affect other waste packages, any structures, systems, and components important to safety, or the repository's ability for waste isolation.
- The canistered waste form must be designed for criticality safety assuming occurrence of design-based events.
- The canistered waste form must not contain or generate materials that are explosive, pyrophoric, or chemically reactive in a form or amount that could compromise the repository’s ability to perform its isolation function or satisfy its performance objectives.
- The canistered waste form must not contain or generate free liquids in the waste package to an amount that could compromise the ability of the waste package to achieve performance objectives related to containment of the waste form or result in spillage and spread of contamination in the event of waste package perforation during the period from placement in a waste package through permanent closure of the repository.

In summary, to satisfy these requirements, a criticality-safe, canistered, consolidated solid waste form, free of combustibles, explosives, pyrophorics, chemically reactive materials and water or water-forming materials must be produced. Of particular note is that these requirements do not impose any performance requirements on the waste form.

3.2.2 Repository Waste Acceptance Requirements

The DOE-EM is responsible for establishing the specifications for meeting the WA-SRD requirements. These specifications, which expand on the WA-SRD requirements, are defined in the WAPS. This document requires estimates of chemical composition and radionuclide content of the waste to provide the repository with information necessary to make projections on inventories and performance; this information has no direct bearing on the waste loading that the producer can accommodate in the waste form. These documents also require a specific canister material that serves as the container for the consolidated waste form; these requirements also have no direct bearing on the waste loading that the producer can accommodate in the waste form, with the exception of one interaction that will be discussed below. A third type of information

required relates directly to the waste form itself and contains all the requirements imposed by the regulatory requirements discussed above and specific requirements related to the compositional and radiological aspects of the waste form. These latter specific requirements, discussed below, do place restrictions on type and condition of the waste form that can influence the waste loading. The following requirements can result in restricted waste loading:

- **The waste form is borosilicate glass**: Other waste forms may have lower volumes for all or some of the compositions existing in the storage tanks.

- **Waste form compatibility with canister**: The waste form must not jeopardize canister performance. This would need to be demonstrated for non-borosilicate waste forms.

- **Product consistency requirements**: If the definition of this requirement is relaxed, additional waste loading may be possible, and other waste forms would require development of a similar type of test. Elimination of this requirement would permit production of highly soluble waste forms that could significantly reduce waste volumes.

- **Waste form phases**: This is a reporting requirement but would define development requirements if the waste is in significant quantity or the crystals are highly complex. Higher waste loading has a higher probability of increased crystal formation. Distribution of radionuclides between the waste phases would have to be demonstrated to ensure that release rates are comparable to a homogeneous waste form.

- **Hazardous waste loading**: Elimination/modification of this criterion (toxicity characteristic leaching procedure, etc.) could increase waste loading, but is not likely. This criterion may be the limiting requirement on waste loading if the product consistency requirement were eliminated.

- **Heat generation**: Heat generation is limited to 1500 watts per 3-m canister and 2540 watts per 4.5-m canister.

- **Dose rate**: Maximum dose rate is limited to a surface gamma dose rate of 10^5 rem/hr and a maximum neutron dose rate of 10 rem/hr.

3.2.3 Processing Constraints

The ability to produce an acceptable glass or glass ceramic form not only depends on the composition of the product but also on the facilities necessary to produce the form. The following process constraints can be limits on waste loading.

- **Liquidus**: The temperature at which crystal formation is initiated on cooling or the temperature at which dissolution of crystalline phases takes place on heating. If the process cannot remove the crystals that form, then the equipment may plug with nontransferable material, forcing process shutdown. The ability to vitrify compositions that have a higher liquidus as a result of having higher waste loading would reduce production requirements.

- **Solubility limits in glass**: Solubility limits impact waste loading since they may result in an unacceptable secondary glass phase. They may also result in a secondary phase within the processing equipment that could cause deleterious corrosion and processing instabilities.

In addition, the following properties, although they may not impact waste loading, are important for

overall system performance:

- **Glass viscosity**: Glass viscosity may impact the ability to process the waste form by affecting settling characteristics, pouring control, and internal heat flux for melting and throughput.

- **Materials of construction limits**: Various glass/glass-ceramic compositions have higher corrosion rates or require operating temperatures where corrosion rates are greater, reducing the availability of the process.

- **Volatility of components from the melter**: Volatile components are recovered in the off-gas system and must be recycled to the process because of their radionuclide content. This is akin to a solubility limit that can increase total glass requirements.

- **Resistivity**: The resistivity governs the electrical requirement and the ability to generate heat input to the melter.

3.2.4 Waste Compliance Strategy Effects

The producer must demonstrate control of waste form production by comparing, either directly or indirectly, production samples to the Environmental Assessment benchmark glass. The producer must describe the method for demonstrating compliance in the Waste Compliance Plan and shall provide verification in the production records. The producer must demonstrate the ability to comply with the specification in the Waste Qualification Report.

This is the criterion that must be satisfied by the product consistency requirement and does not directly impact the ability to increase waste loading. However, the parameters associated with this criterion and the respective error bands do influence the waste loading (e.g., the wide error bands for liquidus values force a conservative waste loading). In addition, this criterion does directly impact the program required to demonstrate compliance and would be more complex for processes that produce different or more complex waste forms with potentially higher development costs.

3.3 Factors Affecting Costs of HLW Immobilization and Disposal

The cost of immobilizing and disposing of HLW is a compilation of

- research and technology cost of developing and qualifying the immobilization waste form and melter technology
- capital and operating costs of the production facility
- capital and operating costs of the canistered waste form interim storage facility
- repository cost for disposing of the canistered waste form.

Improving waste loading reduces the number of canisters that need to be produced. However, depending on the waste form type, the program cost for HLW disposal could be influenced either positively or negatively by waste loading. Following is a summary of the impact expected for the various cost elements as a result of increased waste loading.

- Research and technology costs would be increased since the new or modified waste form and melter technology would require more testing to ensure that it would meet the program requirements (even if some of the requirements were relaxed). It is not expected that this cost would be significant enough to

eliminate a waste form unless it caused a significant delay in the program.

- The capital cost for the facility remains relatively constant, although it may increase if the melter technology is changed. It is expected that even a 10% increase in capital cost would be less influential compared to shortening the operating duration.

- The waste loading increase would directly affect the facility operating cost since the operating period could be reduced. Operating costs are expected to be the producers' major cost item.

- The storage costs would also be reduced proportionally by improved waste loading, assuming that all canisters had to be stored prior to shipment to the repository. This is not expected to be a major cost impact since storage costs are small compared to production costs and (assuming a repository is approved) storage for all the canisters would not be required.

- The repository cost for disposal is a major cost item. Although this cost is significant, the overall cost benefit from increased waste loading depends on whether the cost is considered an incremental cost or fully proportioned cost based on repository space consumed.

It is expected that waste-loading improvements [i.e., reduction in canister production (assuming a constant process throughput)] would have its biggest cost impact from reduced operating time resulting from fewer canisters. This would definitely be true if an incremental repository cost were used in the analysis instead of the current cost allocation formula.

4.0 Status of Baseline HLW Processing at DOE Sites

4.1 Savannah River Site

One hundred thirty million liters of HLW are stored in 49 storage tanks at SRS in Aiken, South Carolina. This waste consists of three general forms: (1) a supernate consisting of nonprecipitatable salts; (2) salt cake; and (3) metallic oxide sludges. Waste operations at SRS are performed at the tank farm prior to transfer of the waste to the Defense Waste Processing Facility (DWPF) and are the result of two processes; therefore, the HLW sludges basically consist of two types, high iron and high aluminum. These sludges were only partially segregated over the years, thus the compositions vary across the entire range of aluminum and iron concentrations. Wastes high in aluminum are treated with caustic to solubilize part of the aluminum, since aluminum is more restrictive on borosilicate formulations than iron. The sludges are also washed to reduce the alkali content, which could increase glass quantity if the original interstitial liquor were fed to the melter system. Current operations at SRS do not process the salt or supernate wastes since the proposed process for removing cesium, strontium, and plutonium produced unacceptable flammable benzene concentrations.

The sludges at SRS are produced in macro batches (1 to 3 million liters) in a feed tank to the DWPF. The feed tank is thoroughly characterized for composition and radionuclides, as required to meet WA-SRD and WAPS reporting requirements. This tank, which can be completely homogenized, is sampled and the sample is processed through the Savannah River Technology Center to establish that an acceptable glass that will meet the PCT can be produced and meet the Glass Product Control Program parameters. The DWPF processes this sludge through its system in batches of approximately 20,000 liters. After processing to remove mercury and adjust redox ratio, frit is added and the product sampled. The sample is tested for acceptability relative to Product Composition Control System parameters and, if acceptable, approved for addition to the melter feed tank. The melter feed tank is analyzed after each addition and an average of these analyses for the macro batch is reported to the repository. The DWPF uses a Joule-heated ceramic melter for melting of the waste form and is typically limited to operation in the range of 1150 to 1200°C.

The expected range of feed compositions, from high iron to high aluminum, were tested in the production melter on simulated waste material to demonstrate the ability to produce a product that meets the PCT prior to radioactive operation.

The DWPF has processed in excess of 1000 canisters or about 1.8 million kilograms of glass using the first melter. Waste loading for the DWPF is approximately 25 wt% waste oxides. The limiting operating parameter for waste loading identified in the Product Composition Control System is maintaining a satisfactory liquidus temperature. The DWPF melter does not have agitation capability; therefore, it has a limited ability to remove crystalline precipitate by other means than internal heat flux circulation.

Increasing waste loading at the DWPF would require providing agitation capability to permit operation at higher liquidus compositions or converting the system to a high-temperature melter configuration.

4.2 West Valley Demonstration Project

The West Valley Demonstration Project (WVDP) in West Valley, New York, stored approximately 2.3 million liters of HLW in two waste tanks. One of the tanks contained an acidic waste, while the other tank contained an alkaline waste, both of which were generated during reprocessing of commercial nuclear fuels. The tanks were mixed prior to processing through the melter system. The waste feed composition was well defined, and control of the feed composition was maintained similar to that at the DWPF, with the exception of shard samples that were taken from the canisters and analyzed for composition as a method of satisfying the compositional reporting requirements of the WA-SRD and WAPS. The WVDP uses a Joule-heated ceramic melter for glass production and typically operates at approximately 25 wt% waste oxide loading.

The WVDP produced about 350 canisters in its production operation and is currently in a system cleanup mode prior to plant decontamination and decommissioning

4.3 Hanford

The Hanford Site in Richland, Washington, stores 204 million liters of HLW in 177 underground storage tanks. This waste was produced by numerous processes at the site over its 60-year history. This study estimates that the waste can be divided into 17 compositional groups that would impact glass formulation (based on current waste characterization status). The current planned facility for processing Hanford HLW, the WTP uses a Joule-heated ceramic melter as the baseline. This site recently underwent a change in the major waste contractor, and as a result the facility scope and requirements were modified.

The Hanford Site has defined a sequence for feeding the waste to the production facility that generates about 89 different batch compositions. Whether this sequence will result in actuality or if internal recycles between the pretreatment, HLW, and low-level systems will impact the operation is uncertain. The original contractor had not selected a method of assuring product consistency as required by the WA-SRD or WAPS. The current process flow diagrams do not have facilities adequate to satisfy any of the three proposed product control systems.

The ability to improve waste loading at the Hanford Site will depend on whether the design is flexible enough (as outlined in this study) to handle higher liquidus compositions or accommodate alternate melter technologies.

4.4 Idaho National Engineering and Environmental Laboratory

The Idaho National Engineering and Environmental Laboratory stores approximately 5.7 million liters of SBW and 4,000 cubic meters of calcine produced from the reprocessing of naval fuels between 1952 and 1991. The SBW is stored in eleven stainless-steel underground tanks as acidic liquids with some settled solids. The calcine, obtained by processing liquid wastes at 400 to 600°C, is stored dry in six stainless steel bin sets. Vitrification of both of these wastes is being planned, with the SBW to be vitrified from 2007 to 2012 and the calcine to be vitrified in 2017 and beyond. Specific processes for these treatments have not yet been selected; however, waste loading is currently based on current perceived limitations for Joule-heated ceramic melter-type operations. Any relaxation in requirements or change in technologies would probably not impact SBW vitirification but could impact calcine vitrification.

The ability to improve waste loading at Idaho will depend on whether the vitrification process and plant

design is flexible enough to handle characteristics as outlined in this study to handle higher liquidus compositions or accommodate alternate melter technologies.

5.0 Potential for Enhancement of DOE HLW Processing

5.1 General Approach

This study focused on identifying enhancements or alternatives for solidification of Hanford Site HLW with potential for implementation to achieve major cost reductions within reasonable long-term program risks. As identified in previous sections, waste loading has the largest impact on overall system cost, although processing rate is also important. Therefore, a major effort in this study was directed to establishing a clear picture of the key technical limitations that affect waste loading, especially at Hanford. Clear definition of limitations provides a basis from which alternative technological approaches could be identified and evaluated. The objective was to make a comparison of alternatives to a well-defined baseline, so the potential cost implications could be defined. To pursue this objective in a disciplined manner, the approach to identification of promising technical innovations followed a path consisting of the following steps:

- Define the current requirements and constraints that govern glass formulations to support an understanding of how these factors affect waste loading.

- Establish a quantitative model for approximating the range of compositions found in Hanford tank wastes to establish a consistent basis for comparing alternative waste form materials and melting technologies.

- Establish a baseline model, using the best currently available data and constraints for formulating borosilicate waste glasses, to identify the baseline waste loading and limiting factors for a reasonable set of groupings of Hanford tanks with compositional similarities.

- Identify alternative waste forms that may represent a potential for increased waste loading, if current repository requirements (or interpretations) could be modified and suitable melting (or processing) technologies could be made available.

- Identify and evaluate alternative melter processing technologies, relative to the baseline of the current DWPF-/WVDP-type Joule-heated ceramic melters.

- Match melter technology features and capabilities to the processing requirements of enhanced borosilicate glasses and alternative waste forms.

- Assess the cost implications of waste loading enhancements and alternative melter technologies relative to the current conceptual design and program plans for the Hanford WTP and, on a limited basis, other sites.

The full scope and detailed results of the above steps are reflected in the series of reports developed, and later compiled into a final report by the Study Team (Perez, Jr. et al. 2001). Combining the summary results of the evaluations on glass waste loading, alternative waste forms, and alternative melter technologies resulted in a set of discrete options that appear to have potential for providing cost savings if the essential technical elements are successfully developed. Judgments were also made on the nature and level of risks to successful development of these options.

Criteria for screening the technology alternatives were identified as needed to fit the specific area of evaluation. The criteria and factors used in the assessment of waste forms and those applicable to the assessment of melting technologies are identified below.

5.2 Optimizing Waste Form Materials

The basic factors that must be considered when approaching the optimization of waste form materials were presented in Section 3. For optimizing waste form materials, the critical factors come from two sources:

- The Waste Acceptance Requirements for disposal, which define specific properties and configurations that the waste form materials must fall within.

- Processing constraints, which are determined primarily by the capabilities of a selected process technology and its design features. There can be interrelationships between the properties required by Waste Acceptance Requirements and the behavior of the waste materials in processing.

The specific approach to identifying how factors in each of these areas affect or constrain waste loading is described below.

