**VITRIFICATION DEVELOPMENT PLAN
FOR U.S. DEPARTMENT OF ENERGY MIXED WASTES**

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SUMMARY

This document is a general plan for conducting vitrification development for application to mixed wastes owned by the U.S. Department of Energy. The emphasis is a description and discussion of the data needs to proceed through various stages of development. These stages are (1) screening at a waste site to determine which streams should be vitrified, (2) waste characterization and analysis, (3) waste form development and treatability studies, (4) process engineering development, (5) flowsheet and technical specifications for treatment processes, and (6) integrated pilot-scale demonstration. Appendices provide sample test plans for various stages of the vitrification development process.

This plan is directed at thermal treatments which produce waste glass. However, the study is still applicable to the broader realm of thermal treatment since it deals with issues such as off-gas characterization and waste characterization that are not necessarily specific to vitrification. The purpose is to provide those exploring or considering vitrification with information concerning the kinds of data that are needed, the way the data are obtained, and the way the data are used. This will provide guidance to those who need to prioritize data needs to fit schedules and budgets. Knowledge of data needs also permits managers and planners to estimate resource requirements for vitrification development.

Vitrification has already been developed for high-level waste and other types of radioactive and industrial waste. Based on this experience, development for mixed waste should also be feasible. One distinguishing aspect of mixed waste, however, is variability and uncertainty in composition. Production of a glass acceptable for land disposal will require some knowledge of the waste composition so that appropriate glass-forming chemicals can be added where necessary. Process safety will also be a factor when vitrifying unknown waste materials. Another special feature of mixed waste is that it consists of regulated hazardous materials as well as radionuclides. Vitrification development should thus result in equipment systems and process chemistry flowsheets that satisfy regulatory requirements for waste form product consistency, product quality, worker safety, equipment performance, and environmental discharges. The required product quality is not yet defined beyond certain minimal limits. Through vitrification development, the glass waste form can be tailored to any desired level of quality.

1. INTRODUCTION

The U.S. Department of Energy (DOE) is actively investigating methods for treating mixed waste to yield enhanced waste forms through the Mixed Waste Integrated Program (MWIP). To this end, various treatment alternatives are being explored, including vitrification, which results in a glass waste form. Vitrification is attractive because hazardous organic compounds are destroyed at the high process temperatures (typically 1000–1500°C), and toxic metals and radionuclides can be incorporated in the leach-resistant glass waste form. Vitrification has been successfully applied to high-level wastes from the nuclear fuel cycle in France and Germany (Chapman and McElroy 1989). DOE is planning to use vitrification on its high-level waste (HLW) at West Valley (New York), Hanford, and Savannah River. Similarly, it is expected that vitrification can be deployed for mixed waste, although the equipment configurations and glass compositions may be different from those used for HLW.

The purpose of this report is to lay out a plan for development of vitrification technology to treat mixed low-level radioactive wastes (mixed waste). The waste being considered is located at DOE sites and is the responsibility of DOE. The report provides a description of the data needs for bringing vitrification technology to the deployment stage for mixed waste.

The term *vitrification* means “conversion to glass.” The waste glass, however, can include crystalline phases as minor constituents. The plan described in this report covers production of a glass waste form, with the understanding that the waste may not be entirely vitreous because of process conditions. The results are thus relevant to glass-producing technologies including the joule-heated melter, fuel-fired melter, and in-can melter.

The study begins with a description of initial screening activities at the waste site to determine which wastes should be considered for vitrification. This is followed by a vitrification development plan covering waste characterization, waste form development, process engineering, technical specifications for treatment processes, and integrated pilot-scale demonstration. The emphasis of the study is to generally identify and discuss the data needs in a vitrification development program. The appendices provide examples of test plans and data-gathering procedures for treatability/glass development, small-scale melter testing, and pilot-scale testing. These cover both mixed waste vitrification development and testing for the HLW vitrification program.

2. WASTE SITE ACTIVITIES—INITIAL SCREENING

This activity covers the selection of waste streams that should be considered for vitrification. The selection process should involve site staff and those familiar with the technology.

2.1 OBJECTIVE

The main objective of this section of the plan is to describe the process for selection of those low-level mixed waste streams that are potentially amenable to vitrification. The selected wastes will be candidates for further study during vitrification development at a treatment site. An additional purpose of this task is to describe the requirements and issues that must be addressed by the project from the generator-site perspective. The screening exercise initially covers stored and newly generated wastes; remedial and decontamination and decommissioning waste treatment needs will be determined when these waste streams are better defined.

The objective of the initial phases of characterization is to gain sufficient compositional data to determine applicability of the waste forms to vitrification. This information should include the Resource Conservation and Recovery Act (RCRA)-listed constituents, radionuclide analysis, and as much detail as possible about the chemical composition. Knowledge about the processes which generated the waste can be used if there is sufficient documentation. By using the results of the characterization activity, a screening process will provide a selection and prioritization of those low-level mixed waste streams that have the highest potential for treatment by vitrification. This screening will include the advantages and disadvantages of vitrification when compared to other technologies such as incineration, grouting, and polymer encapsulation.

The following steps are discussed in this phase of the plan:

- Screening and selection of the mixed wastes for vitrification or vitrification testing development
- Preliminary characterization of the waste to allow for estimates of process chemistry and process equipment design and preparation of surrogate materials for testing
- Packaging and shipment of waste samples for treatability studies on actual waste at the vitrification site or the vitrification testing site if different from the waste originator site

2.2 METHODOLOGY

Each DOE site has completed at least a preliminary listing of the compositions and amounts of its mixed waste streams. Compositions of these streams are based on process knowledge in the majority of cases. Process knowledge has been the method of choice in the recent past because of the general lack of analytical capabilities for radioactive mixed wastes. The initial screening activity is planned as a coarse selection process, so the existing process knowledge will be used as the initial information base. Selection criteria will include radionuclide composition, RCRA constituents and U.S. Environmental Protection Agency (EPA) codes, chemical composition, physical form, total amount to be treated, ability to obtain samples, ability to perform analyses, pretreatment requirements, ability to ship, application to other sites, and political interest. After the initial list of candidates has been selected, the limited compositional information known at that point will be shared with those developing vitrification treatment technologies.

Surrogate materials can be identified for preparation of simulated waste streams for use in preliminary glass development and testing. This initial testing is typically performed with nonradioactive material due to cost and schedule constraints. These "cold" tests can be

accomplished at the vitrification developer sites while additional characterization, testing, and preparation for shipment of samples of the real waste for treatability testing are taking place at the waste originator site.

Characterization will provide information required by the process as well as that needed for shipping. This includes the main constituents, presence of materials that may be an advantage or a disadvantage to vitrification, materials that could cause shipping problems, the RCRA-listed constituents, and a radionuclide analysis. A preliminary test using the toxicity characteristic leaching procedure (TCLP) and possibly other evaluations of the rough waste will provide a basis for comparison to the final waste form. Some type of pretreatment may be required prior to shipment. Finally, the waste samples must be properly packaged in suitable shipping containers that comply with all applicable regulations at the shipping site, the U.S. Department of Transportation (DOT), and the receiving site. This final waste form verification activity will ensure that the waste has been converted into a robust form that complies with all applicable regulations. The minimum compliance is verification that the treated waste is low-level waste (LLW), rather than HLW or TRU (transuranic), and that it meets land disposal restrictions. Further verification may include a compositional analysis to determine hazardous constituents, a radionuclide analysis to determine activity, and a TCLP to verify encapsulation.

2.3 PREREQUISITES

In general, a comprehensive inventory of the types and quantities of low-level mixed waste at a particular site will serve as the basis for this portion of the plan. At the Rocky Flats site, the inventory information required as input will be provided by the Comprehensive Treatment and Management Plan (CTMP) and its supporting documents. The CTMP has been prepared as a requirement of the Federal Facilities Compliance Agreement (FFCA) and describes DOE's strategy and commitments for bringing Land Disposal Restricted (LDR) mixed waste at Rocky Flats into compliance with applicable regulations.

2.4 REQUIRED RESULTS

The information to be developed as a result of this screening activity is as follows:

- List of wastes under consideration for treatment at the site
- List of selected waste streams to consider for vitrification
- EPA listing and RCRA constituents for the selected wastes
- Description of the waste through process knowledge and documentation, including chemicals and radionuclides, if possible

2.5 DECISION POINTS

The key decision in this task is selection of wastes as candidates for vitrification development. The criteria on which this decision will be based are as follows:

- **Chemical composition and physical form.** This information will be required for process development as well as for shipping. It includes the main constituents; presence of materials that may be an advantage to vitrification (silica, alumina, calcium, etc.) or that could be a disadvantage (chlorides, sulfates, metals, etc.); materials, like free liquids, that could cause shipping problems; the RCRA-listed constituents; and a radionuclide analysis. Wastes that are predominantly metal or dilute wastewater may not be

candidates for vitrification; however, the residue from decontaminating the metal or wastewater could be vitrified. Also wastes that contain high levels of volatile material such as mercury are not candidates for vitrification.

- **Total amount to be treated.** Includes both the backlog and newly generated wastes. This is used for economic analysis and equipment sizing.
- **Ability to obtain samples for analysis.** It will be much easier to sample current processes as opposed to backlog wastes, which may not be homogeneous and will probably not have current sampling plans.
- **Pretreatment requirements and ability to ship.** This hinges on good characterization and the ability to package the waste samples in limited-quantity DOT Type A containers.
- **Political interest.** Some waste streams have gained this interest level for a variety of reasons: perceived hazard, amounts in backlog or being generated, desire for “some action/any action,” and individual VIP opinions. There may be site-specific concerns and national-need issues to consider.

3. VITRIFICATION DEVELOPMENT FOR MIXED WASTES

The following section describes general activities needed to develop vitrification for waste treatment.

3.1 WASTE CHARACTERIZATION AND ANALYSIS

3.1.1 Objective

The objective of this activity is to characterize those waste streams previously selected during the initial screening process (Sect. 2) as being likely candidates for crucible studies. State and federal regulations may require some level of waste characterization prior to engaging in waste management activities such as storage, transportation, treatment, and disposal. Any or all of these data should be made available to those exploring vitrification as a treatment option for a particular waste type.

Beyond the regulatory requirement, there are technical needs associated with characterization. Knowing the constituents in the waste facilitates selection of proper additives to be introduced during vitrification. A target waste glass formulation is sought which has the appropriate processing properties (e.g., viscosity at melt temperature and electrical conductivity) and also yields a final waste form with adequate structural integrity, leach resistance, and other attributes. It is also useful to identify constituents that are not incorporated into glass, such as metals, chlorides, sulfates, and combustible materials. Techniques to manage these materials must be employed, such as combustion, volatilization, and draining of metals. Waste variability information is needed for process design. Finally, some testing will be accomplished using surrogate materials, and characterization will provide the information needed to select and formulate appropriate surrogates. The key deliverable for this activity is sufficient characterization of each waste stream selected in the rough screening process to decide if vitrification studies are warranted.

3.1.2 Methodology

Characterization of stored waste occurs by process knowledge or by sampling and analysis. As mentioned above, process knowledge will probably be the only initial information available on the constituents in the majority of mixed wastes. In some cases this information may be enough. Other wastes, such as those with a requirement for determining levels of certain contaminants, may require more detailed analyses, and an analytical laboratory with specific mixed waste capability must be utilized.

3.1.3 Prerequisites

To proceed with characterization, a decision on which wastes to consider for vitrification is needed. This should be established in the rough screening exercise.

3.1.4 Data Needs and Required Results

Characterization should include information sufficient to select and size waste-handling equipment, formulate glasses, develop a process flowsheet, and define process operating parameters. The information should also be sufficient to allow formulation of surrogate materials for testing of various technologies at the bench or pilot scale. Table 1 lists the principal types of information about waste that can assist in vitrification development. Many of the procedures for chemical analysis are well established and are commonly used in commercial laboratories. To determine water content and combustible content for the purpose of vitrification testing, a specific procedure has been developed at Pacific Northwest Laboratory (PNL) for industrial and institutional wastes and is also applicable to DOE mixed wastes. It is provided in Appendix A.

