HIGH-LEVEL WASTE MELTER REVIEW

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ABSTRACT

The U.S. Department of Energy (DOE) is faced with a massive cleanup task in resolving the legacy of environmental problems from years of manufacturing nuclear weapons. One of the major activities within this task is the treatment and disposal of the extremely large amount of high-level radioactive (HLW) waste stored at the Hanford Site in Richland, Washington. The current planning for the method of choice for accomplishing this task is to vitrify (glassify) this waste for disposal in a geologic repository.

This paper describes the results of the DOE-chartered independent review of alternatives for solidification of Hanford HLW that could achieve major cost reductions with reasonable long-term risks, including recommendations on a path forward for advanced melter and waste form material research and development. The potential for improved cost performance was considered to depend largely on increased waste loading (fewer high-level waste canisters for disposal), higher throughput, or decreased vitrification facility size.

The review addressed the following questions:

- Are there other glasses or glass-ceramic compositions, including borosilicate glass variations, which could handle segments of DOE high-level waste 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 high-level waste with greater efficiency, cost savings, or lower program risk?

The principal conclusions and recommendations of the Review Team include the following:

- There are no other glasses or glass-ceramic compositions that are obviously better than borosilicate glass, and a modest research program on other silicates and iron-phosphate glass was

recommended, primarily as an insurance policy in case substantial problems arise in the use of borosilicate glass.
- The Joule-heated ceramic melter is the best approach for vitrification, and substantial improvements to the current technology were recommended. A short but intense research and technology development program on the Advanced Cold Crucible Melter was recommended, as an insurance policy.
- 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.

INTRODUCTION

This study was organized for DOE by the Tanks Focus Area office in Richland, Washington. Two separate but interactive teams were established: a Study Team and a Review Team. The Study Team participants were comprised of technical staff throughout DOE laboratories and site contractor organizations. The Review Team was made up of independent consultants with substantial collective experience in glass and high-level waste (HLW) processing for disposal. Information gathering and technical analyses were performed by the Study Team, with data and results compiled in a report (7). These studies were guided by the Review Team, which developed conclusions and recommendations consistent with their charter from DOE. This paper presents a summary of the study, key elements of the Review Team's evaluation, and the results (1).

HANFORD SITE TANK WASTE TREATMENT CHALLENGE

Beginning in 1944 and continuing until 1988, the United States government operated facilities at the Hanford Site for the production of plutonium for nuclear weapons. During that time span, various processes were used to separate plutonium and uranium from other byproducts. Several other chemical processes were also used in support of work at the site. By the early 1990s, the waste generated from these processes amounted to more than 55 million gallons of solid and liquid high-level radioactive waste. This waste was stored in 177 tanks (149 single shell, 28 double shell) ranging in size from 55,000 to 1,160,000 gallons. The waste consisted of a variety of soluble and insoluble salts, organic compounds and complexed chemical species. This waste contains more than 250 million curies of radioactive materials.

In 1994, the DOE began a strategy to privatize the pretreatment and immobilization of the tank waste at Hanford. This led to the signing of two competitive contracts in 1996: one with BNFL, Inc (BNFL) and one with Lockheed Martin Advanced Environmental Systems to establish technical, regulatory, and business elements to accomplish this project. A contract was awarded to BNFL in 1998 to design a plant to vitrify 10% by volume and 25% by curie content, with a HLW fraction intended for disposal in Yucca mountain and a low-activity portion separated for disposal on site. Both HLW and low-activity waste products would be incorporated into borosilicate glass. Although that financial approach ended in May 2000, the technical strategy of waste vitrification has continued with a cost–plus incentive fee contract awarded to Bechtel-Washington in December 2000.