5.3 Addressing Repository Requirements

A systematic assessment was made of the implications for waste loading and waste form processing from each specific requirement in the WAPS and WA-SRD. The basis for each requirement was identified, and it was determined whether a modification to the requirement could affect waste loading or other processing cost contributors. The criteria applied were as follows:

- **Primary**: Could a modification of the requirement allow increased waste loading?

- **Secondary**: Could modification of the requirement provide a basis for significant increase in glass production rate or decrease in the cost of processing?

Particular emphasis was focused on DOE-RW-imposed requirements related to repository design and performance, as distinguished from requirements derived from specific regulations (Code of Federal Regulations or statutes).

In consideration of the risks associated with departure from current institutional baselines, potential changes to requirements were first related to the current borosilicate glass standard waste form. Further consideration was made as to whether the requirement might restrict or need to be modified if nonborosilicate waste forms appear to be attractive based on assessment against other criteria.

This assessment identified only one repository requirement that has a direct effect on waste loading for borosilicate glass: the PCT requirement (WAPS 1.3, WA-SRD 4.2.3), which involves a measurement of glass durability. Based on review of the DWPF and WVDP strategies for compliance with this requirement, it was determined that details of the compliance approach (sampling points and levels) could influence waste loading. Other requirements that may impact processing costs, depending on interpretation and compliance strategy, are those involving reporting of composition, phases present, and phase stability. More detailed descriptions of the relationship of these specifications to specific waste loading enhancements for Hanford HLW are presented in Section 8.

For any nonborosilicate waste form identified as attractive for waste loading optimization, there would need to be revisions to the waste acceptance requirements. In addition to the change in WAPS 1.1, WA-SRD 4.2.2, and WA-SRD 4.2.3, which requires the waste form to be borosilicate glass, there would need to be changes in the consistency/durability test specification and probably changes in the requirements associated with reporting of compositions, phases, and phase stability. Another requirement that could impact alternative waste forms is WAPS 3.5, which addresses protection from canister internal corrosion.

As part of this assessment, a set of questions on the potential for flexibility and implications of changes to the Waste Acceptance Requirements were addressed to DOE-RW. The results of that inquiry are discussed in Section 10.

5.4 Addressing Processing Constraints

Processing constraints to waste loading were also systematically assessed through the same methodology as applied to the repository requirements. The processing constraints considered arise from the range of properties that allow acceptable melting and pouring behavior for a specific melter design, as described in Section 3. The properties considered in the evaluation matrix were liquidus temperature, glass viscosity, solubility limits, materials limitations, and volatility. Experience to date on the manner in which these constraints have affected the waste loadings and processing rates achieved during production at DWPF and WVDP were considered in the assessment.

Waste loading is affected by these constraints through the application of correlations relating physical properties to glass compositions. Glass composition regions with acceptable properties are mapped out through modeling with these correlations. By appropriate selection, specific amounts of glass-forming additives are mixed with a defined composition of the HLW waste feed to achieve an acceptable glass product composition target. The minimum amount of glass-forming chemicals needed to bring the glass composition into an acceptable range for all the property constraints (both processing and repository requirements) represents the maximum waste loading.

There are three possible courses to follow in pursuing optimum waste loading with any specific HLW waste feed composition:

- For a selected waste form, such as borosilicate glass, refinement in the property-composition relationships can affect the limiting property value that glass compositions must meet. If the limit can be expanded to accommodate more of the components in the waste that influence the property, an increase in waste loading is achieved. This may be accomplished through obtaining more data on the property composition relationships to reduce uncertainties in the correlations. Alternatively, refinement in understanding the relationships between the property and the performance of the melter system can support changing limits to accommodate more of the problem components in the waste.

- The second approach, for a specific waste form such as borosilicate glass, is to change the characteristics of the melter system. The applicable considerations for this approach are discussed in the following section

- The third approach is to find a different waste form material, which offers a less restrictive set of property constraints relative to the constituents of the HLW waste feed. Property-composition relationships will still be important for an alternative waste form material to ensure that it can be processed into an acceptable product with a selected melter technology. The challenge in this option is to find a combination of waste form product compositions and melting system capabilities that minimize the amount of additives needed to obtain acceptable properties for processing and product performance.

In this study, a methodology was adopted that allowed a quantitative assessment of the compositional relationships for the specific constraints that establish waste loadings for Hanford tank wastes. The best available property-composition models for borosilicate glass were employed along with best estimates of pretreated Hanford waste tank compositions. According to the Hanford retrieval schedule, the transport of materials is traced from tank to tank during retrieval and the expected composition then calculated. This process results in 89 batches for feed, which were combined into 17 compositional groups or clusters with similar chemical contents. Borosilicate glass formulations were defined for all clusters, using the currently accepted constraint limits for Joule-heated ceramic melters, which defined the maximum waste loading achievable for each cluster. This allowed a definition of the specific waste components that affect the dominant limiting constraint for each grouping. It was also possible to define a hierarchy of the limiting constraints, allowing assessment of the implications of removing the dominant limit by means of waste form or process changes.

Using this methodology, sensitivity studies were performed for a number of cases involving borosilicate waste form modifications, alternative melter capabilities, and alternative waste forms. The results of these sensitivity studies are summarized in subsequent sections of this report. The methodology provided the basis to evaluate the relative merits of different waste form and melter technology alternatives. The criteria applied in judging the relative merits of waste form modifications and alternatives (including the effect of changes in disposal requirements) are

- size of the reduction in total waste form product volume for the Hanford tank waste inventory

- relative maturity and performance uncertainties of any alternative melter processing features or technologies (more detailed criteria for judging melter technologies are provided in subsequent sections of this report) and severity of potential viability issues

- change in the WTP and process assumptions cost baseline

- relative maturity of understanding on the processing characteristics and properties of alternative waste form materials and severity of potential viability issues

- extent of changes that might be required in repository Waste Acceptance Requirements

- extent to which the alternative would deviate from current repository performance assessment modeling baselines.

5.5 Optimizing Melting Processes

The potential for major reduction of total program cost within reasonable long-term program risks through improved vitrification is primarily through higher waste loading and more predictable processing rate. General considerations in selecting and developing melter technologies are discussed in this subsection, and specific technologies are compared and assessed in Section 7.

One of the three possible approaches described above for maximizing waste loading with any specific HLW feed composition is to change the characteristics of the melter system, which includes both the hardware design and operating practices. Hardware includes all components for (1) feeding raw materials; (2) heating the raw materials to cause reactions and molten glass to lower its viscosity; (3) containing molten glass; (4) homogenizing the molten glass; and (5) delivering molten glass for shaping into a product. Operating practices include (1) the choice of targets for steady-state conditions, (2) the control strategy for maintaining these conditions, and (3) an adaptation strategy for responding to major changes in feed, processing rate goals, or normal deterioration of the melter. Although the hardware features are the most obvious to an outside observer, it is more often the operating practices that determine the degree to which a melter meets its production goals. Thus, the optimization of the operating practices is at least as important as selection or design of the hardware.

The choices involved in changing the design and operation of the melter to increase waste loading also influence its reliability, and thus they impact the predictability of the vitrification processing rate. (Note that the predictability has far more impact on total program costs than the actual level of processing rate, since all processing steps are designed to be most efficient when working together at the design rate. The actual level can be easily modified during the design stage with relatively small impact on cost.) In the discussion that follows, these two goals of higher waste loading and more predictable processing rate will be addressed together, since their effects on choices of melter design and operating practices are so intertwined.

5.5.1 Factors in Selecting Melter Systems

Every HLW glass melter consists of a system combining components that provide the means for feeding, heating, containing, homogenizing and delivering. (Commercial glass melters also have means for removing bubbles, a major point of differentiation from HLW melters.) The lowest risk, fastest, least expensive strategy to develop a new melter is to create a new combination of existing, proven components. The more unproven components that are included, the higher the risk, cost and development time of the melter system. Selection of an appropriate melter design requires balancing the performance criteria for the melter, which include safe and reliable operation, consistent products, flexibility to handle various feeds, and low cost. The prioritized performance criteria employed in this review will be discussed in more detail in Section 7.4.

The design of a melter should be tailored to the properties of the glass to be melted, the quality of the glass, and the required production rate. (Quality in this context means the degree to which the waste product is uniform in space and time.) Thus, both the properties of the molten glass and the quality requirements (uniformity of composition on various dimensional scales, size, and number of acceptable inclusions such as crystals and bubbles) need to be specified before selecting an appropriate melter. When these requirements cannot be precisely defined, the melter must be designed to handle the most extreme cases. The increased flexibility normally comes at the expense of some other desirable characteristics, such as simplicity, operational reliability, low cost, and compact size.

Once a melter design is chosen, the reasoning is reversed and the melter now places constraints on the glasses that can be melted efficiently. Only glasses having properties that fall in certain ranges can be melted

without sacrificing goals for glass quality, production rate, or melter lifetime. These constraints imposed on the glass properties by the melter translate into limitations on waste loading.

5.5.2 Relationships of Melter System Features to Waste Form Materials Properties

The manner in which the melter system design and operating practices are determined by, and limit, the melt properties and behavior, and the product quality, are introduced here and discussed further in Attachment 1. The nature of these limitations and the influence waste loading has on them are discussed for crystallization, molten salt phase separation, foaming, volatilization, viscosity, chemical homogeneity, operating temperature, melter heating methods, and discharge systems. Waste loading has a minor role, except as it affects melt viscosity.

5.5.2.1 Waste Glass Properties and Behavior

Crystallization is most often the process that limits waste loading. If a crystal-free glass is to be produced by the melter, waste loading is limited to the amount of waste that will stay in solution in the coldest part of the molten glass bath. Designing the melter to operate hotter can extend this limit. Alternatively, the melter can be designed to operate with a significant level of crystals kept in suspension in the melt. The largest gains in waste loading are estimated to result from operating with suspended crystals discharged each time glass is poured into a canister. This assumes that a waste form containing suspended crystals is acceptable. Further crystallization may occur in the canister during slow cooling, but that does not influence the selection of a melter. If necessary, crystallization in the canister could be suppressed by cooling the canister during filling.

Crystallization of noble metals (most often ruthenium oxide, but also metallic rhodium and palladium) also can occur with some HLW glasses. Because these crystals are electrically conductive, they pose a danger to the electric heating in both Joule- and induction-heated melters. They generally precipitate when the oxidation state of the melt (the amount of oxygen available for chemical reactions) is too low. A low oxidation state is created by high temperatures or by the addition of reducing agents to the feed (conditions normally employed to suppress foaming). Means are needed to prevent the accumulation of noble metal crystals in the melter by removing them to the canister with the waste glass.

Liquid phase separation is similar to crystallization, except that the new phase that forms in the glass melt is a liquid rather than a solid. In HLW melts, the phases most likely to separate are molten salts containing sulfates or halides (chlorine, fluorine). Although they can be removed from the melter by volatilization, high levels of sulfur or halides in the waste could limit waste loadings.

Foaming limits melting rate. A layer of foam forms just under the cold cap, where it blocks heat transfer from the bath to the unmelted feed. This occurs to some degree in all cold cap melting and is a key determinant of the melting rate. In HLW vitrification, it can be especially troublesome because of the high concentration of elements (such as iron) that easily change oxidation state, producing gases in and under the cold cap. It is normally addressed by batch additives rather than by reduced waste loading.

Volatilization could limit loading of wastes containing halides. Materials volatilized in the melter are captured in the off-gas system. If all volatilized radionuclides can be separated and recycled to the melter, high volatilization only makes the process more complex. But if their separation is impractical, then they create a highly undesirable secondary waste stream. Melters that present little free melt surface, such as those with cold caps, have such low volatilization losses that this behavior is not waste limiting, but it essentially

eliminates from practical consideration those heating methods or melter designs that have very hot or very large exposed surfaces.

Viscosity does not normally limit waste loading unless the nature of the feed changes very markedly. A melter can be designed to handle any viscosity in a very wide range (e.g., varying by a factor of 100), but any given melter is only efficient in a fairly narrow range (e.g., a factor of 5). The viscosity range of a melter can be extended by adding special features, such as multiple delivery systems designed for different flow rates.

A number of other melt properties could limit waste loading in glass waste forms other than borosilicates but are unlikely to pose major problems with Hanford wastes. Electrical resistivity (or high frequency impedance, for cold wall induction melting) is unlikely to limit waste loading for Hanford HLW borosilicate because of their relatively high alkali content and low resistivity. Corrosivity toward refractories is primarily related not to chemical effects but rather to transport processes (diffusion and convection). Corrosion is strongly increased by lower melt viscosity and by higher convection velocities, but can often be countered by cooling. Corrosivity toward electrodes and other metal components is primarily a chemical process, and usually imposes a narrow oxidation state range on a melter, but does not limit waste loading.

5.5.2.2 Waste Glass Quality

The glass quality parameter that is limiting for a waste glass is chemical homogeneity, since leachablilty (e.g., in the PCT) is quite sensitive to small-scale inhomogeneity. Better homogeneity results from better melt convection or longer residence time, both of which are determined by melter design. Homogeneity can be adversely affected by waste loadings high enough to cause formation of second phases.

5.5.2.3 Melter Temperature Capability

The operating temperature of a melter is limited by the temperature-dependent mechanical properties of the melter materials of construction. The selection of these materials is in turn limited by their chemical reactions with the molten glass, and is thus influenced to a degree by waste loading. Although slowly dissolving oxide ceramics can provide containment, they are too brittle for reliable stirrers, bubblers, level probes, and thermocouple wells, for which metal components are needed. For Joule-heated ceramic melters, metals are also needed for electrodes. Unfortunately, the metals that have better chemical properties also have poorer strength at higher temperatures. The best compromise for HLW is Inconel™, a nickel-chromium alloy with a maximum use temperature of around 1200°C. German studies have shown that air cooling of electrodes could permit their use in melts nearly 150°C hotter than this use temperature. Aggressive air or water cooling of the electrodes and other metal parts has the potential to safely extend the present operating temperature limit of about 1150°C on the DWPF and WVDP melters to 1350°C, high enough to permit melting glasses with significantly higher waste loadings. Temperatures above about 1350°C probably are impractical to achieve just by cooling Inconel™. Other metals are needed, but significant efforts to develop metals having higher use temperatures in HLW melts have thus far been unsuccessful.

The maximum operating temperature of a melter in turn limits the glass compositions that can be melted, primarily through the effect of temperature on viscosity and crystallization.

5.5.2.4 Melter Heating Methods

The fundamental conflict in heating glass melters arises from the fact that most of the essential reactions to make glass from raw materials proceed to completion at relatively low temperatures (well below 1000°C), but the thermal conductivity of the materials is so poor that high temperatures (or large areas, or intensive stirring) are needed to achieve reasonable heat transfer rates. Most of the troublesome reactions, such as volatilization and refractory corrosion, become important only at higher temperatures. Thus, low temperature, distributed heat sources are much more useful than high-intensity sources.

Broadly, melters can be heated by two methods: (1) externally, with heat transferred into the melt, and (2) internally, with heat generated within the melt. The critical melt property is its thermal conductivity. For HLW glasses, which have poor infrared transmission, the thermal conductivity is similar to that of snow and is only a few times higher than that of wood. Thus, external heat sources require very high surface temperature plus good melt convection, or else heat transfer (and the melting rate) will be very slow.