Table 1. Data Needs: Waste Characterization and Analysis

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Quantity	Equipment sizing and selection, identify opportunities for blending wastes that are complementary with respect to vitrification, establishing cost and schedule for treatment campaign	Plant records, inspection (i.e., count number of containers), volume or weight measurements	Mass, volume, and density
General material description	Screen waste categories for applicability of vitrification or other thermal processing	Plant processing records, inventory records, visual inspection	Qualitative: sludge, liquid, bulk solid, trash, contaminated metal, general heterogeneous material, etc.
Physical form	Determine materials conveyance requirements, feed systems, melter sizing requirements	Plant records, inventory records, visual/manual inspection of waste	Qualitative: flowable solid, liquid, slurry, bulk solid, heterogeneous material, etc.
Physical properties	Determine materials conveyance requirements, feed systems, melter sizing requirements	Measurement of specific weight, viscometer measurement, handling characteristics	Density, viscosity, angle of repose
Rough size distribution	Determine materials conveyance requirements, feed systems, melter sizing requirements	Plant records, inventory records, visual/manual inspection of waste	Size distribution: weight percent versus dimension
Combustibles content	Melter plenum sizing and design, off-gas system sizing and design, melter heat loads, selection of technologies (incinerator, etc.)	Plant records, visual/manual inspection, char/oxidation weight change, organic analysis as needed	Weight percent carbonaceous material or fuel content
Water content	Determine process energy requirements, off-gas sizing, process rate estimates, secondary effluent quantities	Sample and analyze: weight loss on drying, firing	Weight percent H ₂ O
Primary metal content	Determine materials conveyance requirements, need for sorting, feed systems, melter sizing requirements, melter design requirements, treatment technology selection, design of waste glass	Plant records, inventory records, visual/manual inspection, sorting of waste, analysis for metals as needed using metallurgical or chemical methods	Weight percent metals by metal type

Table 1. Data Needs: Waste Characterization and Analysis (continued)

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Volatile metal content	Off-gas system design, plant flowsheet development, secondary waste evaluation	Plant records, inventory records, visual/manual inspection, sorting of waste, analysis for metals as needed using metallurgical or chemical methods	Weight percent metals
Metal cation/oxide content	Melter decontamination factor (DF) determination, waste glass formulation, additive requirements, flowsheet development	Sampling and analysis of waste: inductively coupled plasma (ICP) (EPA 3050, 6010)	Parts per million or weight percent metals, converted to equivalent oxides or glass compounds
Hazardous organic compound content	Air quality and other EPA permit requirements, melter plenum sizing and design, destruction and removal efficiency determination, off-gas system sizing and design, melter heat loads, selection of technologies (incinerator, etc.)	Sampling and analysis of waste: gas chromatography/mass spectrometry (EPA 8240, 8270)	Parts per million by compound
Anion content	Air quality requirements, off-gas scrubber design, scrub solution recycle management, secondary effluent quantities, waste glass formulation, additive requirements	Sampling and analysis of waste: anion chromatography	Parts per million, weight percent, or mole percent anions, associated with corresponding cations (use ICP data as necessary)
Radiochemical analysis	Determine radionuclide retention (DF) in melter, evaluate criticality safety, establish radiation protocols, establish material balances for radionuclides across process, meet air quality requirements	Gross alpha counting, gamma scan	Activity per unit mass (Ci/g) by radionuclide
Radiation field	Determine personnel shielding requirements	Exposure rate measurement using hand-held or remote ion chamber probes	Exposure rate (R/h)

It should be pointed out that not all of the data categories in Table 1 are required. Ideally, there would be minimal requirements to characterize the waste prior to treatment. However, this may not be realistic regardless of the treatment technology for reasons of safety and waste form quality. Blindly treating waste is a safety issue because there may be highly reactive or sealed containers that could explode upon thermal treatment. The safety systems to contain such an event in a radioactive processing facility may be economically unfavorable compared to the alternative of opening containers and conducting sorting/sampling. Waste form acceptance requirements may also prevent treating without some knowledge of the waste. For example, if the waste is dominated by sodium or calcium, then it is necessary to add glass formers in the correct proportions in order to arrive at glass that is not highly soluble in water.

The extent to which waste needs to be characterized depends on the waste form criteria, the uniformity of the waste feedstock, the waste loading, and the treatment process. The need for detailed elemental analysis information about the waste increases with the quality and consistency requirements imposed on the waste glass. This is due to the need to blend appropriate glass formers with the waste. If the waste is highly variable, then the frequency of the sampling and analysis for characterization will correspondingly increase. The sampling and analysis frequency can be reduced if there is a provision in the treatment process for accumulating and batching waste. This dampens out variability and results in a uniform and predictable product. Accumulation and blending can be done in feed preparation tanks prior to vitrification. This is done in the HLW program, where there are stringent requirements for waste glass quality control. Another approach is to utilize a melter with a sufficiently long residence time or a large glass melt bath. Temporary fluctuations in waste composition are dampened by a large inventory of molten glass which is within acceptable composition limits.

A vitrification process can also be chosen that does not depend on the waste for applying heat. The joule-heated melter requires a range of electrical conductivity for heating molten glass. This conductivity is dependent on glass composition. It is thus necessary to analyze the waste to make sure that the material to be vitrified has the appropriate composition to ensure joule-heating. This is avoided by indirect heating such as fuel-fired or arc furnaces. (In the case of arc furnaces, however, it is not clear that homogeneous glass can be produced. This is currently being evaluated by DOE Office of Environmental Restoration and Waste Management programs.) Also, heat applied externally, as with an in-can melter, can be used to vitrify waste without dependence on glass composition or electrical properties.

The extent of characterization for a variable feedstock can also be reduced by formulating a glass with low waste loading. In this case, known glass formers dominate the glass composition. The disadvantage of this approach is that the lower the waste loading is, the higher the amount of waste glass to handle, store, and dispose of.

The distinction between essential versus desirable data will depend on the specifics of the waste in question; the type of vitrification technology being applied; and the criteria for treatment in terms of cost, waste loading, schedule, and perhaps other factors. Some generalities can be made, however, regarding the data types that are needed to proceed with glass development, process design, and evaluation of the performance of the process.

3.1.4.1 Glass Development

The key information needed here is the waste composition in terms of elements that form glass compounds ("metal cation/oxide content" in Table 1). The glass-soluble compounds in the waste determine the ultimate waste glass composition. They also determine whether additives are

needed to achieve a nonleachable glass and to meet requirements for viscosity and other thermal properties to accommodate processing. The elements that are generally abundant in mixed waste and affect glass composition are Li, Na, K, Mg, Ca, Zr, Fe, Al, Si, P, Pb, and F. All of these except fluorine are oxides when dissolved in glass. Fluorine can replace oxygen in the glass structure and bind with metal atoms. The elements sulfur and chlorine tend to volatilize when introduced into a thermal process, although they can be incorporated into glass at low percentages. Those that are less abundant but may affect processing constraints include As, Cd, Hg, and Cr. Other elements are generally trace contaminants including heavy metals; radionuclides such as Cs, Sr, and Tc; various other fission products; activation products; and transuranics.

3.1.4.2 Process Chemistry

Certain waste constituents do not play a role in glass development since they either vaporize during vitrification or form another phase aside from molten glass. However, these constituents influence process design and operation. Materials that volatilize include compounds with H, C, and N. Nitrate and most organic and combustible materials have no influence on glass composition, but they can affect the process. If nitrates are present in the waste, then it may be necessary to employ NO_x abatement devices, depending on the facility permit requirements and the quantities to be processed. Combustion of organic material will generate heat and gases that must be dealt with in the off-gas system. The presence of organic material in the feed may also affect the redox conditions of the glass. Reducing conditions can result in metal phases that include toxic heavy metals and generate waste form material that would have difficulty passing TCLP.

Some elements have a tendency to form another phase that is not soluble in glass. This includes metals with a tendency to remain in the primary state at vitrification temperatures ($>1000^\circ\text{C}$) such as Rh, Pd, Ag, Cu, Cd, As, and Hg. Arsenic and mercury have high vapor pressure, have low solubility in glass, and may volatilize from the melter. These metals would likely require capture in the air pollution control system.

Under reducing conditions, iron can reside as a separate phase in a melter. In the glass industry, iron-rich tramp metal is often found in melters. If there is a potential for molten metal phases, then the design of the melter and its operating temperature must be able to accommodate this. The refractory must be able to resist erosion due to metals. There must be provisions to withdraw metals. An alternative approach is to oxidize the metal using an oxygen lance, in which case the glass formulation will need to be adjusted accordingly.

Depending on the glass and feed chemistry, sulfur can dissolve into the glass, form a separate molten sulfate salt layer in the melter, form a metal sulfide phase, or all of the above. If the concentration of sulfur is low enough, then it may dissolve into the glass completely. Silicate glasses typically can dissolve 1 or 2 wt % of sulfur (as SO_3 in glass). If there is a high level of sulfur in the waste, then provisions for its capture in the air pollution control system and management of a sulfate-bearing scrubber liquid need to be considered. The strategy for managing a molten sulfate layer in the glass melter may be a separate tap from the glass tank or use of a reducing agent to promote conversion to SO_2 and volatilization into melter exhaust. Phosphorous in the feed can result in a phosphate salt layer; however, phosphate has a higher tendency to dissolve into glass than sulfate. Phosphate glass compositions have been developed for high-level waste (Sales and Boatner 1988). Phosphate glasses also have a higher solubility for sulfur than silicate glasses.

3.1.4.3 Subsystem Designs

To design the feed system, off-gas system, and radiation protection system requires knowledge of the waste stream to be processed in the vitrification facility. The general approach will perhaps be to design systems that can handle most or all of the envisioned mixed waste slated for vitrification, rather than tailor the design to a particular type of waste. This allows the greatest flexibility and may avoid the need to build or retrofit a facility to handle a new waste stream.

The physical form of the waste will determine the waste-handling requirements. If the waste is liquid or slurry, then the feed system will utilize appropriate pumps and piping. If it is a bulk solid, then a conveyer and screw feeder might be used. Large solid objects such as trash or cement blocks may require size reduction prior to feeding.

The radiation field associated with waste is necessary information to determine shielding requirements during handling, storage, shipment, and processing. Typically, this information is easy to obtain with hand-held instruments and is documented for stored radioactive waste. Whatever facility is used for treatment, it will likely be designed for the worst condition in terms of radiation field. Shielding will be inherent in the design, and changes in administrative controls and levels of shielding to accommodate a new waste will be costly. It is therefore important that all available radiation field information be available on potential wastes to be treated so that these data can be considered in the criteria for design of the treatment facility.

The presence of water in the feed material will require additional energy for vaporization. The sizing and design of the off-gas system will depend on the water load because of the steam volume and the necessity to avoid the dew point downstream of the scrubbers. It may be necessary to assume the feed is entirely water as a design basis. Provisions for removal of NO_x , SO_x , acid fumes, particulate, and various radionuclide species will be required of the vitrification off-gas system. Performance requirements for the off-gas system should be general enough to cover most envisioned mixed waste.

3.1.4.4 Process Evaluation

Determining the quantities of radionuclides, heavy metal contaminants, and hazardous organic compounds in the waste is needed in order to evaluate the overall success of the process and the resultant waste form. The leach resistance of the waste form as compared to the raw waste can be determined. The degree to which the hazardous organic compounds in the waste are destroyed can be assessed. It is also necessary to determine a material balance around the treatment process and individual units. The radionuclide and heavy metal content of the waste glass and the off-gas emissions can be compared to that of the untreated waste to complete a mass balance. During full-scale operations, process evaluations at predetermined intervals can be done to show compliance with permit requirements.

3.1.5 Decision Points

Based on knowledge gained from characterization, waste streams need to be selected for glass development and treatability studies. There are some wastes that may not be amenable for vitrification. It is expected that these will be identified in the initial screening (Section 2). This includes contaminated scrap metal, mercury, and brines or sludges with high levels of chloride and sulfate. Each waste stream should be considered on a case-by-case basis, however, rather than by establishing a general policy which either prohibits or requires certain treatment technologies for certain wastes. The decision to proceed with vitrification development on certain wastes will involve consideration of how readily the waste stream chemistry lends itself to

conversion to glass and how readily the waste glass can be produced in a melter which is available for testing and/or deployment.

3.2 WASTE FORM DEVELOPMENT AND TREATABILITY STUDIES

3.2.1 Objective

The objective is to develop glass compositions based on waste compositions selected for vitrification studies. The objective is also to perform crucible-scale tests with the waste or surrogates to determine the feasibility of treatment. The waste glass should have performance standards higher than those required to meet environmental regulations.

At present, the recognized criteria are EPA-TCLP and the general standards identified in DOE Order 5820.2A, which essentially follows those of the U.S. Nuclear Regulatory Commission (10 CFR 61). The DOE standards are qualitative and deal with free liquids, flammable material, reactive material, compressive strength, and other basic criteria. They are met almost automatically by glass waste forms. There is no established leach performance criteria beyond TCLP for mixed waste. TCLP was originally designed as a method to determine whether a substance is hazardous.

There is an incentive to minimize the leach rate of waste forms that is independent of conformance to TCLP or other established criteria. The measured or predicted leach rate will provide the near-field source-term data in a performance assessment model. The lower the rate is, the lower the calculated dose to the biosphere. The desire to minimize leach rate for waste glass must be balanced against other factors such as additive requirements (i.e., low waste loading) and the cost and schedule of the development phase to optimize the glass composition.

3.2.2 Methodology

To a first approximation, it is necessary to formulate a glass for every inorganic waste stream to be vitrified. If the waste stream is small (i.e., on the order of the size of the molten glass inventory in the melter), then this development may not be necessary since small waste streams in this case may be dominated by larger waste streams. The steps to develop a waste glass for a specific mixed waste composition are described as an example. Table 2 shows specific data for mixed waste sludge from the Oak Ridge Reservation West Tank Farm sludge (WTFS).