The BNFL plan for the Hanford Waste Treatment Plant (WTP) was considered to be a robust design that met or exceeded technical requirements. The design incorporates a Joule-heated melter technology, similar in concept to those which the DOE uses at the West Valley Demonstration Project (WVDP) in New York and the Savannah River Site (SRS) in South Carolina. The DOE currently plans to fully utilize and build upon the BNFL design as the baseline approach. However, the DOE is also dedicated to evaluating and incorporating technology alternatives and treatment strategies that are more expedient, less costly, and less risky. The Hanford Site is scheduled to complete cleanup by 2046, with an estimated $53.3 billion life-cycle cost for the Office of River Protection (the DOE office in charge of tank waste cleanup at Hanford). DOE's Office of Environmental Management (EM) maintains a viable technology development program (EM-50, Office of Science and Technology) to search for process improvements and enhancements, as well as alternatives to baseline strategies.

PREVIOUS STUDIES OF HANFORD TREATMENT ALTERNATIVES

In January 1999, DOE initiated a study "Technical Alternatives to Reduce Risk in the Hanford Tank Waste Remediation System Phase I Privatization Project" (9). This evaluation, completed in September 1999, concluded that the overall HLW melter system planned for Hanford presented a moderate level of technical risk, based mainly on possible failures due to noble metal accumulation and clogging by solids precipitation. Concurrent with development of the WTP project using the Joule-heated melter, the DOE's EM-50 program has funded work involving a variety of melter-related technologies that may be considered alternatives to the baseline, including induction melters, in-can melting, and phosphate glasses. The DOE continues to evaluate solicited and unsolicited technology proposals. In late 2001, it was desirable to have an independent assessment of specific melter technologies and waste forms to guide the technology development program and recommend the preferred alternatives for continued research. This was considered in part due to possible changes in the requirements of the HLW repository in drafting of 10CFR63 (issued November 2001), and the possibility of cost savings by attempting increased loading of waste into glass or from some alternate waste form.

A study of cost drivers was carried out for the EM program, which estimated that the incremental cost per Hanford HLW canister to the EM program was about $1 million, with a potential savings to Hanford on the order of $2 billion if waste loading were increased from the current baseline of about 30% up to 45% (6). This estimate was roughly supported by a cost analysis in the present melter study. Coincidentally, another impetus for the melter study was a recommendation to the DOE from a committee appointed by the National Research Council (5) encouraging "research on alternative melter techniques" as one of four research areas for developing a long-range science plan. That committee, chartered by the DOE to provide recommendations on the development of a long-term basic research agenda to address HLW problems at the DOE sites, formally issued their recommendation in an interim letter report in November 2000.

In April 2000, the DOE requested that the Tanks Focus Area (TFA) conduct a technical review of alternatives for waste solidification (focusing on glass and glass ceramic waste forms) to achieve major cost reductions within reasonable long-term program risks. This review was to provide recommendations for future research and development activities to address types of waste formulations, waste forms, waste loading, waste packages, waste canisters, and melters for cost savings in vitrification, storage, and disposal. The processes and technologies were to be compared to the Joule-heated melter concept but were not to be limited to incremental improvements over the baseline. The study was targeted primarily for Hanford, but could also be applicable to HLW treatment programs at the Idaho National Engineering and Environmental Laboratory (INEEL) and Savannah River Site. The study was to encompass near-term and long-term options, alternative technologies to the joule-heated melter, and waste forms beyond borosilicate glass, such as ceramics. The recommendations of the report (1) will be used by the DOE to support funding decisions for technology development, but could also be used to address internal policy matters concerning waste forms and performance of an HLW repository.

STRUCTURE OF REVIEW ACTIVITY

As described above, waste loading largely drives overall system cost, although processing rate is also important. 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. Therefore, a major effort in this study was directed at establishing a clear picture of the key technical limitations that affect waste loading as 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 utilized the following steps:

- Define the current requirements and constraints that govern glass formulations to support an understanding of how these factors affect waste loading.
- Utilize 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 waste loadings 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 Joule-heated ceramic melters (at SRS and WVDP).
- 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.

CONSIDERATIONS ON TECHNOLOGY SELECTION-WASTE FORMS

For optimizing waste form materials, the critical factors come from two sources: requirements the product must meet, and processing constraints.