The most common internal heating source is electrical resistance. Joule or resistive heating occurs when a voltage field creates ion movement. The rate at which energy can be generated by this process is limited in molten glass by the fact that the electrical resistivity decreases with increasing temperature, creating an inherently unstable condition in which increasing power causes hot channels to form through the melt while other portions lose temperature. Energy input also is limited by irreversible electrochemical reactions that can rapidly destroy the electrodes. High frequency electromagnetic fields cause heating by both resistive heating and atom vibration in glasses. This is used both in microwave heating and cold-wall induction melting, neither of which require electrodes in contact with the melt.

5.5.2.5 Waste Glass Discharge Systems

The most serious operational problems in glass melters usually occur with the delivery system. The ease of controlling glass flow, as well as the numerous problems that arise, are both a result of the unique flow behavior of glasses. Viscosity and infrared emissivity are the only significant physical properties. (Surface tension also can be important, but only for very small streams, as in fiber pulling.) The unusual behavior of glass is due to the fact that the viscosity changes exponentially with temperature, roughly doubling for every 100°C cooling. Surface heat loss by radiation is extremely rapid for high reduced-iron waste glasses, so the surface viscosity increases rapidly as soon as a glass stream can “see” cooler surroundings. This makes it difficult to avoid stream deviation or buildup on orifice rims. In general, the most reliable delivery systems are intensely heated well beyond the last point of stream contact and are thermally symmetrical about the axis of the stream.

5.5.3 Tools for Development and Optimization of Melters

A key factor in the success of a glass melter is the method for experimentally determining which of many ideas yield the best design and operating practices. The chemical and physical processes occurring inside glass melters are far too numerous and interactive to permit design from first principles. Even the best lab tests and computational methods are only sources of ideas and directions, not definitive answers, for the many questions that must be answered. Successful designs depend on either many generations of evolution, as is the case with most industrial melters today, or on well-planned programs of testing prior to production. This latter approach is necessary for HLW vitrification because of time constraints and the severe consequences of unsatisfactory melter performance.

A critical decision in development of new melter technology involves the timing and extent of trials

conducted in melters intended to simulate the behavior of the final production melter. These development melters can be full- or reduced-scale, and they can have all or only part of the features and components (e.g., devices for feeding raw materials and removing product, stirrers, auxiliary heat sources, etc.) of the production melter. Typically, they have additional instrumentation and observation and sampling ports to gather more information on conditions in the melter. Not only the trial melts but also post-test autopsies of pilot and failed production melters are especially rich sources of information.

5.5.3.1 Simulants in Testing

Simulants should be used whenever possible because of the high cost of testing in radioactive facilities. However, the term simulant takes on a new meaning when applied to testing of melting processes, and especially of the process of converting cold feed to molten glass in the cold cap. For this, not only must the overall chemical analysis be correct, but also the individual compounds, their particle size distributions, surface chemistry, and contaminants must match the actual waste after pretreatment. This is a daunting technical task and major expense. It cannot be accomplished by detailed characterization of actual wastes and proposed simulants alone, but must include paired hot-cell and cold melting tests in pilot melters to verify that the difference is small enough to be corrected for or ignored. Even with this precaution, tests with actual waste are a very important part of the development process. Although extremely expensive, the cost of such testing is greatly exceeded by the cost of vitrification processes that fail to perform as intended.

5.5.3.2 Laboratory and Pilot Testing

Laboratory melters (smaller scale and with some features or components missing) are most useful at both the early and late stage of development of a new melter technology. Their role is primarily to (1) identify potential show-stopping problems when the melter technology is largely unknown, and (2) answer very complex and specific questions when the overall melter process is relatively well understood. For example, the cold cap with all its complex chemical reactions can be satisfactorily simulated in a bench-scale melter, but only when appropriate melt velocities and temperatures (just below the cold cap) are known and when the equilibrium cold cap thickness is known. With this information, gained from observing production melters, a good simulator can be developed to test offline the effects of changes in raw materials, feeding practice, etc.

At the intermediate stages in development of a melter technology (where many of the issues with Joule-heated ceramic melters are today), a full-scale pilot melter that includes all key features and components is the only reliable tool to predict overall performance of the production melter. Valid comparisons can be made between melters of significantly different scale only when all the critical internal processes (chemical reactions, heat transfer and fluid flow, with all coupled) are well understood. Simulation of a melter requires that all of the significant processes not only be included but that they interact and have the correct relative impacts on the outcomes. When the detailed internal processes are only incompletely understood, a pilot melter operating at a smaller scale or with some features missing is very unlikely to provide a reliable simulation. Very large benefits could accrue from having a full-scale prototypical non-radioactive development melter available throughout the production period for offline tests of ideas for operating improvements. Without such a capability, all significant improvements will be thwarted by the high risk associated with trying them for the first time on a production melter.

Since a pilot melter does not need to be remotely operated, its cost is considerably lower than the production melter it simulates, and small compared with the savings achieved by keeping the production melter continually near optimum output. Measured in dollars per innovative solution, full-scale pilot melters are far less expensive than laboratory melters to develop new or extended technology. Measured in dollars per reliable conclusion, full-scale prototypical pilot melters also are far less expensive and risky than conducting trials in production melters to optimize melter operations. The cost of pilot melter testing (regardless of scale) is comprised of costs of (a) equipment and experimental design, (b) construction, (c) raw materials purchase, preparation and disposal, (d) melter operation and data gathering, (e) analytical measurements, and (f) data analysis and reporting. Of these, only construction and raw materials costs depend very much on scale. Even these costs are not proportional to scale (e.g., a 1/10-scale full-featured melter will cost at least half as much as a full-scale melter). Unfortunately, there is a tendency to focus on the more visible construction and raw materials costs, even though they typically make up well less than half of the total testing cost.

Some examples of melter testing that should be increased to reduce program risks related to waste loading and ensure that production goals are met are:

- Models that predict crystallinity and melting behavior for applicable composition ranges should be developed, using correlations from laboratory and small pilot scale melting tests. Full-scale melter tests with selected compositions will be needed to compare with and calibrate model predictions.

- The effect of suspended crystals on melter operation needs to be tested. A program is needed to determine what specific operating problems result from having some parts of the melter at temperatures well below the liquidus, and to determine the efficacy of measures for removing crystals from the melter. This includes 1) lab tests for characterizing the effect of composition on the formation, growth and settling of crystals in the melter, and 2) pilot melter tests for determining the effectiveness of such measures as stirring and bottom draining, and the impact of prolonged periods of idling without a cold cap.

- Pilot melter tests are needed to establish batch addition strategies and operating practices to avoid foam-related production limitations and precipitation of noble metals, because the control of oxidation state in the melt is sensitive to the dynamics of the complex reactions occurring in the cold cap.

- Glass formers should be adjusted for each batch of pretreated waste to maximize waste loadings. Chemical analyses, trial hot cell melts and property measurements will be needed. The alternative is to continue to use lower waste loadings to ensure that process and product requirements are met without such testing. Present practices would not allow pretesting of feed batches in hot cells after pretreatment and before introducing them into melters, because the long delay would require an unreasonable storage capacity for pretreated waste. Methods need to be developed to reduce the testing time to a reasonable storage period. This may require test methods development as well as resource decisions. Additional storage capacity may be needed for feed to allow for the testing time.

- There is presently an opportunity to reduce DWPF costs, since plant production is limited by vitrification. One of the spare DWPF melters might be set up as a cold (not radioactive) development melter, to run tests of ideas to improve DWPF melt rate and develop a better understanding of simulant characteristics that affect melt rate. This offline development has the potential to repay its cost many times over in reduced operating time and costs.

5.5.3.3 Testing in Production Melters

During production, numerous issues arise that were not anticipated by the testing during design development. For Hanford waste vitrification, the most important issues are likely to be related to unforeseen changes in the composition and character of the melter feed. The combined use of pilot and production melters for testing is an extremely powerful tool for relaxing the constraints such as those on waste loading presently imposed by liquidus and viscosity. A testing program should be planned for each of the DOE production melters as a way to both optimize operations and to gradually adapt to changing feeds and deterioration of the melter. Operating conditions will differ for each batch, and the idea that one operating condition can be learned and locked down should be avoided. An operating strategy is needed that takes full advantage of production operation to generate information for optimization of process conditions.

Since a production melter is the best possible simulator of itself, it is wasteful not to use it to improve the melting process. It can and should be used to suboptimize the process in the vicinity of its normal operating conditions. This can be accomplished at very low risk and cost by the EVolutionary OPerations (EVOP) approach, in which very small changes from the normal operating conditions are made repeatedly, with conclusions extracted from the small change in outputs discernible by statistical analysis. By this method, the operating conditions can be gradually evolved toward their local optimum, without ever making a change large enough to risk unacceptable product or damage to the equipment. In a remotely operated melter, it is more difficult to obtain the process measurements and samples needed to measure the change in outputs. Nevertheless, the cost of such testing can be amply repaid by the benefits of being able to smoothly adjust for changing feeds.

Another related standard method for low-risk, low-cost testing in production melters is pulse testing. This is especially useful for changes in feed. Advantage is taken of the natural inertia of the melter to avoid creating large unexpected changes in melter conditions. A proposed step change in feed (e.g., substitution of frit, change in amount of reductant) is tested by introducing it for a brief time or at a reduced level, then returning to normal conditions. If no unwanted effects are observed, another pulse of longer duration or higher concentration is tried. The duration of each pulse is increased each time no adverse effects are observed, until a decision can be reached to leave the process at the new conditions. This stepwise testing strategy can be used with any variable that can be easily turned on and off. It is appropriate for changes in feed, power input, cooling, stirrer speed, bubbler flow rate, etc., but not generally for hardware changes.

Procedures need to be developed for safe but efficient testing during hot production, using techniques such as EVOP and pulse testing. This will require rethinking of present change control procedures.

A very important opportunity for improvement is lost when design targets (for throughput, operating conditions or lifetime) are retained that were based on information available before production began and before the continuous learning opportunity provided by production was available. Production targets should be reassessed and reset periodically to reflect the <u>best</u> performance achieved to date.

6.0 Waste Form Evaluation

6.1 General Approach

6.1.1 Introduction/Overview

The optimization of the United States' nuclear waste vitrification program is predicated, in part, on (1) maximizing throughput rates in Joule-heated ceramic melters; (2) developing compositional flexibility in the currently accepted waste form, borosilicate glass, or developing new ones that can dissolve wastes to levels not achievable in borosilicate melts or are more suited for unusual waste compositions; and (3) gaining the repository acceptance of vitrified waste products that contain higher volume fractions of crystalline phases, but still meet minimum PCT requirements.

In evaluating alternative waste form materials, it is useful to review the scientific history that led to the choice of borosilicate glass as the primary waste form in the United States and subsequent milestones that have supported this decision. This discussion leads naturally into the chemical and physical variations of nuclear wastes to be immobilized, the current vitrification process that utilizes borosilicate glass and the daunting engineering challenges involved. Several waste forms are then discussed, including variations within the borosilicate definition, nonborosilicate glasses, titanate crystalline assemblages and glass ceramics. The Study Team identified these forms as worthy of further consideration in attempting to meet the objectives of the present review.

6.1.2 Previous Waste Form Selection and Development

Following an intensive and spirited debate in the United States in the late 1970s and early 1980s, borosilicate glass was selected as the primary waste form for the immobilization of high-level nuclear defense wastes. (Berndzskowski et al. 1983) Other waste forms considered in this selection process included high-silica glass, titanate ceramics, tailored ceramics, concrete, and glass marbles in a lead matrix. A titanate ceramic (SYNROC) was selected as an alternative to borosilicate glass. Figure of merit calculations were carried out on each waste form using weighted averages for broad categories including product performance, waste form performance, and processability. The analysis spanned the entire waste immobilization cycle [i.e., an operational (processing) period, a thermal pulse period, and a long-term geologic storage period]. Attributes of borosilicate glass that were persuasive in designating this material as the primary waste form included

- acceptable chemical durability
- flexibility in accepting wide ranges of waste compositions
- suitability for remote processing via a well-known and well-understood commercial glassmaking process - the electric melting of glass
- mechanical stability.

A major concern of using glass as a waste form is that below the liquidus, it is thermodynamically metastable with respect to crystallization and for some compositions, amorphous phase separation (i.e., liquid immiscibility). These phase changes can occur rapidly or very slowly over long periods of time at temperatures below the liquidus, but still above the glass transition temperature. They potentially lead to chemical partitioning and possible reduction of chemical durability. The major arguments against crystalline forms included low processing rates, potential product inhomogeneity, and remote processing concerns.

Relatively recent reviews have been concerned with processability (Lambert and Kim 1994), glass as a waste form (NAP 1996), and solidification technologies (NRC 2001). Other contributions are more narrowly directed at very specific issues such as waste form qualification, composition-property relationships, or engineering insights/problem-solving in the vitrification (melting) process of choice. (Vienna et al. 1996) Still others have addressed potential extension of current technologies to increase melting rates, throughput rates, and overall process efficiency. (Roux and Jouan 1999, Ladirat et al. 1995) Intertwined with these scientific and engineering efforts, considerable progress has been achieved in proposing and ultimately adopting a number of waste qualification and documentation procedures. Among these are the WA-SRD and WAPS.

Since the time the borosilicate glass waste was chosen as the primary U.S. waste form, two processes have emerged the most suitable for vitrification: (1) liquid-fed, Joule-heated, electrode melting, and (2) calcine-fed, hot-wall, induction-heated crucible melting. The former has been employed primarily in the United States, Japan, Russia, and Belgium, and the latter in France and the United Kingdom. Variations of both methods have been used or are under consideration in a number of countries throughout the world. One variation is a cold-wall induction melter, in contrast to the hot-wall types now in use. The cold-wall induction melter is thought to be capable of higher operating temperatures.

In view of these extensive scientific efforts and the development of product documentation procedures, it is not surprising that both a national and international acceptance of the borosilicate glass waste form has emerged. This development was supported in part by the successful vitrification of HLW at both SRS and WVDP. Reluctance to move away from this waste form is not unreasonable given the investment of time and resources to accomplish the above milestones.

The present review deals primarily with examining potential ways to decrease the estimated costs in vitrifying both high and low-level wastes at the Hanford Site and, to a lesser extent, INEEL. It is more holistic than previous attempts in that all aspects of the waste vitrification program could be reviewed, including storage at a national repository. Notwithstanding this breadth, the improvement of borosilicate waste forms or the adoption of new ones must be evaluated in part on the same criteria used in previous reviews of this type: projected chemical durability, processability, flexibility, and phase stability throughout the processing and storage stages. The potential utilization of fully or even partially crystallized waste forms must also be reviewed and evaluated in the same context. The recommendations offered as a result of this review may have applications in the vitrification program at SRS.

6.1.3 Summary of Waste Vitrification

The current overarching United States' flowsheet to produce an acceptable waste product by vitrification of nuclear defense wastes starts with chemical characterization of the wastes to be vitrified, followed by mixing with borosilicate glass-forming compounds in a water-based slurry. These compounds (i.e., oxides) can be added collectively as a premelted frit or as single entities. When heated, a number of chemical and physical changes occur in this slurry, including evaporation, shrinkage, solid-state reaction, sintering, decomposition, volatilization, and if the temperature is high enough, dissolution of refractory components. That is, the slurry-based mixtures are highly reactive, not only within themselves, but also with containment materials, mechanical stirrers, and electrodes used for heating. Reaching a temperature to create a well-mixed molten state followed by pouring into a canister will produce a homogenous glass when cooled. Wide variations of cooling rates in the canister are to be expected.