1. Waste composition data are obtained and expressed as chemical analyses. This is shown in the first two columns in Table 2. Note that the parts per million only adds to 271,800. The glass developer must assume that the balance is water or some other material that does not affect glass composition.
2. The elements in the waste are converted to oxides or other compounds that form glass, as shown in the next two columns. This can be done in the laboratory and the oxide residue analyzed. This is the preferred approach when the waste contains a high mass loading of combustible material. Alternatively, given the chemical analysis of the waste, the oxide equivalent composition can be calculated. In the case of the tank farm sludge, the composition is dominated by CaO.
3. Chemical surrogates are used to make an equivalent composition to match the waste with respect to glass compounds. Lanthanum is used in place of uranium so that bench-scale studies can be done without using radioactive material. MIK (methyl isobutyl ketone) is a solvent that is added. (To prepare a surrogate with representative physical and

Table 2. Formulation of Glass for Oak Ridge West Tank Farm Sludge

Average Waste Analysis		Glass Dry Oxide Compound wt %		Surrogate Waste Compound wt %		Waste Glass WTFS-2 wt %	
Ba	500	BaO	0.5	Ba(OH) ₂	0.24	BaO	0.11
Ca	269,200	CaO	96.2	Ca(NO ₃) ₂ ·4H ₂ O	92.37	CaO	21.0
Cd	100	CdO	0.5	CdNO ₃ ·4H ₂ O	0.23	CdO	0.11
Cr	400	Cr ₂ O ₃	0.8	Cr(NO ₃) ₃ ·9H ₂ O	1.15	Cr ₂ O ₃	0.17
Ni	1,100	NiO	0.8	Ni(NO ₃) ₂ ·6H ₂ O	0.68	NiO	0.17
Pb	200	PbO	0.5	Pb(NO ₃) ₂	0.17	PbO	0.11
Zn	300	ZnO	0.1	ZnO	0.02	ZnO	0.02
U	0.14	La ₂ O ₃	0.6	La ₂ O ₃	0.14	La ₂ O ₃	0.13
MIK	3.7	----		MIK	5.0	Al ₂ O ₃ *	14.0
						Na ₂ O*	14.0
						SiO ₂ *	50.2
Total	271,800	Total	100.0	Total	100.00	Total	100

* Additives.

chemical properties of the raw waste, it is necessary to stoichiometrically match cations and anions, if known from the analysis. This detail may not be necessary if the intent is to evaluate the glass, since anions such as carbonate and nitrate are destroyed in the vitrification process.)

4. A glass composition is sought that most closely matches the equivalent oxides shown in the second two columns. Resources are phase diagrams for ceramics; Intergral, which is a commercial glass database; and the PNL Waste Glass Database. In the case of waste dominated by calcium oxide as in Table 2, it is evident that dilution with glass formers is needed to bring down the melting temperature and to arrive at a nonleachable glass.
5. Melting trials are conducted. The surrogate waste is blended with various glass former combinations and melted in crucibles. Observations on melting temperature, homogeneity, phase separation, foaming behavior, and metals dropout are made. These preliminary studies should provide an indication of the feasibility of making a reasonable glass from the waste and can serve as a treatability study. Many candidate glasses are identified based on this exercise. One preliminary glass, WTFS-2, is shown. The glass formers are alumina and silica, which take advantage of the low-melting CaO-Al₂O₃-SiO₂ ternary phase.
6. Candidate glasses are evaluated for melt properties such as viscosity and electrical conductivity as a function of temperature. If these parameters are unacceptable, then step 5 is repeated until the acceptable values are obtained. The qualitative effect of various constituents on these thermal properties is known in many cases so that the iteration steps to arrive at the correct viscosity and conductivity ranges can be minimized. The HLW programs within EM-30 have developed computer models over some compositional ranges to predict properties (Piepel et al. 1993).
7. A final selection on candidate glasses is done to evaluate leach resistance. Tests methods that can be used include MCC-1 (Materials Characterization Center 1982) and the Product Consistency Test (PCT) (Bibler and Bates 1990).

Figure 1 is a logic diagram for waste characterization and glass development prepared for a company that treats commercial LLW. The steps mentioned above are illustrated in this diagram, which is applicable to mixed waste as well. Appendix B provides an example of a test plan used to conduct treatability studies on vitrifying Fernald OU-4 waste. It includes detailed data sheets for the specific test apparatus used in the study.

Preferred formulations will be developed for various temperatures ranging from 1050 to 1500°C. This is the temperature range which has been found to dissolve common inorganic oxides found in waste into the glass melt. Other waste compositions available for co-processing will be considered if they offer potential economic or formulation advantages (e.g., mixing in a waste high in silica with one high in alkali). For each temperature, an optimum waste loading will be identified.

The efforts to develop glasses for mixed wastes can benefit from previous investigations and accumulated theoretical and empirical knowledge. Wolf (1984) provides a comprehensive summary of the effects of various elements on commercial and technical glasses. Chick et al. (1981 and 1984) and Piepel et al. (1993) provide data for borosilicate waste glass. Leachability can be compromised when certain alkaline and alkaline earth metals exceed 20–30 wt % of the glass. This includes mainly Na, Li, K, and Ca. Because of solubility, it is difficult to make glass when alumina and magnesia exceed 30 wt %. Silica is the most common glass former but additives are generally needed to bring its fraction to below 95% to achieve reasonable viscosity at reasonable melt temperature. Chrome oxide is generally insoluble in glass beyond 1–2%, although the steel industry reports molten slags with up to 15 wt % chrome oxide (Downing and Urban 1965). Zirconia is difficult to dissolve beyond 10–15 %, although it is possible to make high-zirconia glass under certain conditions (Lukacs et al. 1978, J. St-Pierre and Zikovsky 1982). Sulfate is generally only soluble up to about 1 or 2 wt % in glass. High percentages of phosphate can be incorporated into glasses that are acceptable as waste forms (Sales and Boatner 1988).

3.2.3 Prerequisites

The information requirements to proceed with waste form development are as follows:

- Chemical composition of the waste
- General requirements of the treatment process (i.e., operating temperature, materials compatibility)
- Waste form performance requirements

In practice, these three factors may not be completely defined prior to the waste form development phase. Detailed chemical composition of the waste may not be available or may have statistical uncertainties due to limited sample populations. There may be iteration between treatment process design or selection and glass development. Waste form performance requirements may not be fully developed for a particular site or disposal scenario. In this case, the glass developer may need to adopt working standards to proceed with a waste glass composition.

Figure 1. General Glass Formulation Procedure.

3.2.4 Data Needs and Required Results

Table 3 lists general data needs associated with this glass development activity. The results of waste form development should provide a glass composition that optimizes the following factors:

- Waste loading
- Compositional variability
- Melt temperature
- Melt viscosity as a function of temperature
- Foaming/reboil behavior
- Processing rate
- Electrical conductivity (for joule-heated melter)
- Leach resistance
- Homogeneity/phase separation
- Devitrification behavior

The ideal situation is to have a glass with 100 wt % waste loading and with the ability to accommodate variations in composition. The glass would melt at the lowest practical temperature, it would not foam or reboil, and it would have a high processing rate. It would have a viscosity of about 100 poise at process temperature and an electrical conductivity of about 0.3/ohm-cm (for joule-heated melter). The waste glass would have high leach resistance ($< 1 \text{ g} \cdot \text{m}^{-2} \cdot \text{d}^{-1}$ in the 28-d MCC-1 test), it would be homogeneous, and it would not devitrify during cool-down. A glass that simultaneously satisfies all of these attributes is unlikely. However, these targets provide a preliminary criteria for glass developers to use. Precise requirements for glasses to be applied for various waste streams will likely be specified by the sites responsible for the vitrification treatment.

The initial part of glass development can serve as a feasibility study for vitrification or as a treatability study. In this stage, observations of homogeneity and the required glass formers to achieve a glass can be determined quickly and inexpensively without detailed or extensive analysis. A decision as to whether to proceed with more extensive development can be made after this phase of study.

The primary variables controlled in the glass development activity are glass composition and melting temperature. Melter operating temperature for waste vitrification is generally 1150–1550°C. This provides a reasonable melting range for glass development. The higher temperature can provide for higher melting rates and higher waste loading. However, high temperature can also result in increased volatility and greater wear on melter materials. These factors should be considered when selecting vitrification equipment and developing waste glass compositions.

The results of treatability studies and glass development need to be documented in a comprehensive report for peer review and technology transfer purposes. An example is a document prepared for the Fernald OU-4 vitrification studies by Merrill and Janke (1993).

3.2.5 Decision Points

The principal decision is selection of preferred glass formulations for mixed waste. The decision is based on the degree to which the parameters described in Section 3.2.4 can be optimized. If an acceptable glass cannot be made in terms of waste loading and leach resistance, etc., then the applicability of vitrification should be questioned before further investment is made. Aside from the technical requirements, there may be economic or schedule requirements that affect the decision or selection process.

Table 3. Data Needs: Waste Form Development and Treatability Studies

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Glass former composition	Formulate glass composition	Chemical makeup procedures	Weight percent by oxide
Glass composition	Basis for association with glass properties	Chemical makeup procedures and/or elemental analysis using chemical fusion and inductively coupled plasma (ICP)	Weight percent by oxide or glass compound
Effect of compositional variability	Determine ability of glass to accommodate waste feed composition changes since waste is not always well characterized and is subject to change	Statistically design test matrix around target compositions. Conduct limited evaluations of glass properties and performance	Thermal properties, leach resistance, qualitative observations of homogeneity
Melt glass viscosity	Evaluate ability to process and handle molten glass, use as criterion for glass development	High-temperature viscometer	Viscosity versus temperature [poise vs T (in kelvin)]
Melt glass electrical conductivity	Evaluate ability to process glass via joule-heating	High-temperature conductivity cell	Electrical conductivity versus temperature [1/ohm-cm vs T (in kelvin)]
Metal retention in glass melt	Determine viability of glass composition or thermal process to retain metals versus volatilize in off-gas	Analyze glass for metals after melting: fusion-ICP	Parts per million metals
TCLP of glass	Determine or quantify performance of glass relative to EPA criteria	TCLP test (EPA 1311, 6010)	Parts per million heavy metals in aqueous extract
Leaching characteristics of glass	Quantify glass performance relative to radionuclide leaching	MCC series tests, PCT	Normalized release of glass constituents or radionuclides
Metals dropout in crucible melts	Criterion for redox control, need to oxidize if metals are reduced from melt	Visual observations in crucible melts	Mass fraction of metals in glass melts
Melting temperature of glass	Determine processability of glass, criterion for glass development, design of melter refractory and electrodes	Qualitative melt condition versus furnace temperature	Temperature
Glass homogeneity, phase separation	Overall quality and reliability of glass composition, criterion for glass development	Visual observation, microscopic observation as needed	Phase observations
Foaming tendency	Processability of glass, redox control, criterion for glass development	Visual observations	Qualitative descriptions

3.3 PROCESS ENGINEERING DEVELOPMENT

3.3.1 Objective

This phase of vitrification development is testing of glass compositions in small-scale or engineering-scale melter. The purpose is to run through a number of glass compositions or flowsheets at relatively low cost and on a faster schedule than possible in a full-sized or pilot-scale unit. Confidence can be gained in the feasibility of the melter process on a new flowsheet before committing resources to large-scale tests. Also, it may be prudent to test new glass compositions on a small scale rather than risk large and expensive equipment on untried glasses. At the small scale, a process flowsheet for integrated testing can be developed to reliably yield an acceptable product.

3.3.2 Methodology

The strategy is divided into steps as follows:

- Select melter unit for testing based on glass formulation and processing constraints.
- Prepare flowsheet for the overall process including feed preparation, additive requirements, vitrification unit, off-gas system, and secondary wastes.
- Perform engineering studies to determine the effects of process parameters on vitrification reliability and glass quality.
- Characterize melter performance—off-gas emissions, melting rate, glass discharging.

In most situations MWIP will be using available melter test units. Flowsheet preparation involves calculating heat and material balances around the process operations. Key parameters to be varied in the melter tests are temperature, waste composition, and waste loading. Variables to be monitored are glass durability (TCLP and PCT); melt rate; melt behavior (formation of metal precipitates, foaming); off-gas composition and amount; organic destruction; and metals retention. These studies will result in an identification of the preferred process conditions for vitrification of the waste using the melter selected for testing.

3.3.3 Prerequisites

Engineering studies on small-scale melter require identification of waste compositions and glass formulations to be tested. A well-developed glass composition should result from the activity in Section 3.2; however, if this activity has not been completed, then preliminary compositions may suffice. Also, there may be iteration between the engineering-scale work and glass development activities. Unacceptable melter performance may require additional glass development work.