The Waste Acceptance System Requirements Document (WAS-RD) (8) defines specific properties and configurations that waste form materials must fall within for disposal in a geological repository. A systematic assessment was made of the implications for waste loading and waste form processing for each specific requirement in the 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: 1.) Could a modification of the requirement allow increased waste loading? 2.) 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 requirements imposed by the DOE Office of Civilian Radioactive Waste Management (DOE-OCRWM) related to repository design and performance, as distinguished from requirements derived from specific regulations (Code of Federal Regulations or statutes). This assessment identified only one repository requirement directly affecting waste loading for borosilicate glass: the Product Consistency Test (PCT) requirement (WA-SRD 4.2.3), which involves a measurement of glass durability. For any non-borosilicate waste form identified as attractive for waste loading optimization, there would need to be revisions to the waste acceptance requirements. In addition to changes in 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 on reporting of compositions, phases, and phase stability.

Processing constraints, which are determined primarily by the capabilities of a selected process technology and its design features, were evaluated. Interrelationships between the properties required by waste acceptance specifications and the behavior of the waste materials in processing were also considered. The applicable processing constraints arise from the range of properties that allow acceptable melting and pouring behavior for a specific melter design. The extent and characteristics of crystallization which occurs on cooling can also be a factor in determining acceptable glass composition fields. The properties considered in the evaluation matrix were liquidus temperature, glass viscosity, solubility limits, materials limitations, and volatility. 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, the minimum amount of glass-forming chemicals 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.

Three possible courses allow for optimum waste loading with any specific HLW feed composition:

1. 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, improved understanding of the relationships between the property and the performance of the melter system can support changing limits to accommodate more of the problem components.

2. The second approach, for a specific waste form such as borosilicate glass, is to change the characteristics of the melter system. This is discussed below.

3. 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 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 here is to find a combination of waste form product compositions and melting system capabilities that minimize the amount of additives needed to consistently obtain acceptable waste form properties and performance.

CONSIDERATIONS ON TECHNOLOGY SELECTION-MELTERS

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, form a molten glass, and 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.

Every HLW glass melter consists of a system combining components that provide the means for feeding, heating, containing, homogenizing and delivering waste-glass materials. 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 design of a melter should be tailored to the properties of the glass to be melted, the required quality of the glass, and the required production rate. Once a melter design is chosen, the reasoning is reversed and the melter now places constraints on the glasses that can be melted efficiently.

A number of glass properties and melting phenomena are affected by melter design features in such a way as to impact allowable waste loading. Performance of all melter designs, whether heated by resistance or induction or other means, is influenced by these effects. Among the most significant of these properties are:

> Crystallization - 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. The most important composition-dependent property related to crystallization limits is the liquidus temperature of the melt. This is the temperature below which crystal formation (i.e. nucleation and growth) can be initiated on

cooling, or at which dissolution can occur on heating. Also, single component solubility limits can impact waste loading when there is a need to preclude crystallization. Limited solubility of noble metals in silicate glass is an example of this problem.

Liquid phase separation – Liquid (amorphous) phase separation is similar to crystallization, except that the new phase that forms in a glass-forming melt is liquid-like, rather than crystalline. In HLW melts, the phases most likely to separate are molten salts containing sulfates or halides (i.e. chlorine, fluorine).

Foaming - Foaming can involve formation of a layer of foam just under the cold cap. This foam layer blocks heat transfer from the bath to the un-melted feed, limiting the melt rate.

Volatilization - Volatilization could limit loading of wastes, especially those containing halides. Materials volatilized in the melter are captured in the off-gas system. Volatilized radionuclides involve process complexity if separated and recycled to the melter, or they may create an undesirable secondary waste stream.

Viscosity – 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). Therefore, once a melter has been selected, waste loading can be affected by glass constituents which tend to significantly increase or decrease viscosity. The maximum operating temperature of alternative melter designs can limit or extend the glass compositions that can be melted, relative to a reference operating temperature (such as 1150^o for a typical Joule-heated ceramic melter).