In practice, vitrified waste products made by this method contain small volume percents of refractory crystals (e.g., spinel). These crystals may form during heating of the starting mixtures or may precipitate and

grow either in the melt or during canister cooling. In principle, they may be dissolved by reheating the glass or its parent molten liquid above the primary thermodynamic liquidus. Dissolution, however, is a time-dependent process and can compete with other processes, such as settling to the bottom of the melter.

This propensity towards crystallization undergirds the WAPS requirements that time-temperature-transformation diagrams must be established for each glassy waste form. These diagrams, in turn, help establish important processing and storage constraints (i.e., minimum allowable centerline cooling rates for canisters when being filled, and maximum waste loading allowed due to internal heating of the canisters by radiation decay processes).

As previously noted in Section 5.5, other inclusions may be found in the cooled glass, such as noble metals, which can settle to the bottom of the melter and cause electrical shorting. Once formed, they are not expected to dissolve in the melt. Depending on the starting waste composition, an undesirable alkali sulfate liquid may form that is immisible with the borosilicate melt at the melting temperature.

In current melting units, the reaction of the starting mixture to form a molten liquid is preceded by evaporation of the water portion of the slurry, often exceeding 50% by weight. This process is sequential in that evaporation is followed by melting, whereas, in the European induction melting process for commercial wastes, evaporation normally (but not necessarily) occurs prior to melting (i.e., the mixture is calcined before introduction to the melter). Thus, an important principle is established: both slurry-based and calcined waste feeds can be vitrified to produce an acceptable waste product. The drying of waste feeds by evaporation is thought to be a major rate-limiting step in maximizing throughputs in Joule-heated melters. It is recognized that not all wastes are easily dried (e.g., high alkali bearing wastes) and in these instances, continued use of slurry-fed melters may be the best course of action. Alternatively, compositional changes in these high alkali feeds, for example, by the addition of alumina, may be beneficial in solving this drying problem. There is extensive technological experience with calcination in France, and to a lesser extent, in the United States at INEEL.

6.1.4 Nuclear Wastes to be Processed

According to the Hanford retrieval schedule, the transport of materials is traced from tank to tank during retrieval and the expected composition then calculated. This process results in 89 batches for feed, which were combined into 17 compositional groups or clusters with similar chemical contents. These clusters encompass some 204 million liters of HLW. At INEEL, approximately 4,000 m^3 of calcined nuclear wastes are stored in bins, and an additional 5.7 million liters of high alkali nuclear waste are stored in steel tanks. One hundred thirty million liters of waste are also stored at SRS.

Upon reviewing the wide variations of the chemical makeup of the nuclear wastes now stored at all sites, there is growing concern that the borosilicate glass waste form can satisfactorily vitrify all known wastes. A more credible engineering approach is to consider compositional clusters (and eventually batches) to be vitrified on a case-by-case basis. If it makes sense from both a cost and process efficiency viewpoint to use a variation of the borosilicate glass, or another glass waste form, then these options should be pursued. Similar comments hold true for the use of other waste forms beside glass. It is noted, however, that a trade-off most likely exists between the cost of increased waste product volume due to using the reference borosilicate waste forms for all wastes, and the cost of learning how to process different glass-forming compositions of crystalline assemblages.

This comparison is not within the scope of the present review.

6.2 Variations Within the Borosilicate Waste Form

6.2.1 General Aspects

It is appropriate to inquire if the vitification of nuclear waste using the baseline borosilicate glass (i.e., alkali-aluminoborosilicate) is an optimized process. This is a multifaceted question that can be answered in part by noting that there are processing constraints associated with this waste form, including the properties of the intermediate molten liquid state, such as viscosity, electrical conductivity, redox state, corrosivitity, and liquidus. All of these depend on composition and temperature, except the liquidus, which is only dependent on composition. As a matter of current melter practice, which may be unduly conservative, the liquidus must be less than the operating melt temperature. Otherwise, crystallization of the melt could occur, potentially interrupting (1) the melting of new slurry feed, (2) heat transfer and mixing within the melt, and (3) pouring the melt into a canister. It is generally held that higher waste loadings produce higher liquidus temperatures. That is, one must melt at higher temperatures to dissolve refractory reaction products to maintain the same volume percent of crystals found when melting at lower temperatures. Therefore, to increase waste loadings in the borosilicate waste form while still maintaining comparable product quality, melting units capable of achieving higher temperatures must be employed. This capability could be achieved in current Joule-heated melters by developing advanced electrode systems or through the adoption of cold-wall induction-type melters.

It is possible that increasing the waste load will produce greater concentrations of undissolved inclusions in the melt, such as spinel or zircon even when melting at higher temperatures. Yet, it is also recognized that these phases, if not directly precipitated during cooling, may have little or no effect on the chemical durability of the residual glass. Thus, the Review Team arrived at an important assertion, namely, that vitrification of nuclear waste using the borosilicate waste form that results in a biphase waste form (i.e., chemically inert crystalline phases embedded in a glassy matrix) may still be an acceptable alternative. Clearly, final product quality (chemical durability), as revealed in PCT, is determinant in such situations.

6.2.2 Measures to Support Variations

6.2.2.1 Increased Melting Temperatures

Increasing the operating temperature of the current Joule-heated melter to 1200 - 1300°C would be valuable in supporting a wider application of the base borosilicate waste form. With wider application and increased waste loading, microcrystals of spinels, chrome oxide, and zircon present in the melt may have to be removed periodically or maintained in a state of suspension during transfer (pouring) of the melt into a canister. Removal can be effected by introducing drain or pouring valves in the bottom of the melter, whereas suspension can be promoted by mechanical stirring or melt agitation induced by bubblers. These potential modifications would also promote increased melting and throughput rates.

6.2.2.2 Pre-Treatment of Wastes to be Vitrified

Wastes high in iron and chrome promote the formation of spinels within the cooled glass. Unless they are removed from the melt, they can accumulate and potentially decrease total operating efficiency (TOE). Other problematic wastes are those high in zirconium, noble metals, phosphorous, chlorides, fluorides, and sulfur. Like chrome, phosphorous oxide and sodium sulfate have limited solubility in borosilicate melts. Undissolved liquid sulfates can accumulate at the surface of the melter, and phosphorous oxide can react during melting with other constituents, such as lime, to form insoluable refractory phases. Clearly, upstream processing to remove these troublesome components is a desirable strategy. If the concentration of sulfates,

chrome, or phosphorous cannot be sufficiently reduced, then it may be necessary to handle these wastes in a nonborosilicate waste form. That is, variations within the borosilicate definition may not be sufficient to remediate this problem. Stated otherwise, it cannot be anticipated that the borosilicate waste form will act as a universal solvent for all nuclear wastes. There are two alternatives: (1) increase the quantity of vitrified waste (i.e., glass volume) to stay within solubility limits, or (2) utilize another waste form that has the prerequisite solubilities for these troublesome wastes. Force-fitting could be counterproductive. It is recognized, however, that a change from borosilicate glass to a new waste form would significantly impact planned schedules for final storage of vitrified wastes at the Yucca Mountain Repository. (The WA-SRD specifically identifies borosilicate glass as the standard HLW form.) Obviously, additional engineering work and policy changes would be needed to bring about this modification, and since borosilicate glass dissolution products are included in the repository release scenarios, the impact of changing to new waste form on storage costs, schedules, and licensing procedures cannot be taken lightly. The preferred path forward is to continue to use the reference borosilicate composition wherever possible, and develop new waste forms in those instances where the borosilicate composition has a low probability for success. Amendments to the License Application to accommodate changes in waste form would have to be obtained at a future date.

6.3 Non-Borosilicate Compositions

6.3.1 General Aspects

The study team identified three other waste forms worthy of additional consideration in this review. They are (1) alkali-aluminosilicate glasses, (2) iron-phosphate glasses, and (3) titanate ceramics. Each are discussed below.

6.3.2 Alkali-Aluminosilicate Glasses

The Study Team asserted that low-melting, boron-free silicate glasses would accept about the same amount of waste loading as the baseline borosilicate glasses. Higher melting alkali-aluminosilicates, however, can accept up to 80% waste loading while maintaining acceptable PCT results. These glasses may contain appreciable volume fractions of crystals and would require higher melting temperatures presently obtainable only with induction-type melters. The Study Team also noted that even small additions of boron oxide to alkali-aluminosilicate melts would lower melt viscosity and may provide gains of 10 to 20% in waste loading, relative to the alkali-alumino-borosilicate case studies, for some waste cluster compositions. On the other hand, boron-free glass melts should be able to dissolve more sulfate depending on the redox state of the melt. The assertion here is that variations in the base glass composition (with or without boron), coupled with a capability for higher melting temperatures, is favorable to achieving increased waste loading. This approach is worthy of future development. In addition to extensive melter design and testing, it would also require determination of the liquidus temperatures of all phases developed during crystallization, and time-temperature-transformation diagrams that could be applied to melts cooling in a canister. Properties of the melt would have to be determined including viscosity, waste solubility, corrosivity of refractories/electrodes, and electrical conductivity – all as functions of composition and temperature. To some extent, the alkali-aluminosilicate waste form can be regarded as an extension of the baseline borosilicate glass.

The Study Team was unable to perform waste-loading estimate cases, based on cluster compositions, for alkali-aluminosilicate glasses because there is insufficient property data to define viable formulations. As noted above, if improved melters could allow operation in the 1200 to 1300°C range and have the capability to discharge glasses with relatively high volumes of crystals, alkali-aluminosilicate glasses could be advantageous.

As basically silicate materials, they would involve minimal deviations from a repository licensing basis with borosilicate glass. Melter processing requirements and performance should be similar to the enhancements being recommended for increasing waste loading and processing rates for borosilicate, especially with respect to accommodating crystallinity. Further exploration of this waste form variation should be focused on the waste cluster compositions with high waste volumes, where modest gains in waste loading could have the largest benefit. Such work should initially address the minimal sets of properties versus composition data that would allow determination waste loading increases relative to enhancements allowed in alkali-alumino-borosilicate glasses processed in equivalent melters.

6.3.3 Iron-Phosphate Glasses

During the last several decades, several families of phosphate-based glasses have been considered for vitrification of HLW, including sodium phosphate, aluminophosphate, lead and iron-phosphate, and most recently iron phosphate. The latter has emerged as the most suitable for waste vitification. Phosphate glass waste forms have been produced in Russia for some time.

The data available to date in the United States regarding the properties and melting behavior of phosphate-based waste glass compositions have been almost entirely derived from melting studies carried out with crucibles. These glasses have a number of attractive attributes: low melting temperatures; low viscosity; the ability to dissolve heavy metals such as uranium and bismuth; acceptable chemical durability; and in some cases, an ability to accommodate relatively large waste loadings compared to the baseline borosilicate glass. Some compositions can be crystallized substantially without degradation of chemical durability. The Study Team has pointed out that an iron-phosphate glass waste form may be particularly suitable to vitrify waste clusters that have high concentrations of iron, phosphorus, or chromium. On a mass basis, these clusters represent almost 30% of the total Hanford waste to be vitrified. Moreover, the Study Team concluded that the uncertainty of the final chrome content in these wastes and limited chrome solubility in borosilicate melts has potentially the largest effect on the amount of waste glass product to be produced by vitrification. Developing a backup iron-phosphate waste glass form that can dissolve greater amounts of chrome than the baseline borosilicate glass would appear to be a prudent engineering strategy.

On the down side, phosphate glasses tend to crystallize more readily and are more corrosive to metal-based electrodes (Jantzen 1986). These attributes, while not necessarily fatal, must be examined extensively if an iron-phosphate-based waste form is to be adopted. Another concern is their electrical conductivity at melting temperatures. Being high in iron, chrome, and other multivalent elements, an intrinsically high electrical conductivity could be problematic depending on the type and design of the melter employed.

Time-temperature-transformation diagrams must also be developed for the envelope of compositions now under consideration. It is possible that the low melting temperatures of these glasses would allow crystallization to occur during geologic storage as a consequence of internal radiation decay heating. This behavior could limit the amount of waste loading.

For phosphate-based waste forms, the present situation is that preliminary studies have indicated potential for higher waste loading, especially for compositions where chromium is limiting for borosilicates. However, for single-phase glasses, the decrease in glass volume provided amounts to only about 300 canisters from the base case for this study (from Table 4.22 of the Study Team report). Development of the recommended enhancements for borosilicate glasses would remove any advantage for phosphate glasses, unless the unexplored possibilities of partially crystallized phosphate compositions could be successfully developed. The information compiled by the Study Team leaves significant uncertainty as to whether the cost of phosphate material, development of waste form qualifications, repository data development and analysis,

repository licensing amendments, and production change-over would yield net benefits for the best estimate waste feed chromium concentrations used by the Study Team.

There is, however, a significant incentive to perform further development work focused on the viability of producing higher waste loading phosphate waste forms. Recognizing that uncertainties exist in the leach factors for chromium removal in pretreatment and also for the inventory of chromium in Hanford tanks, a phosphate glass option should be further developed as a backup. If additional characterization and testing on actual tank wastes indicate that chromium removal is much less efficient than the 0.77% used in the study, the reduction in this volume of HLW waste produced with a phosphate glass could become very attractive. At the same time, additional engineering efforts are necessary to achieve their full acceptance as a waste form.

6.3.4 Titanate Ceramics

The Study Team identified a titanate-type, crystal waste form produced by melting as worthy of future consideration. This waste form, if processed via the molten state, would require high-temperature melting units. This approach would potentially remove a major impediment for utilizing crystalline waste forms - low processing rates. Development of this waste form, however, is not a small undertaking. In light of scarce waste loading data, it would appear to be more practical to concentrate on variations within the borosilicate definition and the other alternatives listed above.

6.4 Glass Ceramics Waste Forms

The study team has alluded to the potential crystallization of alkali-aluminosilicates and iron-phosphate glasses to point where the resultant waste products might be described, more appropriately, as a glass ceramic (i.e., a partially or wholly crystallized glass product containing at least 50 volume percent of crystals). In industry, glass ceramics are made by heat-treating a preformed, homogenous glass article below the liquidus, but above the glass transition temperature. In most instances, the process requires the addition of nucleating agents such as TiO_2 to ensure uniform crystallization through the product. In nuclear waste vitrification, however, neither comparable homogeneity nor uniform thermal treatment of the product is expected. That is, the thermal history of solidified glass in a canister will be varying from the center to the edge. Because of this variable thermal history, it will be necessary to develop models that predict the composition by phases of cooled glass as a function of composition, meting temperature, and an envelope of projected cooling rates. This will not be an easy task. Another point of concern is potential chemical partitioning of the waste product during crystallization. This partitioning could affect PCT results depending on composition and thermal history. Despite these technological difficulties, the development of these waste forms that are more glass ceramic-like is desirable. The key driving force for this effort is their potential for higher waste loadings.