3.3.4 Data Needs and Required Results

Table 4 lists the various data needs that are addressed by the process engineering development phase. In some cases the data objective is a prerequisite to doing the experiment and has no inherent value for the treatment program. "Feed composition" is one such entry. This needs to be determined so that comparison with the glass can be made and material balances can be performed, etc. Other data are specific to the melter unit such as cooling water flow and temperature, power settings, and various other parameters. These need to be monitored and recorded so that the process can be operated and conditions reproduced. All other entries besides these have value that extends beyond the immediate need for operating the equipment.

Another discriminating factor characterizing data objectives is the distinction between independent variables and dependent variables. The term *dependent variable* means the factor

Table 4. Data Needs: Process Engineering Development

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Feed composition	Compare against product composition, establish material balance for treatment process, reference data for evaluating off-gas composition and decontamination factors (DFs)	Sample and analyze: inductively coupled plasma, water content, density measurement	Weight percent water, wt % solids, density, composition (wt % glass compounds)
Fate of metals in feed	Determine ability of process to accommodate metals (i.e., oxidation, melting)	Sample and analyze glass and off-gas. Test metal withdrawal methods if needed. Inspect melting tank for metals at end of test. Perform mass balance	Weight percent recovery of metals fed to melter, condition of melting tank with metals, melting temperature of metals, composition of glass and metal withdrawn from melter
Volatility	Determine viability of glass composition or thermal process to retain metals versus volatilize in off-gas	Collect isokinetic sample, analyze solids and compare to glass and feed material through a mass balance	Weight percent by constituent for entrained solids, glass and feed material
Effect of combustibles	Determine how combustibles behave in the melter in terms of redox conditions and effect on volatility of other feed components. Determine combustion efficiencies	Analyze glass for reduced phases, measure off-gas temperature and CO/CO ₂ content, pyrolysis product content	Mole percent gases, wt % composition of glass, temperature data
Organic compound destruction efficiency	Evaluate ability to de-list hazardous waste and meet air quality regulations	Collect off-gas sample or slip stream, analyze with gas chromatography/mass spectrometry via EPA method if warranted	Destruction and removal efficiency expressed as percent destruction of organic compound

Table 4. Data Needs: Process Engineering Development (continued)

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Off-gas flow	Variable affecting off-gas entrainment and combustion process—control parameter, size off-gas treatment system	Flow meters on inlet air or combustion air, flow meters on exhaust gas flow (orifice plates, anemometers)	Standard m ³ /s (scfm), mol % condensable
Off-gas temperature	Variable affecting off-gas entrainment, volatilization, combustion process, and organic destruction efficiency—control parameter	Thermocouple in exit gas pipe (away from radiant shine in furnace)	Temperature (°C)
Off-gas solids loading	Determine DF for species representing radionuclides, determine scrubber solution recycle requirements	Pull isokinetic sample through filter, weigh filter	Mass per unit volume (e.g., grains per dry standard cubic foot)
Off-gas condensable gas loading	Determine material balance around melter, size off-gas system, determine secondary effluents (scrubber brines)	Pull isokinetic sample through cold traps, weigh condensate	Mole percent gases
Off-gas noncondensable composition	Variable depending on combustion or calcination processes in melter, indicator of reactions occurring, used to monitor or control the treatment process, select or design off-gas system for acid gases if needed	Pull sample into mass spectrometer	Mole percent gases
Specific melting rate	Size melter to achieve production requirements, determine feasibility of feed composition (data at small or engineering scale may not be reliable)	Monitor feed rate and glass production rate over sufficiently long period to obtain average rate with low standard deviation	Mass/time-area: kg/h-m ²

Table 4. Data Needs: Process Engineering Development (continued)

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Adaptability to compositional variability	Determine ability of process to accommodate waste feed composition changes since waste is not always well characterized and is subject to change. Evaluate glass quality as a function of feed variation	Systematically alter surrogate waste composition during melter test. Monitor feed rate and glass production rate versus changes in feed. Analyze feed and glass compositions as feed is altered. Observe cold cap or melting conditions	Weight percent by constituent for feed and glass versus time; feed rate and production rate (kg/h); qualitative observations of melt conditions; leach rate (normalized release) and glass properties (viscosity, electrical conductivity) versus composition
Characterization of secondary waste streams	Determine the nature and extent of streams such as wastewater, spent materials, and contaminated equipment. Factor in calculation of plant life-cycle cost. Establish criterion for selection of treatment technology	Analyze scrubber brine composition, identify quantities and types of contaminated equipment or materials generated	Mass, volume and composition data on wastewater and other contaminated material
Materials compatibility	Select materials of construction, establish thickness tolerances, establish operating temperatures	Insert corrosion coupons in glass melt, off-gas exhaust pipe, and other high-corrosion/erosion locations	Corrosion rate: mm/year, qualitative observations for pitting, erosion and corrosion
Utility requirements	Determine heat loads and energy loads for equipment, size equipment for pilot scale	Collect current, voltage, and power consumption data using instrumentation and data logging software or equipment. Measure cooling water requirements using flow meters and thermocouples. Perform heat balance around treatment process	Amps, volts, watts, water flow rate (kg/h), temperature (°C)

Table 4. Data Needs: Process Engineering Development (continued)

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Gross material balance	Determine retention efficiencies for heavy metals and radionuclides, evaluate secondary effluents, support production rate determinations	Measure feed rate and glass production rate. Analyze feed and glass composition. Analyze off-gas entrained solids composition	Composition feed, glass, and off-gas aerosols (wt % by constituent)
Glass product quality evaluation	Determine ability of process to achieve product quality objectives. Verify glass performance as projected from glass development samples. Help determine process stability. Facilitate design of glass-handling system to minimize devitrification	Periodically sample glass product and conduct performance tests (MCC series, PCT). Inspect glasses for homogeneity, crystallinity. Use optical microscopy or other more sophisticated methods as needed	Leach results: normalized release, qualitative results from glass inspection, percent crystallinity
Time to steady state	Indicator of overall stability of thermal treatment process	Monitor temperatures, feed rate, and electrical power demand until steady-state conditions are achieved. Constant composition will require glass tank turnover	Temperature (°C); flow rate (L/h, kg/h); electrical (volts, amps, watts); composition (wt % glass compounds)

depends on the particular experimental arrangement and is a meaningful observable. The operator has control over a limited set of parameters, such as feed rate, power setting, and off-gas blower vacuum setting. With these settings, factors such as melting rate, off-gas temperature, and off-gas flow can be influenced. Other parameters cannot be directly influenced by the operator, such as glass quality, off-gas composition, and organic destruction efficiency. These factors are governed more by chemical reactions, thermodynamics, heat transfer, etc., and are dependent variables. For the purposes of this discussion, the entries in Table 4 are considered to be dependent variables, with the understanding that some observations can be influenced more than others by the operator. The objective is to genuinely and systematically vary the conditions of an experiment to allow for meaningful observations.

The key required results from the process engineering development phase are as follows:

- Mass balances for the preferred process sufficient to proceed to integrated testing
- Functional performance requirements for process equipment (type of melter, required throughput, off-gas system requirements, treatment equipment for secondary wastes) sufficient for procurement
- Processing limits [precipitation of metals, solubility of salts, range of waste loading, and type(s) of waste] sufficient for safe operation of process equipment
- Identification of secondary waste streams
- Organic destruction efficiency
- Heavy metal retention
- Refined cost estimate ($\pm 25\%$)

The extent of engineering testing and experimentation required will vary depending on the specifics of the vitrification development needs for a particular waste. It will also be constrained by schedule and resources. Thus Table 4 identifies numerous data objectives that likely need to be prioritized to meet program budgets and schedules.

3.3.5 Decision Points

At the conclusion of engineering development, it should be possible to make selections on the promising flowsheets and glass compositions associated with various waste streams. The decision to carry a technology and a flowsheet into integrated testing can be made.

The criteria on which to base this decision are as follows:

- Process reliability (projected uptime of process, tolerance of process to variations in feed composition and other parameters)
- Waste form quality and conformance to acceptance criteria
- Project costs (operational costs—including treatment and disposal of secondary wastes, capital costs, disposal and monitoring costs)
- Other site-specific considerations

3.4 SPECIFICATIONS FOR TREATMENT PROCESSES

3.4.1 Objective

This phase of the plan outlines how to define functional specifications for the vitrification process, prepare a material balance, define treatment processing parameters, and develop a specification of pilot-scale equipment for treatment of the subject waste. This is required for deployment of the technology in a process operation, and it is also necessary for pilot-scale

testing, which should simulate real plant operation as accurately as possible. To properly demonstrate the technology in a nonradioactive pilot test, it is necessary to utilize surrogate materials that are physically and chemically similar to the waste and to operate at flows and temperatures that are representative. Equipment performance can thus be evaluated under realistic conditions.

3.4.2 Methodology

The functional criteria for the vitrification process need to be defined. The following are attributes and criteria that are relevant to selection of the treatment technology and its design features.

- **Convert leachable waste into nonleachable final waste form.** This is necessary to generally meet the objectives of the final waste form task in MWIP.
- **Provide a waste form with mechanical and biological stability.** General criteria for waste forms as promulgated by DOE Order 5820.2A will require this.
- **Reduce waste volume.** This is a factor in cost-effectiveness and is identified in DOE Order 5820.2A.
- **Meet treatment standards to allow for disposal.** Certain treatments may be required in order for disposal to be allowed. For example, LDR wastes may require treatment with the best demonstrated available technology (BDAT). Treatments that provide an opportunity to "de-list" the waste will also be favored.
- **Destroy toxic organic materials.** The ability to destroy organic materials will ensure a waste form that is free of such agents and will improve performance for risk assessment.
- **Accommodate a wide variety of feedstock.** Mixed waste streams are heterogeneous, and it is generally preferable to accommodate a spectrum of wastes in one process rather than have a separate process for each waste type.
- **Consistent product quality.** This is important to regulators in proving that the waste form properties are consistent and thus predictable in terms of meeting waste form criteria.
- **Ability to recycle rejected products.** This is an important aspect of product consistency and implementation of production quality control.
- **Minimal secondary streams.** Considering the cost of handling potentially mixed waste streams, this is important in controlling proliferation of more waste.
- **Sufficient throughput capacity.** The process must be able to attain production rates so that campaign schedules are met and/or equipment sizes are manageable.
- **Mature technology.** Mature technologies are desirable for near-term implementation to avoid uncertainties and to minimize research and development costs and schedules.
- **Operate safely.** Technologies with inherently safe features should be sought for worker and environmental safety and to facilitate compliance with stringent DOE standards.

- **Cost-effectiveness.** Capital and operating costs will be a factor in the selection of technologies due to budget constraints. The technology should not be labor or capital cost intensive.
- **Reliability, low maintenance requirements.** This is a major factor considering the cost and downtime associated with repairing equipment in radiation zones.
- **Minimal pretreatment.** This is important in keeping facility, equipment, and operating costs under control.
- **Minimal off-gas treatment demands.** This is important in keeping off-gas equipment costs down and in minimizing atmospheric discharges.

The selection of the vitrification equipment for further consideration in pilot-scale testing should be made based on the criteria listed above.

Another aspect of specifying a process for integrated testing is identification and selection of the mixed waste streams that will be vitrified. This is discussed in Sections 3.1 and 3.2. The Enhanced Waste Forms Group in MWIP has tentatively decided to evaluate vitrification of sludges, ashes, and cement-blend wastes (pondcrete, saltcrete, and contaminated concrete). The pilot testing will be with nonradioactive material since the cost and schedule for conducting large-scale tests with radioactive materials are often prohibitive. Also, the physical and chemical properties of the waste are generally determined by "inerts," or nonradioactive and nonhazardous constituents. For example, mixed waste sludge is dominated by inorganic materials such as silica, calcium hydroxide, and magnesia. This approach assumes that the waste has been adequately characterized to allow one to prepare simulated waste.

The challenge in using simulated waste is that there may be minor constituents in the real waste that are difficult to analyze and that can complicate the treatment process. Because of inadequate sampling and analysis, these constituents would be left out of the surrogate recipe. The potential for such disruptions can be reduced, but not eliminated, by conducting treatability studies on a small scale using actual waste samples (see Section 3.2). Observations on phase formation, outgassing, foaming, devitrification, and other phenomenon can generally be made in treatability studies that provide insight to the scaled-up process. Disruptions can also be minimized by maintaining a significant percentage of glass formers in the flowsheet. Sufficient additives with favorable vitrification characteristics can overwhelm constituents in the waste that detract from glass quality and process stability. However, the use of additives has an impact on the waste form volume that is generated and that must be subsequently stored and disposed of. Soils are high in silica and can serve as a good glass-forming additive. If contaminated soils are used as an additive, then the overall waste volume impact is favorably affected.

To establish the processing parameters for the pilot-scale flowsheet, data obtained during glass development and treatability studies must be utilized. These studies should reveal target waste glass compositions, additive requirements, processing temperatures, and devitrification behavior. Decisions regarding blending waste and additives, melter operating temperature, and the design of the melter and other equipment can be made using data from treatability studies.

Establishing the flowsheet is a critical step in sizing all of the equipment to be used in the pilot process. The flowsheet defines nominal flow rates, temperatures, and energy loads for all

streams and equipment in the process. From this, design values are established that typically account for maximum variations in the process parameters. A data sheet that includes basic information necessary to procure or design the item is then prepared for all items in the process.