Waste Glass Quality - The glass quality parameter that is limiting for a waste glass is leachability (e.g., in the PCT) which can be 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.

Electrical Conductivity – The electrical conductivity of typical nuclear waste melt is strongly influenced by composition, temperature and redox state of the melt. A predictable range of conductivities, commensurate with available power supplies and melter design, is highly desirable in nuclear waste vitrification.

EVALUATION OF WASTE FORM OPTIONS

The strategy for evaluation of waste forms consisted of two major elements. The first element was a review by the Study Team of previous DOE waste form selection activity reports. A major reference point was the DOE assessments in the late 1970s and early 1980s, resulting in the selection of borosilicate glass as the primary waste form for the immobilization of high-level nuclear defense wastes (2). 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. A more recent evaluation of similar scope assessed more than 70 different waste forms for use in disposal of surplus weapons plutonium (4).

As part of this effort, a literature survey was performed to determine the extent of any more recent development and certification on promising waste form materials. This re-evaluation recognized that 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 was also reviewed and evaluated in the same context. The activity concluded with a down-selection of materials for further assessment. Criteria used for this waste form selection were: 1) must be processed through a glass melter; 2) must have been evaluated in previous down selection activities by DOE; and 3) must have attributes which suggest potential for success in immobilizing Hanford HLW. The following materials were selected for detailed evaluation: alkali-alumino-borosilicate glass (AABS), alkali-aluminosilicate glass (AAS), phosphate glass, and titanate glass/ceramics.

The second element of the evaluation strategy was determination of a current best-basis waste feed compositions for Hanford wastes and derivation of waste glass compositions to allow estimates of total waste glass volume. A methodology was adopted by the Study Team which 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 used, 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 batch composition then calculated. Batch compositions are also adjusted to account for the pre-treatment washing or leaching steps designed to reduce the concentration of problem constituents such as Na and Cr. This plan results in 89 batches of discreet feed compositions, which involves some incidental but no deliberate blending. In order to make case studies manageable, the 89 batches were combined into 17 compositional groups or clusters. The waste volume in each cluster represented a grouping of tanks with similar chemical contents. Borosilicate glass formulations were defined for all clusters, using 21 accepted property and composition constraint limits for Joule-heated ceramic melters. These formulations represented the maximum waste loading achievable for each cluster as a base case. This allowed identification of the specific waste components or limiting property constraint which controlled waste loading for each compositional grouping or cluster. Thus, 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 modifications to waste feed components, borosilicate property limits and alternative melter capabilities. To the extent that data available for alternative waste forms could support estimates of viable glass compositions for each of the cluster compositions, total glass volumes for the alternative waste forms could be compared to the borosilicate base case and ranges. This methodology provided the basis to evaluate the relative merits of different waste form and melter technology alternatives.

Borosilicate Glass (AABS)

Results of the Study Team's analysis showed that the total volume of waste glass at Hanford is most influenced by the processing limit set by the liquidus temperature for spinel phases and by the Cr_2O_3 concentration limit. Both of these limits are intended to prevent formation of crystals in the glass melter and canister. The liquidus limit is related to the melter operating temperature, which was also an important influence on total glass volume. Since the glass volume set by these limits is directly dependent on the Cr content of the waste feed, it is apparent that the efficiency of Cr removal in pretreatment (Cr leach factor) has a dominant influence on the amount of glass produced.

Review Team conclusions were:

- Increasing the acceptable limits of crystallized phases in the waste glass offers a major opportunity to minimize the total volume of glass needed to immobilize all the Hanford HLW tank waste.
- The presence of crystals in cooled glass should be acceptable, under current waste acceptance requirements (WA-SRD), if the product consistency test (PCT) is not impacted and crystal formation is known and predictable.
- The 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 Office of River Protection (ORP) baseline.