6.5 Summary

The baseline borosilicate glass waste form has performed as predicted and continues to show wide ranges of applicability in the vitrification of waste now stored at Hanford, INEEL, and SRS. The development of other silicate compositions which contain smaller amounts of boron, melt at higher temperatures, crystallize more readily during processing, and allow increased waste loadings, should be pursued. An iron-phosphate glass waste form may be particularly suited for Hanford wastes that contain large amounts of iron, phosphorus, and chrome. The development of these glass families as a waste form, or as a glass ceramic, is a desirable engineering strategy. Preparatory to a wider applicability of the baseline borosilicate glass and alkali-aluminosilicate glasses, is the development of a melter with a higher temperature capability. Accurate determination of residual chrome contents in some of the Hanford wastes would be exceptionally worthwhile from both an engineering and cost viewpoint.

7.0 Assessment of Melter Technologies for HLW Processing

7.1 Overview of Melters In Use (World-Wide) for HLW Processing

This section discusses complete melter systems that are already used in HLW vitrification or under development for that purpose.

7.1.1 Joule-Heated Ceramic Melters

Nuclear waste vitrification using a liquid-fed ceramic-lined Joule-heated melter began at the Pacific Northwest National Laboratory in 1973. The first production of radioactive waste glasses began in 1985 in Mol, Belguim. Joule-heated ceramic melters have been processing radioactive feed in the United States since 1996 at SRS and WVDP. These melters use Inconel™ (nickel-chromium alloy) electrodes and are limited to bath temperatures of 1150 to 1200°C by creep failure of the electrodes and other immersed hardware. Melters similar in concept, but using different metal and ceramic materials, have been used commercially for a century, quite extensively for the past 40 years.

Joule-heated ceramic melters have proven to be rugged and not subject to catastrophic failure. They are suitable for a wide range of low-melting glasses, including high-alkali borosilicates, aluminosilicates, and phosphates. With forced convection, they could accommodate significant levels of crystals suspended in the melt. The main problems in HLW processing with this type of melter have been with lower-than-expected melting rates, sensitivity to feed characteristics, electrode shorting caused by large deposits of conductive noble metals, and pour spouts that clog. In addition, disposal of a failed melter is complicated by the large amount of residual waste glass and corrosion-resistant refractories in the melter. This may require a separate melter disassembly cell in the Hanford WTP.

The melter design currently planned for installation at the Hanford WTP incorporates lessons learned from previous melter use, plus a large amount of development work conducted recently by Duratek under BNFL contract.

All HLW Joule-heated ceramic melters are fed with a slurry containing less than 50 wt% solids. Both flow control and sampling for compositional verifications are simpler and more reliable with slurries than with dry powders, especially considering the very fine and variable nature of the particles in HLW and its high soda content.

7.1.2 Induction-Heated Melters

Two fundamentally different melter technologies are sometimes lumped together under this label. It is important to distinguish between cold-wall high-frequency induction melters, such as those presently under development in France and Russia, and hot-wall low-frequency induction-heated Inconel™ crucible melters, such as those long used by the French and British. Both types of melters have typically used dried or calcined feed, but that is not a fundamental limitation of the melter type, since slurry feed could also be used, albeit at a markedly reduced production rate.

7.1.2.1 Cold-Wall Induction Melters

In this type of melter, the glass itself is heated by a high-frequency electromagnetic field, while the container is kept cool by extensive water cooling. Because the power is generated in the glass only near the surfaces where induction coils are placed, forced convection is needed for melters that are large enough to be practical for Hanford HLW. This technology is interesting primarily because the melt temperature is not limited by electrode materials, since there are none. The need still remains for immersed metal components, such as stirrers, bubblers, level probes and thermowells, so the temperature of a practical melter is more constrained than is sometimes admitted. The most practical configuration developed to date is the French ACCM, in which the bottom surface of the bath is heated, rather than the vertical sides. This may allow easier scaleup, although effective stirring is needed with either configuration for melters of the size needed at Hanford. Current designs use calcined feed and a bottom delivery, but testing has been conducted with slurry feeds.

The principal limitation of this technology is its technical immaturity. It has been under development for over 20 years in France and Russia, with recent work directed at HLW. There is no experience operating remotely and no production experience with large scale melters, nor is there any commercial experience. Only two groups world-wide are working on development of this technology, and both are outside of the United States. Although some work has been done in these areas, three major areas need further technical development, each with its own serious technical problems: (1) the cold-crucible melter design and operating practice; (2) megawatt radio frequency power generators; and possibly (3) methods for drying or calcining Hanford high-soda HLW, feeding the powder to the melter, and distributing it over the cold cap. The first two issues each require extensive development. Even for the melters tested to date, the power supplies are pushing the state of the art. Large generators are needed because the power efficiency of an induction melter is very low (typically less than 20% versus 90% for electroded melters). Feeding and distributing powders has proven to be a troublesome problem, even for commercial hands-on cold-cap melters. The problem of drying feed can be eliminated by feeding slurry, but at the expense of doubling both the cold cap area and the capacity of the RF generator. From a technical point of view, this technology offers freedom from the electrode temperature limitation of the Joule-heated ceramic melter in exchange for RF power supply problems.

The French ACCM technology is the most promising alternative to the Joule-heated ceramic melter, but almost nothing is known about it from firsthand experience in the United States.

7.1.2.2 Hot-Wall Induction Melters

Hot-wall induction melters are Inconel™ crucibles that are heated by low-frequency induction, into which dried or calcined raw materials are charged, melted to a homogeneous glass, and cast into a canister. Production began in this type of melter in France in the late 1970s and has continued successfully since. In spite of this long and successful production experience, this technology was rejected for Hanford HLW during a review held in 1994 (Calmus 1995) because of its low production rate, even at the maximum melter size. Both problems stem from the difficulty of transferring power from the crucible to the bath, exacerbated by the poor infrared transmission of the reduced iron waste glasses. Unlike a Joule-heated (electroded) melter, the production rate of a hot-wall crucible melter cannot be increased by simply increasing melt surface area because of this heat transfer limitation. This limitation applies to any melting process heated only through the side-walls, regardless of the source of energy.

7.1.3 Stirred Melters

Stirring in glass melters is commonly practiced using bubblers to encourage slow convection rolls and mechanical stirrers to homogenize glass before delivery. One unique applicaton of stirring is the Stir Melter™ technology developed in the 1960s by Owens-Illinois and now owned by Glasstech. A high-speed stirrer operated at several hundred revolutions per minute is used to intensively mix feed with the bath, overcoming the heat transfer limitation of cold cap melting. Because the melt surface temperature is kept low, volatilization is fairly low. In all testing to date, the bath has been heated with immersed electrodes. A separated portion or chamber is generally needed to obtain complete dissolution of feed solids and partial removal of the numerous entrained gas bubbles.

Temperature is limited by the electrode and stirrer materials, as in any Joule-heated melter. Even with intensive stirrer cooling, temperature in melters with Inconel™ components has been limited to about 1100°C by high stresses in the stirrers. Because of this low temperature limitation, the limited testing that has been performed, and the lack of remote or production experience, stirred melters are less attractive as a complete melter system than a less intensively stirred Joule-heated ceramic melter.

One special case in which the Stir Melter™ might have a unique advantage is in melting high-phosphate wastes at INEEL. The intensive mixing might disperse any high-melting phosphate phases that form during batch reactions and distribute them harmlessly through the melt.

The concept of intensively stirring the feed reaction zone of a melter is worth considering as a feature of more conventional Joule- or induction-heated melters.

7.1.4 Other Melter Technologies

Several other types of melters have been partially developed or proposed for HLW vitrification. Most of the inventiveness has been directed toward alternate methods of introducing energy to the glass. These are discussed in detail in the Study Team report. Since none of them are considered to be serious candidates for further development for Hanford HLW, they are mentioned only briefly here.

The most promising of the alternatives to the melter systems discussed above is the Joule-heated melter with electrodes made of a material having adequate mechanical properties at a higher temperature than Inconel™. The barrier to taking this approach is the inability to date to identify an electrode material with the necessary chemical and mechanical properties. It appears that a basic materials invention would be needed for this to succeed.

Cyclone melters, in which feed is introduced as a spray into a chamber filled with very hot gases, are fundamentally limited by high volatilization losses. In principle the volatilized materials can be recovered from the off-gas and reintroduced to the melter. However, this will add significant complications, requiring separation of the radionuclides from the volatilized materials captured in the off-gas system and recycling to the melter, increasing glass production requirements.

Melters using electric arcs or plasmas similarly are limited fundamentally by volatilization. Like cyclone melters, they create very hot molten glass surfaces, encouraging rapid evaporation of the alkalies and many of the low-melting metallic elements, including radionuclides.

In-can melters, in which either the canister or an electrically-conductive lining for the canister is heated by low-frequency induction, have the same limitations of low production rate and little scaleup potential as the

hot-wall induction melters discussed above, plus the additional problem of ensuring adequate homogenization in a melter in which observation and internal measurements are very limited.

Microwave heating, in which waste is heated in drums, has essentially the same fundamental limitations as in-can melters.

7.2 Essential Components of Melters Systems

In this subsection, melter systems are examined in terms of some of the means for feeding, heating, containing, homogenizing and delivering glass. Because the means for accomplishing each of these functions can be combined in many ways, it is useful to discuss them separately from the total system.

7.2.1 Feeding: Melters with Dry Feed

The choice of slurry feeding or predrying is a trade-off between the difficulty of handling powdered feeds and of introducing sufficient power to the melt. With a cold-cap slurry-fed melter, evaporation of water represents over half the thermal load, so at least twice the melt surface area is needed for the same melt rate when feeding a 50 wt% slurry rather than dry feed. Dry feeding has been used with both hot- and cold-wall induction melters, because of the difficulty of introducing enough energy to the bath in these melters. Slurry feeding is more practical in Joule-heated HLW melters, since adequate energy to both evaporate water and melt glass can be introduced through the electrodes.

Slurry feeding is not used in industrial practice simply because the raw materials are already dry, and adding water would double the energy costs, which are typically half the total cost of melting. In contrast, HLW feeds are already wet due to prior processing (except for INEEL calcine), and energy is a negligible part of total melting cost.

Because of the high soda content of the Hanford HLW feed produced by pretreatment, drying or calcining tends to produce hydroscopic powders and a risk of caking. This problem is very difficult to remedy in a remote operation, so the risk of process interruptions is high. One approach is to add large amounts of alumina to react with the soda, but this approach decreases waste loading. For Hanford HLW feed, it appears to be more attractive to increase processing rate by enlarging the melter than by the added complexity of drying or calcining.

7.2.2 Heating: Secondary Heating

Secondary heat input (i.e., energy supplied to the top of the cold cap, heating also the plenum and off-gases) reduces the amount of heat that must be supplied to the bath, but at the expense of additional complexity and failure-prone components.

7.2.3 Containing: Cooled Ceramic-lined Melters

Present HLW melters use thick refractory walls, like commercial glass melters in which minimization of energy cost is a primary goal. The refractory walls are multilayer structures with corrosion-resistant materials on the inside, and better thermal insulation materials in the outer layers. In contrast, cold crucible melters consist only of a water-cooled metal crucible, relying on the poor thermal conductivity of glass to contain the melt. A thin layer of solid glass prevents leakage, but at the expense of very high heat losses, requiring substantially more power input to the bath. A combination of these two approaches is possible, since a thin refractory lining inside a water-cooled jacket will have a much lower corrosion rate, yielding a better compromise between the disposal problems of massive refractory melters and the problems of supplying the large amount of heat to the bath needed by cold-wall melters.

7.2.4 Homogenizing: Stirring Methods

Forced convection increases very substantially the flexibility of a melter, allowing a wider range of feeds to be handled efficiently. Convection is necessary for both chemical homogenization (for better PCT) and for thermal homogenization (to eliminate cold regions, thus minimizing devitrification, and to increase heat transfer to the cold cap).

There are three methods to force convection: bubblers, mechanical stirrers, and hot spots.

- Bubblers are simpler to install and maintain, but many are required for intensive mixing of a large volume, and only limited control over the velocities and direction of convection rolls is obtained.

- Stirrers are much more positive and stronger in their effect on convection, but they are more complicated to install, and they may have a limited life (or if well-cooled to extend life, they extract much heat).

- Hot spots are simply regions of intentionally high power input, such as electrodes operating at high current density, to create natural convection rolls by creating temperature gradients. Although they are the simplest to install and maintain, the control obtained over convection is limited.

A combination of these methods is often more effective than any one alone.

7.2.5 Delivery: Bottom-Drained Melters

Nearly all commercial glass melters are bottom-drained because of the simplicity, thermal uniformity, and freedom from surface defects. However, bottom-drained melters normally require frequent hands-on intervention to maintain consistent flow. For remote operation, the need for frequent attention underneath the melter is a serious limitation. Bottom-drained melters also increase the height required in the cell for the melter, and they are attractive for HLW primarily because of the advantage of having a bottom discharge for glass laden with noble metal and other crystalline precipitates. For this reason, bottom-drained melters have been developed extensively in Germany, and used in HLW production in France, the United Kingdom, and Japan. The most successful design required a steeply-sloped melter bottom, adding further to the height requirement.

7.3 Review of Previous DOE Melter Technology Assessments

Westinghouse Hanford performed a comprehensive HLW vitrification review in 1994 (Calmus 1995). Earlier assessments of HLW melter technologies were incorporated in this review. The recommendations and

reasoning of this review were reexamined by the Study Team, other experts, and the Review Team to determine if the conclusions are still valid in light of vitrification technology developments since 1994 and the latest results of the Hanford Waste Characterization Program. In reevaluating the information of the 1994 study, the Study Team relied heavily on its understanding of previous and ongoing technology efforts in the United States and internationally. The intent and result was to bring forward for the Review Team new information and developments, along with the most applicable technologies identified by previous reviews, without attempting anew a comprehensive review of all possible technologies. From this reevaluation of the 1994 study, the Study Team concluded that the following melter technologies evaluated in 1994 warrant reconsideration in the present review:

- low-and high-temperature Joule-heated ceramic melter (high-temperature in this context means using electrode materials with higher use temperatures than Inconel™)
- cold-crucible induction-heated melter
- enhancements applicable to both types of melters, including stirring, feed drying or calcination, and sloped melter bottom with bottom delivery systems.

None of the other technologies examined in 1994 appear to warrant further consideration for Hanford HLW.

7.4 Methods and Criteria Used in this Assessment

The scope of this review is limited to vitrification processes that produce molten waste glass that can be cast into standard canisters. The molten glass may contain suspended crystals and may crystallize further during cooling in the canister.

The information sources for the Review Team's assessment consist of the following materials gathered by the Study Team:

- the extensive data gathered for the 1994 assessment of HLW technologies for Hanford (Calmus 1995)
- responses by vendors to a January 2001 Request for Information
- searches of melter-related literature (journals, presentations, and patents) since 1994
- knowledge of Study Team and other experts gained from their continuous involvement in the field of waste vitrification.

The ongoing involvement of the Study Team and their contacts provided significant information on several of the technologies. Neither the vendor Request for Information nor the literature searches identified any technologies that were not already available to the Study Team.