The design of the melter for the pilot plant begins with knowledge of the required throughput, the physical form of the waste, the type of glass being produced, the glass temperature, and other operational constraints and criteria. For radioactive waste treatment, the design criteria for a melter is substantially different from that of the conventional industrial glass furnace. The typical industrial glass furnace uses a well-known and constant batch charge, operates at fixed power and temperature, does not have radiological protection concerns, has routine and relatively well-characterized maintenance characteristics, and discharges highly viscous glass gobs into forming equipment (bottle machines, etc.). The radioactive melter must be designed to accommodate variations in glass composition, radionuclides, tramp metals, flammable feed materials, and discharge of low-viscosity glass. These differences have led the national laboratories studying vitrification down a different design path than that taken by the commercial glass melter industry. As a result, high-duty refractories are used throughout the tank, they are designed for remote (versus "hands-on") maintenance, the glass discharge section uses a trough block, and the melter shell is water cooled.

3.4.3 Prerequisites

The required input data to proceed with flowsheet and equipment specification are as follows:

- Definition of waste and processing rates
- Established treatment process criteria
- Waste glass composition
- Results of glass waste form development (Section 3) and vitrification process development (Section 4) studies
- Waste form criteria
- Effluent constraints

3.4.4 Data Needs and Required Results

With the defined waste, required processing rate, and established criteria, it should be possible to make reasonable selections regarding the vitrification equipment and the type of design features to use for further pilot-scale development and testing. Selections need to be made such as batch versus continuous, high-temperature versus low-temperature melter, stirred versus unstirred melt cavity, materials of construction, and electrode configuration. Once these basic selections are made, then technical specifications can be developed.

Technical specifications define the following: required unit process capacities, equipment sizing and duty requirements, process temperatures, definition of process material, functional requirements, and operational constraints (i.e., personnel protection requirements, maintenance constraints). Technical specifications are needed to proceed with detailed design and construction of an integrated pilot plant. After operation of the plant, the specifications may be modified based on information and experience gathered. The revised specifications will be used to design, construct, and operate the initial or prototype mixed waste treatment facility.

Associated with this equipment data package are various drawings and attachments to define the process, including the following:

- Process flow diagram
- Piping and instrumentation diagram
- Equipment layouts
- Equipment assemblies
- Mechanical drawings of equipment
- Interface drawings showing how equipment is connected
- Facility drawings
- Catalog descriptions or vendor brochures for procured items

3.4.5 Decision Points

To proceed with the pilot-plant specification, the principal decisions are what technologies to demonstrate and what simulated waste to process through the pilot equipment. For the purpose of this plan, it is assumed that vitrification has been selected for pilot-plant evaluation. The wastes are specified in the "Rough Screening (1)" and the "Characterization/Analysis (2)" sections.

3.5 INTEGRATED PILOT-SCALE DEMONSTRATION

3.5.1 Objective

The integrated pilot-scale demonstration is the culmination of technology development, waste form development, and selections as to how specific wastes are to be treated. The pilot plant provides valuable data and operating experience that determines the overall feasibility and effectiveness of the proposed process scheme. Operating characteristics and process data are collected on large-scale equipment that is representative of the actual plant. The primary treatment equipment should be connected to other relevant components, such as feed systems, off-gas systems, and product-handling systems, so that interactive effects of the combined process train can be observed and characterized.

3.5.2 Methodology

The steps required to arrive at a pilot scale demonstration are as follows:

- Select waste types to demonstrate.
- Select treatment technologies to demonstrate.
- Select support systems (off-gas and feed system, etc.).
- Establish material balances and flowsheets.
- Select facility.
- Specify equipment.
- Design and fabricate or procure equipment. Install pilot plant.
- Prepare test plan and other required documentation.
- Conduct demonstration.

3.5.3 Prerequisites

The input requirements are essentially the results of Specifications for Treatment Processes (Section 3.4) and include selection of waste streams to process in the pilot plant, selection of treatment technologies, selection of off-gas system, selection of feed system, selection of facility, and definition of flowsheet.

3.5.4 Data Needs and Required Results

The results of the demonstration activity are an installed pilot-plant facility that has been functionally tested. Simulated waste feedstock is processed through the equipment, operational

data are collected, equipment operation is characterized, and overall plant experience is gained. This information is used to make corrections or adjustments in equipment design and operating parameters.

The following types of data or information are collected at the pilot scale for the joule-heated melter:

- Behavior of slurry or bulk materials in melter cold cap
- Bridging or boiling phenomenon
- Melting rates versus type of feed
- Entrainment and volatilization from the melter
- Performance and failure modes of ancillary equipment (feed nozzles, glass discharge, electrode holders, power feeds, instrumentation, etc.)
- Interaction of linked process equipment
- Durability of melter tank lining and electrodes

These and other data needs are summarized in Table 5. Appendix D provides a pilot-scale test plan outline used for the HLW program (Freeman 1992). Other test plans for melter studies have been prepared by Janke et al. (1992), Pohl (1989), and Eschbach (1983).

At the end of test campaigns, equipment can be closely examined by personnel since it is nonradioactive. Materials compatibility can be evaluated, and corrosion and wear phenomena can be determined. This information allows for a more reliable full-scale plant design and minimizes maintenance problems. The risk of failure, downtime, environmental releases, and worker injury or exposure is minimized through proper pilot-scale testing and equipment operating experience on surrogate materials.

A vital part of pilot-scale testing is preparation of a report that describes the results and addresses the test and the specific data objectives. Melter test reports have been written by Cooper et al. (1993) and Perez et al. (1983).

3.5.5 Decision Points

Upon completion of the pilot-plant testing, there is a backlog of operational experience which allows for more informed decisions regarding selection of technologies for certain types of waste and determination of operating parameters (i.e., temperatures, throughputs) for plant equipment.

The technology selection is a key decision since it will determine which treatment processes to deploy in the prototype treatment facility. The decision will utilize information gained from the pilot plant: waste form quality, versatility of feedstock, equipment reliability, maintenance requirements, etc. The decision will also include consideration of process safety, worker exposure, and overall compatibility of the equipment with radioactive operations.

Table 5. Data Needs: Pilot-Scale Testing

<u>Data Objectives</u>	<u>How Data Are Used</u>	<u>Method</u>	<u>Form of Data</u>
Off-gas analysis	Select and size off-gas equipment. Determine process flowsheet material balances. Quantify performance of melter for organic destruction. Provide input data for environmental assessments or environmental impact statements	EPA-approved methods for aerosol sampling and organic destruction efficiency. Sample points: after melter, after scrubber	Particle size distribution versus mass loading for aerosols, composition of aerosols, composition of volatile materials, destruction and removal efficiency
Processing rate	Size melter for prototype or operational plant, develop schedule for treatment campaigns	Monitor feed rate and glass production rate over sufficiently long period to obtain average rate with low standard deviation	Mass/time-area: kg/h-m ²
Glass quality	Determine product consistency for regulatory agencies and for performance assessment purposes	Sample and analyze glass from melter	Leach resistance, crystallinity, homogeneity
Fate of metals in feed	Determine ability of process to accommodate metals (i.e., oxidation, melting)	Sample and analyze glass and off-gas for metals or metal-bearing compounds. Test metal withdrawal methods at high capacity. Examine melting tank at end of testing campaign	weight percent recovery of metals fed to melter, condition of melting tank with metals, melting temperature of metals, composition of glass and metal withdrawn from melter
Dynamic system responses: power, feed rate, inlet air	Evaluate treatment unit operation as a function of controllable parameters, define operational envelope for process operation	Monitor key process parameters: melter power, feed rate, etc. Correlate perturbations and associated responses	Current and voltage of secondary transformer, feed rate (L/h, kg/h)
Maintenance requirements	Determine maintenance schedules and costs for melter, develop radiation protection protocols for plant workers, provide input for improved equipment designs for minimal maintenance and risk	Install instrumentation to detect failures, periodically inspect equipment for wear or pending failure	Service life of component, visual observations of equipment, temperatures, flows, or pressures indicating equipment performance

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Appendix A

Sample Characterization Procedure for Waste Vitrification Studies—
Density, Moisture Content, Combustible Content:

Waste Sample Characterization Procedure,
Pacific Northwest Laboratory, 1992

Waste Sample Characterization Procedure

26 May, 1993

Unique sample ID (AA-ddmmvv hhmm)

Contact Name		Company	
Phone		Street	
Fax		City, State zip	

Concise title, identification and description of waste

Measurement of Sample's Apparent Weight Fraction Water

Estimate Bulk Density of Raw Sample	Today's Date	& Time	
Activity	Weight	Units	Initials
B. Weigh empty container			
C. Weigh container filled with water			
D. Weigh dried container filled with sample			

As Received Bulk density ~ (Weight D. - Weight B.) / (Weight C. - Weight B.)

(D. - B.) / (C. - B.) = units

⇒ Raw Bulk Density of Sample

Take photo with sample ID # Describe sample's appearance and general characteristics.

Take photo with sample ID in background and record appearance and general characteristics.			

Set oven to drying temperature of 105°C or record different setting here

Measure Sample plus container weight periodically. After no change in weight occurs, assume sample is dry.

Activity	Date	Time	Weight	Units	Initials
Drying weight #1					
Drying weight #2					
Drying weight #3					
Drying weight #4					
Drying weight #5					
Drying weight #6					
G. Final Dried Weight					

Take photo with sample ID # Describe sample's dried appearance and general characteristics. Add other relevant comments that were observed or occurred during the experiment here

(F. - G.) / (F. - E.) =

⇒ Weight Fraction Water of Sample

Measure Dry Bulk Density of Sample

Today's date _____ & Time _____

Activity	Weight	Units	Initials
b. Weigh empty container			
c. Weigh container filled with water			
d. Weigh dried container filled with sample			

Dry Bulk density $\sim$ (Weight d. - Weight b.) / (Weight c. - Weight b.)

(d. _____ - c. _____) / (c. _____ - b. _____) = _____ units

⇒ Dry Bulk Density of Sample

Measurement of Sample's Apparent Organic Content

Today's Date _____ Time _____

	Weight	Units	Initials
e. Weigh empty sample container			
g. Add sample to container and record total weight			

Set furnace to pyrolysis temperature of 400°C or record different setting here _____

Measure Sample + container weight periodically. When no weight change occurs, assume sample has pyrolyzed.

Activity	Date	Time	Weight	Units	Initials
Pyrolyzing weight #1					
Pyrolyzing weight #2					
Pyrolyzing weight #3					
Pyrolyzing weight #4					
Pyrolyzing weight #5					
Pyrolyzing weight #6					
h. Final Pyrolyzed weight					

Take photo with sample ID # Describe sample's pyrolyzed appearance and general characteristics. Add other relevant comments that were observed or occurred during experiment.

weight fraction pyrolyzed: (g. _____ - h. _____) / (g. _____ - e. _____) = _____

⇒ Weight Fraction Pyrolyzed

Measure Pyrolyzed Bulk Density of Sample

Today's date _____ & Time _____

Activity	Weight	Units	Initials
b. Weigh empty container			
c. Weigh container filled with water			
d. Weigh dried container filled with sample			

Pyrolyzed Bulk density $\sim$ (Weight d. - Weight b.) / (Weight c. - Weight b.)

(d. _____ - b. _____) / (c. _____ - b. _____) = _____ units

⇒ Pyrolyzed Bulk Density of Sample

Sample's Apparent Carbon Content

Today's Date _____

Time _____

	Weight	Units	Initials
e. Weigh empty sample container			
g. Add sample to container and record total weight			

Set furnace to pyrolysis temperature of 800°C or record different setting here _____

Measure Sample plus container weight periodically. When a change in weight does not take place, assume sample has oxidized.

Activity	Date	Time	Weight	Units	Initials
Oxidizing weight #1					
Oxidizing weight #2					
Oxidizing weight #3					
Oxidizing weight #4					
Oxidizing weight #5					
Oxidizing weight #6					
h. Final Oxidized weight					

Take photo with sample ID # Describe sample's Oxidized appearance and general characteristics. Add other relevant comments that were observed or occurred during experiment.

Determine weigh fraction Oxidized: (g. _____ - h. _____) / (g. _____ - e. _____) = _____

⇒ Weight Fraction Oxidized

--

Measure Sample's Oxidized Bulk Density

Today's date _____

& Time _____

Activity	Weight	Units	Initials
b. Weigh empty container			
c. Weigh container filled with water			
d. Weigh dried container filled with sample			

Oxidized Bulk density ~ (Weight d. - Weight b.) / (Weight c. - Weight b.)

(d. _____ - b. _____) / (c. _____ - b. _____) = _____ units

⇒ Oxidized Bulk Density of Sample

--

Sample's Loss on Firing

Today's Date _____

Time _____

	Weight	Units	Initials
e. Weigh empty sample container			
g. Add sample to container and record total weight			

Set furnace to firing temperature of 1200°C or record different setting here _____

Place sample in furnace for at least 1 hour

h. Final Fired weight			
-----------------------	--	--	--

Take photo with sample ID # Describe sample's Fired appearance and general characteristics. Add other relevant comments that were observed or occurred during experiment.