Alkali-Aluminosilicate Glass (AAS)

Literature review indicated that only limited work has been performed on AAS waste forms, and data was insufficient to allow a systematic waste loading assessment. In general, these glass compositions require higher melting temperatures than AABS. Also, small amounts of boron seem to improve properties for lower melting temperatures. There is evidence that very high waste loadings may be possible if high temperature melting is feasible and some crystallization in the glass is acceptable.

Iron-Phosphate Glass (FeP)

There was a sufficient data base from literature and recent work with crucible melts of iron-phosphate glasses to allow the estimation, based on liberal application of expert judgment, of glass volumes for the 17 waste composition clusters. Estimates were made for both single phase and partially crystalline glasses. The total volume of FeP single-phase glass was higher than that with the base case AABS glass, but the total volume for partially crystallized FeP was slightly lower than the best case for AABS. Individual clusters which were highest in chromium and phosphorus showed generally higher waste loading with FeP glasses.

Review Team conclusions were:

- 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.
- 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.

Titanate Ceramics

Although substantial literature exists reporting laboratory studies on incorporation of HLW into titanate ceramics, there is little data relevant to processing of Hanford-type wastes. Thus, waste loadings for these materials produced in a glass melter could not be reliably estimated. The potential complexity of the materials and the extent of development needed to assess viability provide little interest in pursuing this waste form.

IMPLICATIONS OF REPOSITORY REQUIREMENTS

An important consideration in evaluating waste loading limitations and alternative waste forms is the implication of geological repository waste acceptance requirements and their importance in repository licensing. In an effort to determine what level of flexibility may exist in current waste acceptance requirements (i.e. WA-SRD), a set of relevant questions developed by the Review Team was formally transmitted by DOE-EM to DOE-OCRWM. Responses to the questions generally indicated that current schedules for development of a Licensing Application leading to repository operation in 2010 could not accommodate a change from the currently specified borosilicate glass waste form. Such a change could have a significant impact on the Performance Assessment and licensing strategy for the repository. It was stated that the amount and type of crystallinity in a borosilicate glass was not a concern, as long as the radionuclide release behavior was consistent with an acceptable glass. However, DOE-OCRWM indicated that alternative waste forms could be considered for disposal, pending sufficient technical information to support the additional performance assessments and design modifications needed for an application to amend an initial license.

EVALUATION OF MELTER TECHNOLOGIES

The scope of this review was limited to vitrification processes that produce molten waste glass for casting into standard canisters. The information sources for the Review Team's assessment consisted of the following materials assembled and reported by the Study Team: 1) the extensive data gathered for a 1994 assessment of HLW technologies for Hanford (3); 2) responses by vendors to a January 2001 Request for Information; 3) searches of melter-related literature (journals, presentations, and US patents) since 1994; and 4) knowledge of Study Team members 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.

Westinghouse Hanford Company performed a comprehensive HLW vitrification review in 1994 (3). Earlier assessments of HLW melter technologies were incorporated in that review. The recommendations and reasoning of that review were reexamined by the Study Team, other experts, and the Review Team to determine if the conclusions still proved valid in light of vitrification technology developments since 1994 and the latest results of the Hanford waste characterization program. In reevaluating the 1994 study results, the Study Team relied heavily on its understanding of previous and ongoing technology efforts in the United States and internationally. Information supplied by respondents to the Request for Information was carefully reviewed and considered, as reflected in the Study Team Report. The literature search provided confidence that the available sources adequately reflected the status of development for existing and emerging technologies. The intent was to identify for the Review Team new information and developments, along with the most applicable technologies identified by previous reviews, without attempting a full replication of prior comprehensive down-selections from all possible technologies.

Most Prominent Melter Technologies

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 problem could necessitate the construction of a separate melter disassembly cell in the Hanford WTP.

Induction-heated melters involve two fundamentally different melter technologies, 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.