The potential for significant cost reduction results primarily from (1) increased waste loading, leading to fewer canisters of waste to store, and (2) increased rate of waste glass production, leading to a shorter operation period. Both of these are strongly influenced by the uncertainties in the character and composition of the pretreated tank wastes. Thus, technologies that can process a wide range of compositions and tolerate unanticipated changes in waste glass properties (e.g., viscosity, liquidus, oxidation state) would be of most value. This means that insensitivity of process conditions (e.g., melting rate, total power input, bath

temperature, internal convection patterns) to changes in feed properties should be given a high priority among selection criteria for technologies. Potential cost increases to be avoided result from extensive development required by immature technologies and disposal of failed melters and melter equipment.

The recommendations in this report are based on the following choice of design goals for the melter system, listed in order of priority. Listed with each goal are some of the melter system characteristics needed to achieve the goals. These characteristics are the criteria by which alternate melter systems were compared and selected:

1. Capability to produce HLW glass meeting all product and process requirements
   - Maximum operating temperature high enough to achieve waste loadings higher than the baseline technology with all Hanford HLW feeds.
   - Homogenization adequate to not influence PCT negatively.
   - Processing rate to meet design goal of 6 MTG/day in two cells

2. Low and predictable downtime
   - Reliability of inputs and outputs (feed, molten glass removal, power input, and off-gas removal and cleaning).
   - Maintainability – long useable lifetime and ease of replacement of components.
   - Operability under remote radioactive facility conditions - simplicity, ability to control and predict process conditions, obviousness of corrective actions, and predictability of responses

3. Flexibility to tolerate load changes
   - Insensitivity of process conditions (e.g., melt temperature distribution, convection flows) and outputs (e.g., melting rate, off-gas flow rate) to changes in feed characteristics and feed solids content, feed rate, drain rate, and to long-term deterioration of the melter.
   - Ability to tolerate or remove crystals (spinels, noble metals)
   - Ability to operate within a broad temperature region.
   - Capability to accept high waste loadings.

4. Continually adapt and improve - benefit from experience
   - Improvability - ease of modification without total replacement, and ease of replacement without extensive facility changes.
   - Information production - ability to monitor the process and ease of extraction of information about internal process conditions.

5. Minimize development cost and risk
   - Cost to develop technology - predictable effort required.
   - Uncertainty of development - unpredictable effort required (how many and how fundamental are the inventions needed?).

6. Minimize melter lifetime cost
   - Melter replacement time as a fraction of lifetime (with lifetime based on production experience or long-term pilot trials, not just on design estimates).
   - Melter replacement cost, including disposal of failed melters, divided by lifetime.
   - Annual operating cost.

7. Minimize melter first cost
   - Design, construction, and installation cost of the melter system.
   - Facility impacts - waste glass production versus melter footprint, volume, and weight.

It is instructive to ask which among these seven goals and related melter characteristics are fundamentally determined by the choice of the basic melter technology. The only ones that are strongly influenced by the initial choice are the development costs and risks, and these have more to do with the present state of development and the past goals of that development. The rest are primarily a matter of persistent engineering effort focused on the present goals.

7.5 Results of this Reassessment of Melter Technologies

With the above goals in mind, the Review Team reached the following conclusions regarding (1) the need for any new melter technology, and (2) the selection of which new technology offers the greatest potential for major cost reduction with reasonable risks.

1. Alternate melter technologies should be judged on their potential to replace the Joule-heated ceramic melters for the Balance of Mission, and developing them as additional melters that might be used in parallel with Joule-heated ceramic melter should not be considered. No Hanford wastes have been identified that exist in large enough quantity to justify development of a specialized HLW vitrification technology. None of the alternate technologies that might address specific troublesome wastes appear to have development costs and risks low enough to compete with the added cost but very low risk of handling those wastes by dilution (lower waste loading).

2. Development effort should be directed to adapting the Joule-heated ceramic melter to more efficiently handle troublesome wastes. The costs and risks associated with such adaptation are far lower than those for developing a fundamentally different technology.

3. Because of the reduction in risk that accrues with production experience, it is very difficult for a new technology to replace a technology already in production, unless continuing improvement of the technology is neglected, or it is fundamentally flawed. The Joule-heated ceramic melter technology is now supported by a massive amount of development and considerable production experience, so any other technology has a high barrier to overcome to replace it.

4. A Joule-heated ceramic melter with Inconel™ electrodes is the best overall technology for both short- and long-term Hanford HLW vitrification needs. A Joule-heated ceramic melter without enhancements (the baseline technology) is adequate technically, for all Hanford wastes, but dilution (lower waste loading) would be needed with some wastes. The largest waste loading improvements are achievable with technically feasible enhancements. A different basic melting technology is not necessary to achieve significant cost reductions at Hanford. Vitrification of SBW at INEEL also can be accomplished with existing Joule-heated ceramic melter technology.

5. There are strong incentives to ensure that production rate targets are attained and that melting rate is maintained for various feeds. This avoids escalation of total costs. Predictability of melting rate for various feeds is more important that the melting rate itself.

6. Considerable improvement in performance can be expected from aggressive development of the Joule-heated ceramic melter. Four areas of potential improvement stand out:

   - Tolerance for crystals in the melter is necessary for higher waste loadings and is best addressed by forced convection (driven by mechanical stirrers, bubblers and hot spots). Bottom drains or bottom withdrawal of product, and operational moves such as flushing, are other approaches.

- Predictability of processing rate is necessary for operating cost reduction and is best addressed by forced convection and an extended temperature capability.

- Operating temperature capability up to 1350°C could be provided by aggressively cooled electrodes, resulting in higher waste loadings and higher and more predictable processing rate. The temperature capabilities of other immersed metal components (e.g., thermocouple wells, stirrers, level probes) also would need to be addressed by cooling or redesign.

- Reduction of the high disposal cost for failed melters is needed. Provision for emergency draining of the melter and reduction of the thickness of refractories by substitution of shell cooling could substantially reduce this cost.

7. Secondary heat inputs to evaporate water are useful to reduce the physical size and power requirements on slurry-fed melters.

8. Drying or calcining feed to boost production rate add complexity that more than offsets their advantages. It is better to simply enlarge the melter if higher capacity is needed.

9. The ACCM (cold-wall induction-heated) technology appears to be the most promising of the alternate melter technologies under development. Its temperature flexibility is its most attractive feature. But while crucible melters eliminate the need for high-temperature electrodes, they have the same problem with other immersed metal components as the Joule-heated melters.

   The ACCM technology is sufficiently advanced to justify a major development effort for Hanford. The program should be long enough (e.g., five years) to bring it to a stage where it can be determined whether this technology can realistically replace an improved Joule-heated ceramic melter for the Balance of Mission.

   There is a small chance that the ACCM could have sufficient advantages over an improved Joule-heated ceramic melter for INEEL wastes to justify its continued development for that application alone. Until the initial development recommended here is more advanced, it is impossible to make this judgment.

   The strong development program recommended here should be accompanied by an equally strong resolve to critically evaluate the results and stop the program whenever there is sufficient evidence to judge that it will not be able to replace the improved Joule-heated ceramic melter.

10. The Stir Melter™ technology contains a feature, very intensive mixing near the melt surface to rapidly entrain and transfer heat to the feed, that could be applied to other cold-cap melters. The potential reduction in melter size and in failed melter disposal costs could be very significant. This melter system has not been developed for HLW, and much more work is needed, but could be included in a broader program on stirring to improve melting rate.

11. Higher temperatures offer some opportunity for higher waste loadings. High-temperature versions of the Stir Melter® and Joule-heated ceramic melter are possibilities, but both require extensive development, including the basic invention of oxidation-resistant electrode materials with adequate mechanical properties at elevated temperatures, or development of electrode cooling systems well beyond anything proposed to date.

12. None of the other melter technologies appear to have a higher potential than the ACCM to completely replace an improved Joule-heated ceramic melter. Development funding should be focused on those technologies that do.

In summary, there appear to be only two practical options to meet Hanford's long-term vitrification needs:

1. the Joule-heated ceramic melter with Inconel™ electrodes, enhanced to handle suspended crystals, and operate at a higher temperature. Problem glasses would need to be handled by dilution. This technology is simple, reliable, well developed, and proven by considerable HLW experience. Aggressive development is warranted to optimize its performance.

2. the ACCM, as it is being developed in France. The slightly higher temperatures available decrease the number of problem glasses. However, neither the melter nor the power supply has been proven at the scale needed for Hanford HLW, and the number of people with any experience with this technology is extremely limited. Development is warranted to learn more about it.

8.0 Assessment of Waste Loading Enhancements for Hanford Wastes

8.1 Hanford HLW Tank General Inventories and Flow Sheet Overview

The Hanford Site has 204 million liters of HLW stored in 177 underground tanks. This waste was generated by a number of different processes over the last 60 years of plant operation.

The cleanup plans for the Hanford Site include removal of the waste from the tanks and processing it to produce both a low-level waste glass form and a HLW glass form. The processing consists of four major activities:

1. Retrieval of the waste from the tanks
2. Pretreatment of the wastes prior to vitrification
3. Vitrification of the low-level waste
4. Vitrification of the HLW.

Both the retrieval and pretreatment processes impact the actual composition fed to the vitrification processes. The retrieval processing sequence will result in some incidental blending of the process streams because a limited number of tanks will be equipped with retrieval facilities (at any one time), and it is impractical to completely empty the pretreatment feed tanks between every tank transfer. The pretreatment processing facility has numerous processing steps that require transfer of material between the salt (low-level waste) and sludge (HLW) processing equipment. These transfers have the potential for additional incidental blending, which alters the feed composition. This report does not evaluate the vitrification of low-level waste. After pretreatment has been performed, the HLW feed is blended with glass formers and fed to a melter to produce a Borosilicate (reference) Waste Form for eventual shipment to a federal repository.

8.2 Hanford Waste Types and Waste Loading Constraints

The Hanford Site maintains a Best Basis Inventory that contains the latest compositional inventory of the waste based on the ongoing Waste Tank Characterization Program. The Hanford retrieval schedule traces the transport of materials from tank to tank during retrieval and calculates the expected composition. This results in 89 batches for feed to the process. As the basis for this study, these 89 batches were combined into 17 compositional groups with similar chemical contents. These groupings were then analyzed to determine the limiting glass characteristic and the volume or number of canisters that would be produced at these limiting restrictions.

The waste loading constraints for determining the number of canisters is a result of numerous years of compositional analysis of alkali-alumino-borosilicate glasses. These constraints are as follows:

- Processability [melter operating temperature, liquidus (crystal formation temperature), viscosity, and electrical conductivity].

- Waste Form Product Consistency Test (leachability of lithium, boron, and sodium).

- Limiting solubility components (chromium, phosphorus, fluorine, sulfur, and noble metals).

- Model validity limits (metal oxide ranges included in the model).

Using these constraints and the 17 compositional groups, the number of canisters produced was determined and used as the basis for this study. The current batch plan for Hanford waste retrieval (Hanford Tank Waste Optimization Simulator) has 89 batches, analysis of these expected compositions produced about 2.5% more canisters than the 17 compositional groups (clusters), confirming that the clustering was reasonable. The 9300 canisters referenced in this report are 10% higher than the quantity determined from the 17 compositional group analysis. This adjustment results from two factors: (1) the effect of incidental blending within the cluster (which understates the variability of some key constituents and would not occur with actual feed batches); and (2) possible sub-optimization of glass formulations, which would likely occur during actual plant operation. The constraints were then varied over a range, for the 17 compositional groups, to determine how the canister production changed as a result of the constraint variation.

8.2.1 Possibilities for Optimizing Waste Loading for Hanford Wastes

The Hanford Best Basis Inventory shows that 90 mass % of the waste has more than 0.5 wt% chromium oxide. Chronium oxide has limited solutibility in borosilicate glass, especially if the iron content is high. When the liquidus must be maintained 100 ^{o}C below the melter operating temperature, to minimize crystallization, the amount of chromium oxide in the Hanford feed then becomes the limiting criteria for the glass formulations. Estimates for incorporating all the chromium oxide in glass have been as high as 24,000 canisters. One method of reducing this glass volume is by removing chromium oxide during pretreatment by water washing and caustic or oxidizing caustic treatment.

The data on both the solubility of chromium oxide in the glass formulations and the effectiveness of pretreatment for the wide range of Hanford wastes have not been accurately determined. This lack of valid data results in a large uncertainty in actual number of canisters that will be produced.

The current ORP baseline is production of 12 700 canisters at a waste loading of 31 wt% oxides. Recent indications are that this baseline may be conservative as to both the effectiveness of washing chrome from the waste and the tolerance for chrome in the borosilicate glass without crystal formation. This study was performed at the more favorable 0.77 chrome leach factor (the fraction of chrome that can be removed by hydroxide treatment) and 1% chrome glass solubility; this results in a production of about 9300 canisters at a waste loading of 46.4 wt% oxides.

At waste loading in excess of this, crystal formation (spinel, noble metals or eskolite) in a Joule-heated ceramic melter operating at 1150°C would occur. Alternative ways of operating at these higher waste-loading compositions include

- employing melt agitation to keep the crystals in suspension so they can be discharged into a canister
- operating at higher temperatures to keep the crystalline form dissolved until poured into a canister
- operating with agitation at high temperature (to improve and maintain solution of the waste formers and crystals respectively) and until the melt is poured into a canister.

Assuming that the crystal formation does not impact the leach characteristics of the waste form (by changing the chemical composition of the adjacent glass), a maximum reduction of about 12.1% (1100 canisters) could be realized by increasing oxide loading to 54.1 wt% and operating at 1350°C. This would require development of melt agitation and/or high-temperature (1350°C) melter technology.

At this time, the chrome leach factor and glass solubility are both quite uncertain. If the chrome solubility were only 0.5 wt%, the canister production would increase about 24.6% or 2300 canisters. If the chrome solubility were only 0.5 wt% and the chrome leach factor only 0.384 (the original Hanford canister basis), the canister production would increase about 158% or 14,700 canisters.

All other variables studied had very little effect on the number of canisters produced.

8.2.2 Possibilities for Optimizing Processing Costs for Hanford Wastes

The cost of disposing of HLW once it has been retrieved and pretreated involves the vitrification system, the interim storage facilities, and the repository. The cost analysis performed by the Study Team assumed that the HLW system could operate at throughputs dependent only on vitrification criteria. Other requirements such as retrieval, pretreatment, and funding did not hinder the vitrification operation.

8.3 Vitrification Costs

Vitrification costs are primarily dependent on the number of years the facility must operate to process the waste. This is mainly a function of the number of canisters that will be produced. There has been a reduction of about 3400 canisters (from the ORP baseline) as a result of new values for chrome leaching and glass solubility. Operating cost, through shorter operating time at a TOE of 60%, should reduce about $480M as a result of this criteria change. In addition, up to another 1100 canisters may be eliminated if melt agitation or higher-temperature melters are developed to permit processing of crystal forming compositions (assuming acceptable leach performance). This could reduce operating costs by an additional $150M.

The vitrification cost basis is a 6 metric tons/day (MT/d) glass production at 60% TOE. A sensitivity analysis of factors associated with vitrification show that the cost is primarily influenced by the throughput rate and secondly by TOE; other factors such as melter life and disposal costs have impacts but not to a significant level. If the development of improved technology to increase the 1.5 MT/d glass production melter to a 3.0 MT/d glass production melter does not materialize, the operating cost would increase by about $1B. Conversely, if one or two more melter cells were added for say $500M, then the throughput rate would not need to be as great per melter and still provide throughput assurance to prevent operating costs from escalating. If the technology did prove out, then the facility could have an 8X capability.