Determine weigh fraction lost on Firing: (g. _____ - h. _____) / (g. _____ - e. _____) = _____

⇒ **Weight Fraction Lost on Firing**

--

Measure Sample's **Fired Bulk Density**

Today's date _____ & Time _____

(use standard technique if not a insoluble solid piece)

Activity	Weight	Units	Initials
b. Weigh sample			
c. Weigh container filled with water			
d. Weigh water filled container with sample immersed totally in the water			

Fired Bulk density ~ (Weight b) / (Weight d. - Weight c.)

(b. _____) / (d. _____ - c. _____) = _____ units _____

⇒ **Fired Bulk Density** of Sample

--

Sample's Loss on Melting

Today's Date _____

Time _____

	Weight	Units	Initials
e. Weigh empty sample container			
g. Add sample to container and record total weight			

Set furnace to firing temperature of 1400°C or record different setting here _____

Place sample in furnace for at least 1 hour

h. Final Melted weight

Take photo with sample ID # Describe sample's Melted appearance and general characteristics. Add other relevant comments that were observed or occurred during experiment.

Weight fraction lost on Melting: (g. _____ - h. _____) / (g. _____ - e. _____) = _____

⇒ **Weight Fraction Lost on Melting**

--

Measure Sample's **Melted Bulk Density**

Today's date _____ & Time _____

Activity	Weight	Units	Initials
b. Weigh sample			
c. Weigh container filled with water			
d. Weigh water filled container with sample immersed totally in the water			

Oxidized Bulk density ~ (Weight b.) / (Weight d. - Weight c.)

(b. _____) / (d. _____ - c. _____) = _____ units _____

⇒ **Melted Bulk Density** of Sample

--

Appendix B

Sample Test Plan for Bench-Scale Vitrification Studies/ Crucible Melt Studies:

*Test Plan for the Bench Scale Vitrification Testing of FEMP's Operable
Unit Four—Silos 1, 2, and 3, Pacific Northwest Laboratory, 1992*

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TEST PLAN FOR THE BENCH SCALE VITRIFICATION TESTING
OF FEMP'S OPERABLE UNIT FOUR - SILOS 1,2, AND 3

Prepared by:	<u>SM Coté</u> SM Coté, Research Engineer	<u>6/2/92</u> Date
Approved by:	<u>DS Janke</u> DS Janke, Project Manager	<u>6/8/92</u> Date
	<u>RDP Peters for CC Chapman</u> CC Chapman, Group Leader	<u>6/9/92</u> Date
	<u>Robert P. Vogel</u> Bob Vogel, WMCO Project Manager	<u>6/23/92</u> Date
	<u>KR Martin</u> KR Martin, Quality Engineer	<u>6-5-92</u> Date
	<u>L Allen</u> L Allen, Radiation Safety	<u>6-9-92</u> Date
	<u>Glenn R. Hoenes</u> Glenn Hoenes, Laboratory Safety	<u>6/11/92</u> Date
Concurred by:	<u>LE Maples</u> LE Maples, Building Manager	<u>6/3/92</u> Date

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TEST PLAN FOR THE BENCH SCALE VITRIFICATION TESTING OF FEMP'S OPERABLE UNIT FOUR - SILOS 1,2, AND 3

INTRODUCTION

The Fernald Environmental Management Project (FEMP) is a contractor-managed federal facility used for the production of purified uranium metal. The FEMP has been segregated into five operable units. Operable unit 4 is defined as a geographic area that contains Silos 1 and 2 (K-65 silos), Silo 3 (metal oxide silo), and the unused Silo 4. Silos 1 and 2 were used for the storage of radium-bearing residues formed as by-products of uranium ore processing. The residues contain uranium, uranium daughter products, and some heavy metals (primarily lead). Silos 3 and 4 were designed to receive dry materials only. Silo 3 contains calcinated residues of various metal oxides while Silo 4 was never used.

Vitrification studies will be performed on the K-65 material by itself, the K-65 material with Bento-grout added, the metal oxide by itself, and a mixture of K-65 material and metal oxide material. The objectives of these studies are as follows; determine the composition of the off-gas generated during vitrification, determine the radon emanation rate both during vitrification and from the vitrified K-65 wastes, determine the volume reduction resulting from vitrification, determine the gamma dose rates of the vitrified wastes, and finally, determine the leachability of the vitrified wastes. The primary goal of these treatability tests is to develop a stable waste form with minimal leachability of all contaminants, including radionuclides and with reduced radon emanation.

TEST DESCRIPTION

The purpose of these tests is to provide a quantitative evaluation of the performance of the vitrification treatment option. As stated in the 'Operable Unit 4 Treatability Study Work Plan for the Vitrification of Residues from Silos 1, 2, and 3', four different sequences of material (A-D) will be tested. Sequence A consists of the K-65 material by itself. Sequence B consists of the K-65 material with Bento-grout added. Sequence C consists of the silo 3 (metal oxide) material by itself. Lastly, sequence D consists of a mixture of the K-65 material and the metal oxide material.

The first run for each of the above sequences will be performed using an open equipment set-up. This allows for continuous monitoring of the radon emanation during the vitrification process. The open system will be as shown in Figure 1 with valves AV2, AV6, BV4, BV5, and BV6 open. Valves AV1, BV1, BV2, and BV7 can be

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either open or closed depending on whether a previous sample is being monitored for radon emanation. (The sample monitoring container is set-up as a separate system so that vitrification and sample monitoring can occur simultaneously).

The second test run for each of the sequences will be performed with a closed system set-up. This allows for collection of off-gas to determine its chemical composition. The closed system will also be as shown in Figure 1, but with valves AV2 and BV4 closed. Valves AV3, AV4, and AV5 will be opened one at a time depending on which gas sample bag is being filled.

During both the open and closed system runs, the valves on the various flow meters will be fully open unless otherwise stated. These flow meters are for measurement rather than control of flow.

After an initial pre-test waste composite preparation, 100 g test melts (or Sequence 0 melts) will be completed. The results of these test melts will help predict the required compositions for the Sequence A-D tests. As described below, two phases will be required to complete each test within Sequences A-D. When running the Sequence A-D tests, all of the open system runs will be done first. Once all of the open system runs have passed a modified TCLP test, all of the closed system runs will be completed.

Phase I: During the first phase of the test, the material will be melted in a bench-scale furnace. Either an open or closed system will be used, depending on whether the radon emanation is being monitored or the off-gas is being collected. Condensate will also be collected for analysis.

Phase II: During this phase, the vitrified material will be analyzed for radon emanation at 7 and 30 days, volume reduction (based on the specific gravity of the glass), TCLP leachate results, conductivity, viscosity, and gamma dose rate.

HAZARDOUS MATERIALS AND WASTES

All materials used and wastes produced will be handled in accordance with the Waste Technology Center Chemical and Waste Management Plan and PNL-MA-8. All waste produced will be low-level, unmixed waste. Such waste will include gloves, paper cloths, glassware, and cleaning supplies. SDAR # 15-11-1B-0301 (latest revision) will be used for waste disposal. All unused and vitrified test material will be returned to Fernald. All containers will be labeled appropriately, MSDS's will be available, and personnel will be informed of the hazards present.

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SAFETY

Activities associated with the tests will be in accordance with the Waste Technology Center Environmental, Safety, and Health (ES&H) Plan and all applicable Standard Operating Procedures (SOP's) and Radiation Work Permits (RWP's). All personnel performing activities are required to understand the safety requirements for the work at hand.

Hazards associated with this work are the high temperature furnace and the associated electrical power, and radiation. The furnace will be continuously manned and all combustibles will be removed from the area during furnace operation. All staff will be formally trained in radiation protection and will be familiar with all applicable RWP's.

QUALITY ASSURANCE

Testing is to be conducted as Impact Level II work and will be in accordance with QA Plan WTC-060 Rev 1. Analyses of samples will be obtained through Analytical Request Forms for PNL services or through a Statement of Work for off-site services.

The procedures for the two phases of tests follow. Data sheets, which need to be initialed and dated as each step is completed, are included within this test plan. Log sheets are also attached at the back of this test plan. These are for recording any observations that are either unanticipated or which may influence the results of the test, and for recording any speculative notes. Both the data and log sheets will be taped into the laboratory notebook (BNW 53877) once each test has been completed. Any exceptions to this test plan that, due to unanticipated events, may be required to achieve the test objectives, will need to be approved by the project manager (Dan Janke). Any major changes to this test plan will be approved by WEMCO. Once the modifications have been approved, they will be noted in the following data sheets and/or logged in the operations log attached at the back of this test plan.

Each test will be given a number that corresponds to the sequence it is under, whether it is using the open or closed system, the run number, and the start date for the test. An example test number is: AO.1-mm.dd.yy. The 'A' is for Sequence A, the 'O' is for an open system run, the '1' is for the first run, and the 'mm.dd.yy' is the start date format. During each test run various items (such as crucibles, condensate bottles, gas sample bags, and sample cans) will be labeled with the test number and an explanation of the vessel's contents.

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I. PRE-TEST PREPARATION

A. K-65 Composite

PNL has been provided with samples of the K-65 material from three zones (A,B, and C) within each silo. This results in a total of six separate samples of K-65 material. Vitrification will be performed on a composite K-65 sample made from equal dry weight quantities of the above six samples. To complete all the required vitrification sequences, approximately 8 kg of composite K-65 material is required.

The required wet weight quantities from each zone will be calculated based on their moisture contents. This data will be recorded in the laboratory notebook. The proper amount from each zone will then be added to a metal can labeled 'K-65 Composite'. The exact amount added from each zone will also be recorded in the notebook. This composite will be mixed thoroughly to ensure a homogeneous mixture.

B. Silo 3 Composite

PNL received 34 cans containing the Silo 3 (metal oxide) material. To complete all the required vitrification sequences, approximately 7 kg (dry weight) of composite Silo 3 material is required. Material will be combined from enough of the 34 cans until 7 kg has been composited.

The required wet weight quantity will be calculated from the moisture content of the Silo 3 material. This data and the amount added from each can will be recorded in the laboratory notebook. The material will be added to a metal can labeled 'Silo 3 Composite'. This composite will be mixed thoroughly to ensure a homogeneous mixture.

C. Sequence 0 Tests

Up to three 100 g test melts will be conducted for each sequence A-D. The glass forming composition will be varied in these melts until a reasonable composition is found for use in the sequence A-D tests. The various compositions used and the results of these test melts will be recorded in the laboratory notebook.

During these 100 g test runs, the furnace will be operated as stated in SOP #81, the Standard Operating Procedure for laboratory furnaces.

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II. PHASE I - Vitrification (Open or Closed System)

A. Complete Test System Readiness

- i. The following items should be present before starting the test.

Date	Initials	
_____	_____	Crucible (labeled with ceramic high temp. marker)
_____	_____	Gas Sample Bags (5 and 22 L)
_____	_____	Condensate Sample Bottles (1000 ml)
_____	_____	Activated Charcoal Canister
_____	_____	Glass Former Chemicals and Waste Composite Samples
_____	_____	Miscellaneous Supplies: sample labeling tags, Sharpie marking pens, work place copy of the test plan, wrenches, face shields, leather gloves, high temperature gloves, normal working gloves, clean-up supplies, waste drums

- ii. The following items should be given an operability check prior to starting the test.

Date	Initials	
_____	_____	Control panel and Instrumentation <ul style="list-style-type: none">- verify that all instruments have power- verify chart recorder settings- verify over temperature limit setting (max of 1550 °C)- verify that thermocouples are closed and reading close to ambient- verify that furnace temp. controller is getting a signal from the thermocouples and it is close to ambient
_____	_____	Furnace <ul style="list-style-type: none">- check condition of the insulation- visually check the power cables and heaters
_____	_____	Off-gas Cooling System <ul style="list-style-type: none">- check water level in cooler- check that power turns on and it pumps water- make sure there are no leaks
_____	_____	Air Pre-heat before Monitors <ul style="list-style-type: none">- visually check the heating cord

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- make sure the power is on for the temp. controller and that it is getting a reasonable signal from the thermocouple

_____ Radon Gas Monitors (and Computer/Printer)

- check that power is on
- check the functionality of the monitors according to the instructions in the operating manual
- verify that there is paper in the printer

_____ Flow meters

- verify that the valves are fully open

_____ Electronic Balances (Mettler BB240 and Mettler PJ6000)

- verify that power is on
- verify that calibration is up to date

B. Formulate Glass for Sequence Tests

Date _____ Initials _____

Add the following materials/chemicals in a stainless steel beaker and mix thoroughly. The desired amounts will have been previously calculated based on the composition results from the 100 g test melts. The moisture content of the following chemicals will be recorded in the laboratory record book.