With the cold-wall (or cold crucible) 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 large enough to be practical for vitrifying Hanford HLW. This technology is interesting primarily because the melt temperature is not limited by electrode materials, since there are none. There is still a need for immersed metal components, such as stirrers, bubblers, level probes and thermowells, so the temperature of a practical melter may be constrained by their performance limits or the ability to cool these components. The most practical configuration developed to date is the French Advanced Cold Crucible Melter (ACCM), in which a special heater geometry is used. This geometry 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 only limited testing has been conducted with slurry feeds.

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. 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 the difficulty of transferring energy from the crucible to the bath. This limitation applies to any melting process heated only at the sidewalls (such as in-can melters), regardless of the source of energy.

One unique application of stirring is the Stir Melter™ technology developed in the 1960s by Owens-Illinois and now owned by Glasstech, Inc. 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. 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^{o}C by high stresses in the stirrers.

Other melter technologies, which were recognized in the study and addressed in the evaluation process, include: cyclone/combustion melters, electric or plasma arc melters, and in-can melters. None were judged to offer sufficient advantages to offset the development costs needed to demonstrate feasibility.

Melter System Features Evaluated

Melter systems have certain essential components, but there are options in the selection and combination of features for accomplishing essential functions. Options considered in this study included:

- The alternative between slurry feeding and pre-drying, reflecting the difficulty of controlling drying and powder handling versus the power requirements to evaporate water from the slurry. This tradeoff affects the size of the melter system.
- The alternative of using secondary heating, in addition to the primary, to supply extra heat for evaporation without increasing the melter surface area.
- Alternatives for minimizing the size and mass of Joule-heated ceramic melters by more aggressive cooling of refractories.
- Different methods of applying forced convection to the melt pool, such as bubblers, stirrers or intentional power concentration to induce hot spots.
- Alternatives for draining glass from the melter, using either over-flow systems or bottom drains. Both methods have been successfully applied in specific Joule-heated and induction-heated HLW melter designs.

The potential for significant cost reduction through melter design 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 critical re-evaluation of melter technologies was performed based on the following choice of design goals, and related characteristics used as criteria, for the melter systems:

1. Capability to produce HLW glass meeting all product and process requirements
2. Low and predictable downtime

3. Flexibility to tolerate load changes
4. Continually adapt and improve - benefit from experience
5. Minimize development cost and risk
6. Minimize melter lifetime cost
7. Minimize melter first cost.

A major conclusion of this review is the finding that only two practical options appear to meet Hanford's long-term vitrification needs:

1. 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. 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. Further development of the baseline Joule-heated ceramic melter is more likely to produce large cost savings than changing to another basic melter technology.

2. The ACCM (cold-wall induction-heated) technology appears to be the most promising of the alternate melter technologies. The higher temperatures available should decrease the number of problem glasses. However, at present, its demonstration in HLW service 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.

A further conclusion is that the current limitations to waste loading at Hanford are related primarily to processing constraints associated with the current Joule-heated ceramic melter (without above suggested enhancements), 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 aimed primarily at higher temperature melting capability could provide waste loading improvements for some streams, but these cases represent a relatively small fraction of the total waste.

It was also concluded that no other technologies are currently being proposed or developed that offer an attractive alternative to HLW vitrification in resistance- or induction-heated melters.

CONSIDERATIONS ON COSTS

The Hanford case studies on waste loading for borosilicate glass performed by the Study Team provided a basis to evaluate the cost implications of total canisters of glass under various constraints and technology options. The dominant factor on canister count was found to be chromium concentrations in the tank waste.

The Hanford Best Basis Inventory (7) shows that 90 mass % of the waste has more than 0.5 wt% chromium oxide. Chromium oxide has limited solubility in borosilicate glass, especially if the iron content is high. If the predicted liquidus is maintained 100 °C below the nominal melter operating temperature (to minimize crystallization), the amount of chromium oxide becomes the limiting criteria for the glass formulations. Previous 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.