8.4 Interim Storage Facility

The Container Storage Building has the capability to store 880 canisters of HLW (the other bay is used for SNF). The need and how many additional Container Storage Buildings are required depends on the canister shipping rate and timing versus the production rate. For example, if shipments start before the 880 positions are filled and can continue at a rate equivalent to production rate, then no new facilities are needed and the operating cost would be $15.9M/yr. Otherwise, a $343M cost will be incurred for each additional 2640 canisters that must be stored until the repository opens.

If the repository does not open until after the operating period (i.e., no canisters are shipped during production operations), then the two canister reductions mentioned above (4500 canisters) would reduce the storage building requirements by about $500M in construction costs. Otherwise, there is no impact from this study.

8.5 Repository

The DOE repository cost is based on an allocation formula that distributes costs between commercial fuel and DOE. The allocated cost for DOE is $400K per canister. Other studies have been done that indicate that the repository incremental cost is about $100K per canister. The reduction of 3400 canisters, as a result of modifying the chromium wash and solubility values, would result in a reduced cost of $340M and $1.4B for the incremental and allocated costs, respectively. For the additional 1100 canister reduction resulting from relaxing crystal content, the reductions would be $110M and $440M for the incremental and allocated costs, respectively.

8.6 Summary

It is not likely that the repository allocation basis will be a true representation of the cost that will be incurred by DOE, since no savings would be realized for the aboveground facility. Repository savings are more likely to be in the $500M to $1.0B range for the maximum canister reduction case. The interim storage savings are essentially unaffected by this study since the savings only materialize if the “no shipping” case occurs. The operating cost savings of $500M to $700M depend on chrome and melter technology improvements that need to be verified. The ability to obtain the melter throughput either though technology improvement or incorporating additional melter or a larger melter that may require changing the cell dimensions needs to be critically reviewed.

This analysis is based on technical methods to improve the waste loading and throughput of the HLW facility. When the waste loading is increased, more waste per volume of glass must be processed through the retrieval and pretreatment processes in a shorter time frame. An increase in low-level waste glass production must also be obtained to not inhibit the pretreatment facility. If these facilities cannot maintain the higher throughput rates, the operating savings will not be realized. Conversely, if the added improvements and funding for the retrieval, pretreatment and low-level waste vitrification can be attained, considerable additional operating savings can be realized from their shorter operating cycles.

9.0 Assessment of Waste Loading Enhancements for INEEL

9.1 INEEL

Over the past three years, INEEL has gone through an Environmental Impact Statement process concerning the path forward for immobilizing the tank wastes and calcine. (DOE 1999b) As summarized in Section 4.4, vitrification was selected as the preferred approach to preparing the INEEL reprocessing wastes for offsite disposal. Staff at INEEL have prepared technology development roadmaps and plans to support vitrification both SBW and calcine. (Murphy and Olson 2000, Murphy et al. 2000)

The issues and constraints that determine waste loading for the SBW compositions are considerably different from HLW at Hanford and SRS. This waste is a nitric acid solution consisting primarily of sodium, aluminum, potassium, sulfate, and phosphate along with some chlorine, fluorine, and minor amounts of other metals. Radioactive species are primarily fission products and decontamination residues. After these solutions are retrieved from the tanks by pumping, residual heels will remain. Retrieval of these heels will provide a waste stream estimated at 1700 m^3 that will be high in sodium, aluminum, zirconium, and silicon.

The Study Team has summarized preliminary glass formulation envelopes identified for SBW. These preliminary formulations provide a 35% waste loading limited by SO_3 solubility. Current technology development activities emphasize formulation and melting behavior to increase the accommodation of sulfate. Only slightly higher loadings would be obtained beyond the sulfate limit because the high sodium content of the waste limits PCT compliance. An independent technical review of the SBW technology development roadmap prepared by INEEL staff was performed for DOE-Idaho[3]. Reviewers concluded that the selection of a melter technology for SBW vitrification would be primarily driven by project schedule constraints to comply with the DOE/State of Idaho Consent Agreement. (USFC 1995) The total SBW glass production at 35% waste loading is projected to be about 700 standard (SRS-type) canisters. The technical demands of SBW vitrification can be accommodated by a Joule-heated ceramic melter. Development and demonstration lead times for alternative technologies, such as ACCM, appear to be inconsistent with the current baseline project schedule. However, if the vitrification plant established for SBW is to be employed for a follow-on mission to vitrify calcine, design features of the base plant may need to accommodate refitting of melter process systems optimized for calcine.

There are two major calcine treatment options under consideration for which technology development and demonstration plans are being developed. One option involves the redissolution of the calcine in acid, followed by a series of chemical separations process steps. Two different chemical separations schemes are under consideration (Law et al. 2001, Herbst et al. 2000): (1) a combination of steps to separate actinides by a transuranic extraction (TRUEX) process, cesium by ion exchange, and other radionuclides by similar processes; and (2) a universal solvent extraction (UNEX) process that partitions all of the radionuclides into a single, organic-based stream. The second major option for immobilization is direct vitrification of the calcine as retrieved from the storage bins. There is a significant difference in the volume of HLW glass produced under the direct vitrification and pretreatment-by-separations options. Preliminary estimates indicate a range of 5000 to 9,000 canisters for direct vitrification and a range of 400 to 2000 canisters with separations, recognizing considerable uncertainty on achievable waste loading with the current status of flowsheet definition.

[3] Letter report, TM Brouns, PNNL, to TP Pietrok, DOE, "Assessment of Idaho Technology Roadmap for Direct Vitrification of Sodium-Bearing Waste."

A draft technology development roadmap, prepared by INEEL staff to address immobilization of calcine as a glass waste form, was also reviewed by an independent review team (TFA 2001). The primary objective of the INEEL calcine technology roadmap was to provide a technical basis for a system optimization, based on risk and cost factors, for selecting a calcine immobilization baseline. Each of the three process options (full separations, UNEX, and direct vitrification) involve different technical issues for glass formulation and waste-loading optimization. Flowsheets are being developed for each of these process options, which will provide an improved basis to project waste feed compositions to the vitrification process.

For direct vitrification, waste loading is a critical factor in comparing system costs against the pretreatment options. In composition, the calcine falls into two major groupings: (1) the largest fraction of the material is high in zirconium, calcium, and fluorine, and (2) a smaller fraction of approximately 20% by volume high in aluminum. Both types of calcine have the usual range of fission product radionuclides and transition metals found in most HLW. The Study Team has summarized glass formulation studies that show potential for a relatively high waste loadings (45% range) for the predominant type of calcine (high in zirconium, calcium, and fluorine). If constraints due to crystallization for these glass formulations were relaxed, even higher waste loadings could probably be obtained (estimated to be 50-55%). Also, the composition versus properties relationships for these glasses indicate that melting temperatures higher than 1150° C would not enhance waste loading. For the smaller fraction of the calcine inventory that is high in aluminum, the waste loading would be lower, limited by effects of aluminum on glass properties. For this material, higher melting temperatures would probably enhance waste loading. There is also the considerable volume of tank heels that, if processed as a separate stream, could have waste-loading limits strongly influenced by high levels of aluminum and zirconium in these heels.

Vitrification feeds from separations processes represent different challenges for optimizing waste loading but also have added issues on processability. The total volume of HLW after separations is considerably smaller than existing calcine, rendering waste loading in the glass a much smaller factor on the total system costs for INEEL HLW processing and disposal. The full separations option, using the TRUEX process, provides a HLW stream that is high in phosphate, molybdenum, and heavy metals (actinides/lanthanides). If this stream is combined with tank heels, it would also have high levels of aluminum, zirconium, and sulfate. The Study Team noted that phosphate and sulfate are the components that limit waste loading for this combined stream, which could be as low as 10 to 15%. The alternative UNEX process results in a waste feed that has high concentrations of organics at levels for which there is little experience in HLW vitrification processing. Organic incineration and glass melt redox issues must be addressed in establishing a vitrification process for this waste stream. Waste loading may be limited by either components in blended tank heels or by the organic content. These issues are recognized and addressed in the INEEL technology development roadmap planning.

Current retrieval planning and flowsheet status at INEEL impose uncertainties on the degree to which the different calcine sources and tank heels may be blended to moderate the influence of problem components. The hierarchy of limiting constraints and components, analogous to Hanford sensitivities (see Section 8), will depend on the extent of blending and the specific flowsheets chosen for calcine.

The following summarizes how the technical approaches identified for improving waste loading at Hanford could apply to HLW vitrification at INEEL:

- Technical advances that have the effect of allowing more crystallization in the glass should be beneficial to waste loading in some of the INEEL process options.

- Technology development directed to higher temperature melting capability could provide waste loading improvements for some streams, but these cases represent a relatively small fraction of the total waste.

- Melters with features that allow processing of higher volume fractions of crystals in the glass, along with justification for repository acceptance, could open formulation ranges or non-borosilicate waste form options advantageous to waste loading.

- A basis to allow higher concentrations of phosphate phases, and possibly other secondary phases, in the glass could enhance waste loading for some specific streams.

- Iron-phosphate glasses may provide higher waste loading for some streams, especially if calcine separations flowsheets are selected that provide vitrification feeds high in phosphate.

- Performing detailed waste loading assessments for projected waste feed compositions, analogous to the cluster analysis performed on Hanford HLW for this study, should be considered as soon as INEEL flowsheets stabilize and retrieval and blending plans have matured.

10.0 Considerations on Waste Acceptance Requirements for Determination Through the EM-RW Interface

10.1 Responses to Request for Comments

Developing the proposed Yucca Mountain Repository has been a long and tortured process. Understandably, DOE-RW, with the responsibility for developing and obtaining licensing for the repository, is cautious about any changes to the approach being analyzed to date. Since the task for the Review Team is to consider advantages that might be possible if changes were made to DOE-RW's approach, the Review Team asked DOE-RW for comments on the effects of going to a different waste form or different size package. Answers were provided in a May 16, 2001, letter from James E. Carlson, Acting Director, Office of Acceptance, Transportation and Integration, to Ken Chacey, Director, Office of Technical Program Integration, EM-22. This letter included detailed responses developed by the Bechtel Science Applications International Corporation Company to seven questions submitted by the Review Team. Mr. Carlson's main points were the following:

"We have not taken a position that a different waste form cannot be accommodated, but note that additional information and analyses would be necessary, none of which can be accomplished before the planned License Application submittal.

….

In summary, changing from a borosilicate glass to another HLW waste form cannot be accommodated within our current schedule for the development of the License Application to support repository operations by 2010. Therefore, an alternative strategy, such as a later amendment to the License Application to include a new HLW form, will have to be considered once more specific information is available on the alternatives you are considering and further evaluation is completed."

The major points from the Bechtel analysis are the following, with Review Team comments where salient:

"The directions suggested by these seven questions, if pursued, could significantly impact the Office of Civilian Radioactive Waste Management's program for disposing of HLW and SNF.

….

This response is based on the current baseline…in the Waste Acceptance System Requirements Document (WA-SRD). The WA-SRD specifically identifies borosilicate glass as the standard HLW form."

….

"The licensing strategy and schedule for the Yucca Mountain Project LA is based on the currently expected waste forms documented in the WA-SRD."

However, this is only a statement of fact, not an absolute position, as further comments demonstrate.

"Change form a borosilicate glass to another HLW form could have a significant impact on the Performance Assessment (PA) of the repository, the strategy and schedule for developing a License Application (LA), the waste package designs for HLW and DOE SNF, the management of the repository thermal operating mode, and the repository costs." Of course this is true, with the key phrase being "could have."

"In addition to a HLW form qualification program similar to that done for qualifying borosilicate HLW glass, the repository would have to undertake an extensive reanalysis program to support a second standard HLW waste form. The forecast LA schedule to support operations by 2010 cannot accommodate the completion of additional analyses…an alternative strategy, such as a LA [sic] amendment would have to be considered." Few knowledgeable people believe operation will begin in 2010. However, it is to be expected that another waste form would have to undergo extensive evaluation.

"The addition of another standard waste form may result in a net reduction in…costs…the potential savings for waste packages is approximately $115 M….[A]dditional analysis is necessary to ensure that the safety margin is maintained to protect the public and the worker."

With regard to considering other than borosilicate glass, "[a]dding another HLW form would require changing the analytic basis and approach to developing the repository's licensing basis, at a minimum, to revise the co-disposal approach for the remaining DOE SNF."

….

"Changing from the borosilicate glass to another HLW form may have a significant impact on the analysis depending on the characteristics of the new waste form."

…

"By itself, the amount and type of crystallinity in the borosilicate waste form should not significantly affect the PA as long as the radionuclide release from the waste package remains the same.

"[A]ny waste form used to immobilize the HLW should have leach characteristics as good as borosilicate glass so that public safety is ensured….Although it may not be crucial for TSPA [Total System Performance Assessment], [glass degradation rate] will likely be one of the issues evaluated during licensing, wherein the repository performance would have to be analyzed for dissolution rates associated with the new HLW glass form."

….

"Although there is no explicit criterion for HLW glass durability, the current glass degradation model assumes a borosilicate glass dissolution model based on the dissolution testing done for the repository program, not just the SRS EA glass model."

….

"Glass composition, as such, is not significant provided the scientific basis for assessing its performance is adequate….Although the phosphate glasses are presumably more durable than the borosilicate glasses, verification would be necessary through QARD-compliant testing."

With respect to going to a larger canister (1.68 m x 5.03 m), "[a] much larger HLW canister would have a significant impact on the current repository design." These impacts could be a net savings or a net cost.

"Components of the licensing strategy include packaging five HLW canisters with a single DOE SNF canister within one waste package. Co-disposal of HLW and DOE SNF should ensure that the fissile mass content of the waste packages would preclude criticality events during the regulatory period."

….

"Dose consequences analyses will be required to determine if the larger canister will meet dose limits at the site boundary given a drop and breach."

"The larger canisters could possibly reduce the number of canisters by a factor as much as 8 resulting in approximately 1,813 large HLW canisters. This includes a higher material loading with the phosphate glass than can currently be achieved with the borosilicate glass."

….

"The bounding waste package, insofar as the longitudinal dimension are [sic] concerned, is the Naval Canistered SNF Long waste package. Since the hypothetical high-level waste package is bounded in dimension by the Naval waste package, there should be no effects on handling by introducing such a waste package."

The response estimates the effect on repository costs to be a reduction of $115 M, but notes "these estimates are quite coarse and represent rough order of magnitude estimates."

10.2 Conclusion

Acknowledging that the DOE-RW response was provided quickly to general questions, the following are indicated:

- A great reluctance was expressed by DOE-RW to consider any near-term changes to the current program to develop a license application, which is based on borosilicate glass and a standard canister.

- However, other waste forms could be considered for the longer term, if they meet the basic repository criteria. Modification of the borosilicate formulas to increase crystal content could potentially meet all the current repository criteria. Phosphate glasses might have advantages over borosilicate glasses, but considerable repository reanalysis would be required. Further research and development is required to assure acceptability of alternate waste forms.