<u>Chemical</u>	<u>Desired Quantity [g]</u>	<u>Actual Quantity [g]</u>
K-65 Composite		=
Bento-grout		
Silo 3 Composite		
Na ₂ CO ₃		
Al ₂ O ₃		
SiO ₂		

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- _____ Label a crucible with the test number using a high temperature ceramic marker, number = _____
- _____ Record the weight of the empty crucible _____ g
- _____ Place the above blend in the crucible and record the weight of the crucible and the blend _____ g

C. Perform Vitrification

1. Open System

a. Pre-Vitrification Preparation

- _____ Flush the Eberline RGM -3 and Pylon AB-5 portable radon gas monitors to clean out any residuals. Valves BV4, AV3, AV4, and AV5 need to be closed and valves BV3, BV5, and BV6 need to be opened. Refer to Fig. 2 for these valve positions.
- _____ Record the background count for each of the monitors.
Pylon AB-5 _____ pCi/L
Eberline RGM-3 _____ pCi/L
- _____ Record the flowrates from flow meters BF1 and BF2
BF1 _____ scfh
BF2 _____ scfh
- _____ Set and record the appropriate parameters on each of the monitors
Eberline RGM-3: _____

Pylon AB-5: _____

- _____ Check the printer to make sure it is recording the radon emanation data

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_____ Program the temperature controller for the appropriate ramp and soak profile.

- Heat from room temp to sample melting temp at a maximum of 250°C/hr
- Record sample melting temperature _____ °C
- Hold at melting temperature for _____ hours

_____ Load the crucible into the furnace. Replace the door and front plate of the furnace and secure them with clamps.

b. Vitrification Test

_____ Adjust valves to allow for monitoring radon emanation in the off-gas. Valves BV3, AV3, AV4, and AV5 shall be closed and valves BV4, AV2, and AV6 shall be opened. Refer to Figure 3

_____ Turn on cooling water for the heat exchanger

_____ Label a 1 L bottle with the test number , _____ and place it in the condensate collection trap

_____ Open valves CV1 and CV2

_____ Begin radon monitoring of the air flow through the furnace for a minimum of 4 hours

_____ Set monitor inlet pre-heat temperature controller to its set-point temperature (100°F)

_____ Power up the furnace

- Turn on the breakers
- Run the ramp and soak profile on the temperature controller

_____ Check all data acquisition equipment (temperature profile and radon concentrations) to make sure they are being recorded

_____ Verify that the temperature profile is being followed as programmed

_____ Periodically check and record the flowrates from flow meters BF1 and BF2. Record this data on log sheet A which is attached to the back of this test plan

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_____ Periodically check that the off-gas temperature is being recorded

_____ Report any out of the ordinary occurrences on log sheet B which is attached to the back of this test plan

c. Post-Vitrification

_____ Disengage breakers

_____ Turn off monitor inlet pre-heat temperature controller

_____ Stop the monitors and download the data if required

_____ Turn off cooling water when the off-gas has stopped (monitors off) and once the furnace temperature has fallen below 200°C

_____ Remove the 1 L bottle from the condensate collection, screw the lid on, and verify that it is labelled with the test number

_____ Remove any condensate collected in the heat exchanger

_____ Verify that the breakers are turned off and then remove the front of the furnace to provide access for removing the crucible

_____ Remove all charts (furnace temperatures, off-gas temperatures, and radon concentrations) and label them with the test number

2. Closed System

a. Pre-Vitrification Preparation

_____ Program the temperature controller for the appropriate ramp and soak profile.

- Heat from room temp to sample melting temp at a maximum of 250°C/hr
- Record sample melting temperature _____ °C
- Hold at melting temperature for _____ hours

_____ Verify that the temperature recorder is recording

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_____ Load the crucible into the furnace. Replace the door and front plate of the furnace and secure them with clamps.

b. Vitrification Test

_____ Turn on cooling water for the heat exchanger

_____ Label a 1 L bottle with the test number , _____
_____ and place it in the condensate collection trap

_____ Open valves CV1 and CV2

_____ Adjust valves for the closed system. Valves AV2 and BV4 shall be closed and valve AV6 shall be opened. Refer to Fig. 4

_____ Label a gas sample bag with the test number, _____

_____ Place the gas sample bag on the gas sample manifold at position A3 and open valve AV3

_____ Power up the furnace
• Turn on the breakers
• Push start on the temperature controller

_____ Verify that the temperature profile is being followed as programmed

_____ Periodically check that the off-gas temperature is being recorded.

_____ Report any out of the ordinary occurrences on log sheet B

_____ Observe that the gas sample bag is filling. If the bag becomes full, place another bag (labeled with the test number - 2) at position A4. Open valve AV4 and then close valve AV3. If this bag becomes full, place another bag (labelled with the test number - 3) at position A5. Open valve AV5 and then close valve AV4.

_____ When the ramp and soak profile is complete (after holding at melting temperature for specified time), close the gas sample bags and close the gas sample valves (AV3, AV4, and AV5)

_____ Open valve AV2 to allow air in as the furnace cools

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c. Post-Vitrification

_____	_____	Disengage the breakers
_____	_____	Turn off cooling water when the off-gas has stopped (monitors off) and once the furnace temperature has fallen below 200°C
_____	_____	Remove the 1 L bottle from the condensate collection, screw the lid on, and verify that it is labelled with the test number
_____	_____	Remove any condensate collected in the heat exchanger
_____	_____	Verify that the breakers are turned off and then remove the front of the furnace to provide access for removing the crucible
_____	_____	Remove all charts (furnace temperatures and off-gas temperatures) and label them with the test number

III. PHASE II - Physical Property Determination

A. Complete Test System Readiness

- i. The following items should be present before starting the test.

Date	Initials	
_____	_____	Fracture Chamber (for breaking up crucible and glass)
_____	_____	Stainless steel mesh basket for apparent density determination
_____	_____	Miscellaneous Supplies: sample labeling tags, Sharpie marking pens, sample cans, fishing line, work place copy of the test plan, wrenches, face shields, leather gloves, high temperature gloves, normal working gloves, clean-up supplies, waste drums

- ii. The following items should be given an operability check prior to starting the test.

Date	Initials	
_____	_____	Electronic Balances (Mettler BB240 and Mettler PJ6000) - verify that power is on

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- verify that calibration is up to date

Hanford Cutie Pie (CP)

- verify that power is on
- verify that calibration is up to date

Pylon AB-5 Portable Monitor with Pylon Model 300A Lucas Cell

- check that power is on
- check the functionality of the monitors according to the instructions in the operating manual

B. Gamma Dose Rate of Vitrified Waste

Place the cooled crucible in a plastic bag and remove it from the hood

Measure the background dose rate using the CP at the measurement location. This location should be away from the hood, sample storage, and other sources of radiation. The background reading should be taken just before each measurement on the vitrified waste.

Record the background dose rate _____ mR/hr

Take the crucible to the measurement location.

Place the window of the CP in contact with the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate _____ mR/hr

Place the window of the CP at a distance of 6" from the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate _____ mR/hr

Place the window of the CP at a distance of 12" from the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate _____ mR/hr

Place the window of the CP at a distance of 24" from the bottom of the crucible with the axis of the crucible in line with the axis of the ionization chamber. Record the dose rate _____ mR/hr

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C. Break up the Vitrified Glass

- _____ _____ Return the crucible to the hood and place it in the fracture chamber
- _____ _____ Break up the crucible
- _____ _____ Place ~ 100 g of the broken glass into a sample can labelled with the test number and an explanation of the contents. This can will be sent to the off-site laboratory for the modified TCLP test. Record the mass of glass put in the can. _____ g
- _____ _____ Place ~ 500 g of the broken glass into a sample can labelled with the test number and an explanation of the contents. This can will be sent to an off-site laboratory for a full TCLP test. Record the mass of the glass put in the can _____ g
- _____ _____ Place the remainder of the broken glass into a sample can labelled with the test number and an explanation of the contents. This glass will be used for the apparent density measurement and the radon emanation measurement at 7 and 30 days. Record the mass of glass put in the can _____ g
- _____ _____ Place all the crucible pieces that have glass residue on them in a sample can labelled with the test number and an explanation of the contents

D. Transfer of Samples

- _____ _____ Send sample can containing ~ 100 g (_____) to the off-site laboratory for the modified TCLP test
- _____ _____ Send sample can containing ~ 500 g (_____) to the off-site laboratory for the full TCLP test
- _____ _____ Send the 1 L condensate bottle to the off-site laboratory for analysis
- _____ _____ Send the gas sample bags to the 325 building for analysis
- _____ _____ Verify that the glass passed the modified TCLP test and then send the glass formation data to the 3720 building for conductivity and viscosity analysis

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E. Apparent Density of the Vitrified Waste

_____ Fill a 2000 ml beaker about three-fourths full with de-ionized water, place it on the electronic balance, and tare the scale

_____ Suspend a stainless steel mesh basket from a fine wire (or fishing line) with a well defined mark to which the basket can be consistently submerged. Submerge the basket to this mark in the beaker and tare the scale.

_____ Lift the basket out of the water being sure to keep it over the beaker so any water that drips off the basket falls into the beaker. Place a known mass of vitrified sample (about 50-100 g) in the basket. The pieces must be large enough to stay in the basket. Record the mass of glass placed in the basket, $m_s =$ _____ g

_____ Submerge the basket to the mark. Record the mass from the electronic scale, $F_b =$ _____ g. This is the buoyant force.

_____ Measure and record the temperature of the water in the beaker. _____ °C

_____ Look up the density of water at the above temperature, $\rho =$ _____ g/cm³

_____ Calculate the apparent density of the vitrified waste as follows: apparent density = $m_s / (F_b / \rho)$

where:

m_s = mass of the vitrified sample submerged

F_b = buoyant force

ρ = density of water at measured temperature

Apparent density = _____ g/cm³

F. Radon Emanation from Vitrified K-65 Waste at 7 and 30 Days

Radon emanation data at 7 and 30 days is only required for K-65 waste (Sequence A, B, and D). This will be measured with a Pylon AB-5 monitor operating with a flow of about 0.1 Lpm. Figure 5 shows the valve positions for flushing the

Test Number _____

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monitor and sample chamber during these measurements. Figure 6 shows the valve positions required during the actual radon monitoring.

_____	_____	Place a known mass of the vitrified sample (~ 100-200 g) into a sample can of 4" diameter. Label the can with the test number and an explanation of the contents. Distribute the material evenly in the can. Record the actual mass of vitrified sample _____ g.
_____	_____	Place the sample can into the sample monitoring chamber and leave the lid ajar. Open valve AV7 and flush building air through the monitoring chamber
_____	_____	Open valves BV1 and BV7 and close valves BV2 and AV1. Flush the radon monitor with clean air and measure the background counts from the plateout of radon daughters in the sample monitoring cell. Leave for about 5-6 hours or until the background has dropped to about 1 pCi/L
_____	_____	Record the monitor's background measurement _____ pCi/L
_____	_____	Close valve AV6 to stop flushing air through the monitoring chamber. Open valves BV2 and AV1 and close valve BV1 to start the sampling procedure.
_____	_____	Seal the lid of the sample monitoring chamber
_____	_____	Record the flowrate at BF3 _____ scfh
_____	_____	Monitor the radon levels until the concentration reaches steady state. Record the steady state concentration, _____ pCi/L
_____	_____	Repeat the above steps at 30 days and fill in the following table

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	Mass of Sample [g]	Background Measuremnt [pCi/L]	Flowrate at BF3 [scfh]	Steady-state Conc. [pCi/L]
7 days				
30 days

Figure 1. Bench-Scale Test System for Vitrification of Operable Unit 4 Wastes. (Figures 2-6 of original test plan show different valve positions and are similar to Figure 1.)

Test Number _____

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LOG SHEET A - OPEN SYSTEM VITRIFICATION

Phase I

[illegible]

B-21

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LOG SHEET B - 'OBSERVATIONS

[illegible]

B-22

Appendix C

Sample Test Plan for Small- or Engineering-Scale Vitrification Studies:

Research Scale Test Plan, PNL HWVP Technology Development Project,
Pacific Northwest Laboratory, 1991

RESEARCH-SCALE MELTER TEST PLAN

September, 1991

Melter Performance Assessment
Equipment Adaptation & Testing Task
PNL HWVP Technology Development Project

APPROVALS:DATE:

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1.0 INTRODUCTION

The Melter Performance Assessment activity is responsible for determining the affect of noble metals on the HWVP melter. The melter (see Figure 1) has been designed by Savannah River to

Figure 1 The HWVP Melter

provide a minimum two year operating life. Therefore, nonreplaceable components, such as refractories, Inconel metal heaters, lid heaters, and electrodes have been designed to assure this minimum requirement. Unless a catastrophic failure occurs, it is reasonable to expect the melter to operate for five years or more before glass contact components fail (Koeqler 1987).

The presence of noble metals in NCAW feed could lead to the early failure of the first melter used within HWVP. The first double-shell tank of pretreated neutralized current acid waste will contain approximately 0.6 wt% (oxide basis) of noble metals. This will account for one to one and one-half years of plant operation, assuming a plant availability of 75%. This is the only feed that contains sufficient concentrations of noble metals to threaten the minimum operating life of the HWVP melter.