At the time of this study, the Hanford baseline was production of 12,700 canisters at a waste loading of 31 wt% oxides. Recent indications suggest this baseline may be conservative as to both the effectiveness of washing chrome from the waste and the solubility of 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 base case production of about 9,300 canisters at an average waste loading of 46.4 wt% oxides.

Assuming that the crystal formation does not impact the leach characteristics of the waste form, a maximum reduction, from the base case, of about 12.1% (1,100 canisters) could be realized by increasing oxide loading to 54.1 wt% and operating at 1350^{o}C. This would require development of crystal accommodation through 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, relative to the base case, would increase about 24.6% (2,300 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.

A cost study of the overall Hanford system was performed by the Study Team, using the glass volumes and production rates from the case studies and technology deployment options. Recognized cost factors included: 1) research and technology costs to develop and qualify waste forms and processing technologies; 2) capital and operating costs of the production facility; 3) capital and operating costs of interim storage facilities; and 4) costs associated with repository disposal.

Vitrification processing 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. A reduction of about 3,400 canisters from the prior Hanford baseline results from using new values for chrome leaching and glass solubility (7). Operating cost, through shorter operating time, should be reduced about $480M as a result of this criteria change. In addition, up to another 1,100 canisters may be eliminated if melt agitation or higher-temperature melters are developed to permit processing of crystal-forming compositions. This could reduce operating costs by an additional $150M.

The vitrification cost is based on 6 metric tons/day (MT/d) glass production at 60% total operating efficiency (TOE). A sensitivity analysis of factors associated with vitrification shows that 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.

The number of Container Storage Buildings required depends on the canister shipping rate and timing versus the production rate. The baseline Container Storage Building has the capacity to store 880 canisters of HLW. If shipments to the repository start before the 880 positions are filled and can continue at a rate equivalent to production rate, then no new facilities would be needed and the operating cost would be $15.9M/yr. Otherwise, a $343M cost will be incurred for each additional 2,640 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 reductions in canister count mentioned above (4500 canisters) would reduce the storage building requirements by about $500M in construction costs. Otherwise, there are no storage cost impacts from waste loading changes.

The DOE repository cost is based on an allocation formula that distributes costs between commercial fuel and DOE. The current cost allocation 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 3,400 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 1,100 canister reduction resulting from relaxing crystal content, the reductions would be $110M and $440M for the incremental and allocated costs, respectively. Recognizing some uncertainty in the cost allocation basis, repository savings could fall in the $500M to $1.0B range for the maximum canister reduction case.

The operating cost savings of $500M to $700M noted above depends on verified chrome and melter technology improvements. The analysis above was 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.

MAJOR RECOMMENDATIONS

As a result of the conclusions from waste form and melter technology evaluations presented above, key recommendations were made regarding DOE technology development programs. Consideration was also given to how the results from the evaluation focused on Hanford might be applicable to HLW processing at INEEL.

Key recommendations on waste form development are:

- 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 for various waste loadings 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
- A program to determine reliable chrome leach factors and glass solubility values should be one of the top priority items for the Hanford WTP because of its high impact on glass volume.
- A modest research program is recommended 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.

Key recommendations on melter technology are:

- DOE should undertake 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. This requires further development in the areas of: forced convection (bubblers, stirrers, etc.), aggressive cooling of electrodes and immersed metal components, bottom drains, reduced refractory thickness via enhanced cooling, intensive mixing beneath the cold cap, and secondary heating.
- A short but intense research and technology program is recommended 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.
- Expanded melter testing is recommended, involving laboratory, pilot scale and full scale testing to optimize process ranges and rates.
- An expanded program for production optimization should be developed, based on establishing procedures for process enhancement testing and production target reassessments during hot operations.

Recommendations on technology application for INEEL are:

- Waste processing at INEEL should apply technical advances in allowing crystallization in glasses to enhance waste loading.
- Flexible melter systems capable of higher temperature operation should be pursued for application at INEEL.
- Analyses similar to the cluster waste loading assessments in this study should be undertaken at INEEL when flowsheets are mature enough to define waste compositions.

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