- A larger canister might not present any major difficulties to the repository and might lead to cost savings. Because this would eliminate codisposal for SNF and HLW, a repository reanalysis of radionuclide transport would be required. Any decision to consider larger canisters would impact the producer and would need to be incorporated in the initial design effort since retrofitting the design might not be possible.

Consequently, there is a basis for research and development on other waste forms, on melters that are flexible and able to use other waste forms, and provisions in new facilities to process larger canisters.

11.0 References

Aloy, AS, VA Bel'yukov, AV Demin, and YA Revenko. 1996. "Experiences with Vitrification of HLW and Development of New Approaches in Russia." In *Glass as a Waste Form and Vitrification Technology: Summary of an International Workshop*, pp. E.50-E.51. National Academy Press, Washington, DC.

Bernadzikowski, TA, JS Allender, DE Gordon, TH Gould, and JA Stone. 1987. "The Development, Evaluation, and Selection of Candidate High-Level Waste Forms." In *Tech. High-Level Waste Disposal*, Vol. 3., p. 3.

Calmus, RB. 1995. *High-Level Waste Melter Alternatives Assessment Report*. WHC-EP-0847, Westinghouse Hanford Company, Richland, Washington.

Herbst, RS, JD Law, TA Todd, DJ Wood, TG Garn, and EL Wade. 2000. *Integrated AMP-PAN, TRUEX, and SREX Flowsheet Test to Remove Cesium, Surrogate Actinide Elements, and Strontium from INEEL Tank Waste Using Sorbent Columns and Centrifical Contactors*. INEEL/EXT-2000-001, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.

Ladirat, C. 1995. "French Nuclear Waste Vitrification: State of the Art and Future Development." *Ceramic Engineering and Science Proceedings*, 16(2): 11-14.

Lambert, SL and DS Kim, 1994. *Tank Waste Remediation System High-Level Waste Feed Processability Assessment Report*. WHC-SP-1143, Westinghouse Hanford Company, Richland, Washington.

Law, JD, RS Herbst, TA Todd, VN Romanovskiy, VM Esimantovskiy, VA Babain, and BN Saitsev. 2001. Flowsheet Testing of the Universal Solvent Extraction Process for the Simultaneous Separation of Cesium, Strontium, and the Actinides from Dissolved INEEL Calcine Slurries. INEEL/EXT-98-00749, Idaho National Engineering and Environmental Laboratory, Idaho Falls, Idaho.

Murphy, JA, and AL Olson. 2000. *Draft Idaho SBW Technology Development Roadmap*. Idaho Falls, Idaho.

Murphy, JA, WJ Melton, AL Olson, and AZ Rogers. 2000. *Draft Calcine Treatment Technology Development Roadmap*. INEEL/EXT-2000-01620, Idaho Falls, Idaho.

Perez, Jr., JM, DF Bickford, DE Day, DS Kim, SL Lambert, SL Marra, DH Peeler, DM Strachan, MB Triplett, JD Vienna, and RS Wittman. 2001. *High-Level Waste Melter Study Report*. PNNL-13582, Pacific Northwest National Laboratory, Richland, Washington.

Roux, R, and A. Jouan, Rad. 2001. *Summary of Waste Solidification Process Technologies*. NUREGICR-6666, U.S. Nuclear Regulatory Commission (NRC), Washington, D.C.

Tanks Focus Area (TFA). 2001. *Technical Assessment of the Draft Technology Roadmap for Treatment of INEEL Calcine Waste*. TFA-0102, Pacific Northwest National Laboratory, Richland, Washington.

U.S. Department of Energy (DOE). 1996. *Waste Acceptance Product Specifications for Vitrified High-Level Waste (WAPS)*. DOE/EM-0093, U.S. Department of Energy, Office of Environmental Management, Washington, DC.

U.S. Department of Energy (DOE). 1999a. *Waste Acceptance System Requirements Document (WA-SRD)*. DOE/RW-0351P, U.S. Department of Energy, Office of Civilian Radioactive Waste Management, Washington D.C.

U.S. Department of Energy (DOE). 1999b. *Idaho High-Level Waste and Facilities Disposition Draft Environmental Statement*. DOE/EIS 0287d, Idaho Falls, Idaho.

U.S. Federal Court (USFC). 1995. Idaho Settlement Agreement Resulting from Public Service Co. of Colorado v. Batt. No. CV 91-0035-S-EJL and United States v. Batt, No. CV-91-0065-S-EJL.

Vienna, JD, PR Hrma, DS Kim, MJ Schweiger, and DE Smith. 1996a. "Compositional Dependence of Viscosity, Electrical Conductivity, and Liquidus Temperature of Multicomponent Borosilicate Waste Glasses." In *Ceramic Transactions*, Vol. 72, pp. 427-436. American Ceramic Society, Westerville, Ohio.

Attachment 1. Glass Properties and Melter Characteristics that Limit Waste Loading

In Section 5.5.2 of this report, the processes by which the glass properties and hence waste loading are limited by the design and materials of the melter itself are discussed. In this attachment, further detail is provided on these processes.

Crystallization

Molten glass crystallizes (a process called devitrification when it is undesirable) whenever the melt becomes supersaturated with a crystal having a melting point above the local temperature in the melter. Supersaturation occurs below a certain temperature because the solubilities of all crystals in the melt decrease with decreasing temperature. For a given glass composition, the temperature at which it becomes supersaturated is called the liquidus. A different liquidus exists and can be measured for each crystalline phase that will precipitate out of the melt; the highest or primary liquidus is the one usually reported. This is the highest temperature at which the first crystals will be seen, but a temperature typically hundreds of degrees lower is required to cause a large volume fraction of crystals to form.

This property of a glass composition is directly related to waste loading, since the main components of the melter feed that have low solubilities are such waste components as chromium, zirconium, and the noble metals.

Spinels are a family of high-melting crystals that form in high-level waste (HLW) melts high in chromium or iron. They can be particularly troublesome because they can form small blocky crystals that pack together, and they are often enough denser than the melts to settle rapidly. This has caused problems in some production melters. Recent studies at Pacific Northwest National Laboratory suggest that crystal sizes of spinels in Hanford HLW glasses should generally be small enough that they should not constitute a serious problem.

If a small number of crystals are acceptable in the glass product, the melter can operate satisfactorily in spite of the fact that some parts of the melter are well below the liquidus. How much crystallization can be tolerated depends on many factors, including the size and tendency of the crystals to form solid masses, their electrical conductivity, their proximity to the delivery system, and the provisions that are made for removing them. These provisions can include means for continuously removing crystals, such as stirring or use of a bottom drain. For some types of crystals occasional measures such as idling to allow local temperatures to rise, or introduction of a temporary glass composition with a higher solubility for the offending crystals (called “flushing”), could permit operation below the liquidus.

In many cases, some crystallization in the melter poses no risk, either because the crystals never settle out, or because they cause no problem when they do. A case is known of a commercial Joule-heated melter operating for years with nearly half its volume occupied by zircon crystal deposits, with no negative consequences other than an occasional streak of stones in the product when some of the deposit got too close to the side delivery. Except for noble metals, crystals that will settle in HLW glasses are not electrically conductive, so they should not perturb the distribution of power in a joule- or induction-heated melter. Even chrome oxide and spinel crystals have electrical conductivities far below the high-soda glass, so their presence should have an insignificant effect on the conductivity of the bath.

Current practice for DWPF is to estimate liquidus of a specific batch of waste glass using statistical

models based on measured laboratory glasses. The uncertainties in this estimation, together with the uncertain knowledge of local temperatures within the melter based on only two installed thermocouples, have led to the adoption of a requirement that the estimated liquidus be 100°C below the nominal melter operating temperature. With this requirement, waste loading is generally limited in DWPF batches by liquidus. A better model for predicting liquidus of Hanford HLW glasses may permit higher waste loadings, as would a relaxation of the requirement that the waste glass be free of suspended crystals. In addition, it would be practical to operate closer to the liquidus if forced convection were used to reduce temperature differences within the melter.

Noble metal crystals are a special case of crystallization in which the crystals are electrically conductive metals or metal oxides. Thus they can potentially not only block flow, like other crystals, but can also disrupt electric power distribution within the melt. The temperature and available oxygen, or oxidation state, together determine the liquidus for the noble metal crystals. Of these two factors, oxidation state is more important. Oxidation state of the melt is determined by a complex series of reactions that occur in the cold cap, and can be controlled to some degree by addition of reducing agents to the feed.

Since avoidance of noble metal crystallization requires a high oxidation state, while foaming is minimized by a lower oxidation state, both undesirable processes cannot be completely prevented in some waste glasses. Because of the high impact of foaming on melting rate, the best strategy is generally to maintain a low oxidation state and find another way to deal with noble metals. The best way appears to be to allow them to form, keep them in suspension, and remove them as soon as possible from the melter into the canister. Stirring and bottom delivery systems are the usual approaches.

Molten Salt Phase Separation

The concentration of a liquid compound in a melt saturated with that compound is called its solubility, which is a function of both temperature and the composition of the melt. If the concentration of that compound in the feed is higher than the solubility, the excess will form a separate liquid layer in a process called phase separation. In HLW glasses, the phases that separate are normally sulfates and halides, which float on the surface of the melt since their densities are lower.

The main concern about phase separation is that if enough molten salt accumulates, it might form a continuous layer between the melt and the cold cap. Because of the high electrical conductivity of high-alkali molten salts, such a layer could cause a major diversion of power to the salt layer. This would be disruptive to stable operation of the melter, although it would be likely to be self-correcting through volatilization. In addition, such a salt layer could cause excessive corrosion where it contacts the containment refractories.

Phase separation is likely to originate only in the lower levels of the cold cap, where lower temperatures cause the salt solubilities to be lower. Sulfate phase separation can be avoided by adding reducing agents to decompose the sulfate compounds to gases, which in turn will be captured in the off-gas system. Halides must be removed in pretreatment, or some free melt surface must be maintained from which they will volatilize.

Foaming

Melting with a cold cap depends on transferring through the bottom surface of the cold cap at least part of the heat needed to evaporate water, and essentially all the heat needed to react batch materials and raise them to melt temperature. This heat transfer can be severely impeded if a thick layer of foam forms in the lower part of the cold cap. Such foam formation is common, and is the result of rapid gas generation at or below a level in the cold cap where a continuous viscous liquid phase has formed. Gas can be generated in the lower levels of the cold cap by a number of processes. The most frequent source is the release of oxygen due to a redox reaction in which some multivalent cations such as iron, nickel or manganese drop from a higher to a lower oxidation state. This can be largely avoided by adding reducing agents (generally organic or carbonaceous materials like sugar, formic or oxalic acid, starch, oil, charcoal or graphite) which create a preemptive reducing condition in the cooler upper part of the cold cap. This causes the multivalent cations to be reduced before they reach the lower levels where foam can be generated. To the extent that this reaction can not be controlled (e.g., because of fluctuating levels of nitrates and organic contaminants), then the waste loading of multivalent components must be reduced.

Because the control of oxidation state in the melt is sensitive to the dynamics of the complex reactions occurring in the cold cap, pilot melter tests are needed to establish batch addition strategies and operating practices to avoid foam-related production limitations.

Volatilization

If their concentration or the temperature is high enough, a number of elements will separate from the melt as gases. The process is analogous to the condition of saturation that leads to crystallization from the melt. If the melt is saturated with a gaseous element, the excesswill escape to the off-gas system by boiling, regardless of the type of melter. Recycling it will simply cause it to be driven off again, so it must be removed in the off-gas system. Elements that have very low solubility in the melt (e.g., iodine and mercury in borosilicate glasses) behave in this manner. At lower concentrations or lower melt temperatures, where the melt is not saturated, volatile elements can still escape from the melt, but by a process analogous to drying, not to boiling. In that case, the free melt surface area, temperature and velocity (due to convection in the melt), and gas velocity above the melt surface, will determine the rate of loss by volatilization.

Viscosity

Physical processes impose both upper and lower limits on the viscosity that can be successfully melted in a given glass melter. Circulation of molten glass within a melter is the primary method for transfer of heat within the melt and for homogenization of the melt. If melt viscosity is too high, circulation will be too slow, resulting in lower production rates and poorer glass quality. If melt viscosity is too low, flow out of the delivery system may be more difficult to control, and refractory linings and electrodes usually corrode more rapidly. Penetration of refractory joints is only indirectly related to melt viscosity, since it is the viscosity of the glass at the much lower temperature near the outer surface of the refractory lining that limits penetration. The present range for melt viscosity of 2 to 10 Pa-s could be enlarged to 0.5 to 50 Pa-s without exceeding commercial practice. To accommodate the larger range in a single melter would require special design features, such as stirrers used only at higher viscosities, dual delivery systems for the upper and lower parts of the range, and perhaps some refractory wall cooling for the lower viscosities.

Chemical Homogeneity

The conversion of slurry or dry feed to molten glass creates large localized variations in the chemical composition of the melt, because of the widely varying melting points of the various chemical compounds in the feed. These inhomogeneities are removed by allowing the glass to circulate in the melter, driven either by temperature gradients that cause natural convection, or by bubblers or mechanical stirrers. More convection and hence better homogeneity results from stronger convection driving forces lower viscosity and longer residence time.

It is advantageous in a waste melter to minimize residence time, since longer times mean more HLW glass remaining in the melter at shutdown or failure. Design residence time should be minimized based on observed homogeneity in pilot melter experiments in which convection velocities are reproduced. In commercial practice residence times as long as 40 hours or more are used only when good fining (bubble removal) or very good homogenization is required. For HLW melting, a much shorter residence time should yield adequate glass quality while reducing the amount of glass held in the melter.

Operating Temperature

The materials in direct contact with the melt must not dissolve rapidly, but also must retain adequate resistance to breakage and deformation at high temperatures.

An upper temperature limit is imposed on melters by the potential for failure of immersed metal components by creep (mechanical deformation) or by chemical attack (corrosion and formation of metal deposits in the melt). Joule-heated melters require large amounts of immersed metals for electrodes, and both Joule- and induction-heated melters need metal stirrers, level probes and thermowells. There is generally no lower limit to the operating temperature of a Joule- or induction-heated melter, other than that imposed by viscosity.

Many metals are rapidly dissolved by oxidation, since all HLW glasses are oxides. The amount of oxygen available for reaction with immersed metals can be controlled to a degree by addition of reducing agents to the feed stream, a practice that also is necessary in HLW glasses to minimize foaming. The amount of reducing agents is limited however by the presence of easily reduced oxides in the waste, the reduction of which would result in high volatilization losses or formation of molten metal and solid noble metal deposits on the floor of the melter. Thus the oxidation state of the melt is confined to a fairly narrow range to avoid foaming (for which it must be mildly reduced) and formation of metal deposits (for which it must not be strongly reduced). Because of the presence of easily reduced metal oxides in the waste glasses, the electrode materials commonly found in commercial glass melters at higher temperatures (graphite, tin oxide or alloys of molybdenum or platinum) react excessively with the melt. Serious attempts to find other electrode materials with the combination of chemical and mechanical properties needed for HLW glasses have not been encouraging. A fundamental materials invention would be needed to remove this barrier to the use of metals immersed in HLW melters at temperatures above about 1350°C, the limit for well-cooled Inconel™ components.

Cold wall induction melters have no electrodes, but may have other immersed metal components such as metal stirrers, level probes and thermocouple wells with similar limitations.