Noble metals can be considered insoluble in the glass and will exist in the glass melt as particles. The size and behavior

of these particles in the glass tank will determine whether a significant quantity will settle to the floor of the melter or will be carried out in the glass discharged to the canister. If a sufficient quantity of noble metals settle to the melter floor the lower electrode pair could be electrically shorted. When this occurs, either the noble metal accumulation will have to be removed or the melter will have to be replaced.

Work being conducted in FY 1991 and 1992 will define the noble metal behavior in NCAW glass and its propensity for accumulating in a ceramic melter. The work logic is shown in Figure 2. This test plan defines the scope to be performed in the Research-Scale Melter (RSM) activity. Laboratory testing that will precede RSM testing will define feed preparation methods that will be followed and analytical techniques that will give the most accurate and precise measurements of noble metals in slurries and glass. Gradient furnace testing will study the behavior of noble metals during the decomposition, calcination, and melting stages of vitrification. RSM studies will provide more prototypic melting conditions than the GFT, i.e., true cold cap and melter conditions, and will provide data on the effects of process variations on noble metal behavior such as particle size, oxidation state, and agglomeration tendencies. Process variations will span the ranges of plant melter operation, such as redox, temperature, slurry properties, etc. Computer modeling studies will be performed as a precursor to RSM testing and will utilize RSM results to further refine TEMPEST and particle tracking models. Testing will culminate with 20 to 30-day engineering-scale melter (ESM) tests in 1/10th-scale melter systems. ESM testing will be conducted at nominal plant conditions.

The performance assessment approach is based on a plan formulated in FY 1990 by PNL and WHC project staff. The main premise is that the noble metals assessment can not be made at a full-scale. This is due to the fact that no full-scale melter will be available until HWVP cold testing and also is due to the high costs of noble metals. For example, based on a FY 1991 cost estimate a 30-day run in a full-scale melter will require almost \$4M worth of noble metals alone. The approach taken then is to rely on smaller test systems and augment scale testing with laboratory and modeling work.

The KfK 1/10th-scale melter was designed to scale critical dimensions as close to the full scale as possible. The glass surface area is approximately 11% of the plant melter and the glass depth of 34 in. is within the minimum and maximum tank depths of the plant melter. Chemical and kinetic effects can not be well simulated or predicted by current numerical models. Therefore, melter parameters that will most affect particle growth were maintained as closely as possible to full-scale. Parameters which were kept as close to the plant melter as practical were heat transfer conditions, glass residence time, and the electrode placement and overflow location. The residence

NOBLE METALS TEST PROGRAM

Figure 2 Noble Metals Work Logic

time combined with the convective mixing and near surface temperatures will provide conditions as close to the plant melter as can be achieved at this scale. If a conductive sludge forms, the lower electrode current will be shorted through the sludge if a sufficient amount has accumulated. Very conductive accumulations could ultimately affect the operation of the upper electrodes. For these reasons the lower electrode height (12 in.) and the separation between the upper and lower electrode set (10 in.) are matched to the plant design.

The tests to be conducted at WSRC will be conducted in the integrated DWPF melter system (IDMS) melter. The two 10-day melter tests will be conducted within the schedule of testing planned to support DWPF. These tests will obtain data on off-gas compositions during feed forming and noble metal melter mass balance. Any operational effects due to the presence of noble metals that occur will also be studied.

RSM testing will provide process results of noble metal behavior as a function of process condition. Testing is planned to operate the RSM between the maximum and minimum operating limits specified for the plant melter or, if not a plant criteria, based on achieving a measurable change. Relevant process parameters that will be evaluated are discussed in the Objectives section of the plan. Test data will be obtained that, given the scale of the melter, will be treated as semi-quantitative. In contrast to this testing, the ESM tests will be conducted largely within nominal conditions; i.e., reference feed composition, noble metals concentration, process temperatures, glass redox, etc. RSM tests will be correlated to ESM test results and modeling work which together will form the basis for the plant melter assessment.

This test plan has been prepared to direct research-scale melter testing under the Melter Performance Assessment cost account, 1.2.2.04.01. This test plan, along with the gradient furnace test plan, will satisfy PHTD FY 1991 milestone 1.2.2.04.01C. Completion of RSM testing will be completed in accordance with milestone 1.2.2.04.01D. This work will be combined with laboratory and engineering-scale testing planned in FY 1991 and FY 1992 to close HWVP Applied Technology Plan issues under section 5.1.1, "Melter Performance Assessment."

2.0 OBJECTIVES

Per the FY 1991 PNL statement of work the objectives of RSM testing are "to establish operating parameters for engineering-scale melter tests at KfK and evaluate glass containing noble metals. Obtain data that provide an understanding of noble metals behavior in conjunction with feed and glass chemistry to predict melter performance....conduct studies of test parameters, including glass melter temperature, residence time, plenum temperature, and glass redox." (Kruger 1991). To perform this scope of work, a small joule-heated test system was designed in

FY 1990. Approximately eight weeks of testing will be conducted in the RSM to obtain process and product data as a function of process variables.

The relevant slurry and process variables will be varied through the ranges of the HWVP operating limits. The following variables will be investigated:

- noble metals concentration,
- slurry oxide loading,
- redox ($\text{Fe}^{+2}/\text{Fe}^{+3}$) of the glass,
- glass process temperature,
- plenum temperature,

Process analytical data obtained from which noble metal effects will be measured. Process data will be used to determine any measurable effects on melter operation, such as glass resistance or process rate. Process data will also be used to support continued validation and refinement of the numerical codes. Analytical data will be obtained for slurry, glass, and in-melter glass/sludge samples. In addition, post-test examination of the melter will occur to recover sludge or metal deposits.

2.1 Establish KfK Operating Parameters

The 30-day ESM test planned at the Kernforschungszentrum Karlsruhe (KfK) will provide, along with testing in IDMS, the largest scale of testing for the HWVP to evaluate noble metals effects on melter operation. The operation parameters should reflect the expected plant conditions such as nominal composition and slurry properties and melter process conditions. However, RSM testing could identify significant changes in noble metals behavior due to a change in one or more process conditions. Verification of this effect may be required at the larger scale to assess the full impact on melter operation. Based on RSM results then, ESM process or slurry variations will be established. Another aspect of RSM testing that may contribute to the ESM testing strategy is the identification of additional data needs not currently conceived. For example, RSM analytical results may show that smaller or larger sample sets may be required to provide the accuracy and precision for closure the mass balance. Also, process data may identify additional instrumentation needs to support modeling efforts and melter performance assessments.

2.2 Understanding Noble Metal Behavior

HWVP process limits have been established for many feed and melter parameters. These include glass temperature, plenum temperature, glass redox, and slurry oxide concentration. Variations of these parameters will alter somewhat the melting and residence time experience of noble metal particles. For example, the rate of temperature increase and the total time

within temperature regimes within the cold cap is dependant on plenum and glass temperature, and cold cap thickness. Particle interaction and growth is known to occur in the cold cap and near glass region (Nakaoka et al 1986, Sevingy 1990). To assess the impacts of these parameters on noble metals behavior, testing will be conducted at the process limits.

Additional variables that can have an affect on particle size and properties are the level of redox and noble metal concentration in the melter feed. More reducing glasses can lead to reduction of noble metal oxides to metal states. These metals could consolidate, alloy with other metals or act as nucleating sites for spinel growth. Higher concentrations of noble metals provides the opportunity for a greater degree of particle growth.

3.0 Technical Approach/Test Description

The approach to the testing is to vary the parameters considered important to noble metal accumulation over the ranges specified by HWVP Technical Data Package the feed specification (Smith 1991) or over some range designed to produce a detectable change in noble metal behavior. The parameters which will be varied during the testing are glass redox, noble metal concentration, oxide loading, glass temperature, plenum temperature. While residence time is not an independent variable parameter, it is considered an important parameter in noble metal particle agglomeration and therefore warrants consideration. It has been estimated that the residence time will vary between 5.3 and 7.9 hours. This is quite short compared to the residence time projected for the plant melter of approximately 57 h. The actual residence time in the melter will depend on the oxide loading in the feed, and the feed rate which is affected by the glass and plenum temperatures.

In addition to the measurements made during testing, after the planned testing has terminated, project staff will decide whether the melter should be turned off and sectioned to inspect the melter tank bottom for signs of noble metal accumulation or the melter should remain operational for further testing.

3.1 Test Matrix

The nominal value and allowable range of the test parameters, either specified in the HWVP Technical Data Package, based on composition revisions (Smith 1991) or selected for this test based on experience, are shown in Table 1 below. The test matrix (Table 2) was designed to provide an opportunity to vary each parameter mentioned above to its extreme values as listed in Table 1. Testing is planned to occur in 5 day segments. Feeding will last approximately 100 hours per segment. At a 1 l/hr expected feed rate, approximately 15 melter volumes of glass will be processed during each segment.

In addition to the parameters above, one of the later tests will increase the amount of silver and tellurium in the waste by a factor of two along with the noble metals. These metals have been seen to alloy with noble metals in the past.

3.2 Measurements required to attain objectives

The testing required to achieve the desired objectives can be divided into three separate types: process characterization, chemical characterization, and TEMPEST verification.

Process Characterization

The measurements which will define the process are glass and plenum temperature, electrode and heater power, glass and sludge (if measurable) electrical resistance, feed rate, glass production, temperature profile, mass balance (feed, glass and sludge elemental analysis), glass redox.

Chemical Characterization

Chemical characterization will be accomplished through mass balance measurements, sludge sample analyses, glass redox. These various measurements will use ICP, SEM/EDX, XRF.

TEMPEST Verification

The TEMPEST model is being refined to suitably predict the behaviour of noble metal particles in the plant melter. To support this work RSM testing is being used to both provide data on noble metal particle characteristics (size, shape, estimated density, etc.) and glass and sludge electrical resistance. Operation of the RSM is also being done to support verification of TEMPEST as it is being refined by comparing predicted and actual melter measurements including bulk glass temperature, glass temperature profiles, and electrode power usage.

The individual measurements are described in more detail below.

Glass Temperature - Glass temperatures will be measured using two thermocouples in a thermowell on the back of one of the electrodes. This measurement will be correlated to bulk glass temperatures by inserting a thermocouple into the glass melt to obtain a temperature profile during checkout of the melter prior to starting the test, and periodically during the testing.

Electrical Measurements - Electrical measurements will be RMS voltage and current measurements for the electrodes, plenum heater, and overflow heater. These measurements will be made continuously during the testing. Power for each of the heaters and glass resistance across the electrodes can be computed from

Table 1

Research Scale Melter Test Matrix

Test No.	Description	Noble Metal Conc. (Table I)	Oxide Loading (g TO/l)	Glass Redox ($\text{Fe}^{2+}/\text{Fe}^{3+}$)	Glass Temp ($^{\circ}\text{C}$)	Plenum Temp ($^{\circ}\text{C}$)
1	Nominal	Nominal	500	0.005	1150	800
2	Low Glass Temp	Nominal	500	0.005	1050	800
3	High Glass Temp	Nominal	500	0.005	1250 / 1200	800
4	Low Plenum Temp	Nominal	500	0.005	1150	650
5	High Plenum Temp	Nominal	500	0.005	1150	950
6	* High Redox	Nominal	500	0.3	1150	800
7	Low Oxide	Nominal	400	0.005	1150	800
8	High Oxide	Nominal	500	0.005	1150	800
9	High NM Conc.	2X	500	0.005	1150	800
10	High NM, Ag, Te	2X	500	0.005	1150	800
11		2X	500	0.005	1050	650
12		2X	500	0.3	1250 / 1200	950

* Test number 12 will be performed only if time and noble metal stocks allow.

these measurements.

Sludge Electrical Resistance - Sludge resistance measurements refer to measuring the resistance across the electrodes, which normally rest on the bottom of the melter, and then comparing this resistance to the resistance measured when the electrodes are raised a set amount to remove them from any accumulated sludge on the melter bottom. This measurement will be made at the beginning and end of each test period.

Feed Rate - Feed rate will be measured using the specific gravity/weight factor dip tube assembly built in the melter feed tank. A measurement of the change in feed tank depth over a period of time along with a tank depth/volume calibration curve will allow the average volumetric flow rate of feed to be calculated for that period of time.

Glass Production Rate - Glass production will be monitored by a small platform scale under the glass canister. The change in weight indicated on the scale over a period of time will allow computation of the average glass production rate.

Glass Temperature Profiles - Temperature profiles in the melter will be determined by manual thermocouple probes. Two ports are available to probe through (see Figure 9), the viewport and off gas line penetrations.

Noble Metal Mass Balance - Mass balance measurements refer to the analysis of the amount of noble metals present in the feed, melter tank glass, melter sludge and glass product. Melter tank glass and sludge samples will be taken with a trigger activated stainless steel syringe sampler. Section 8.0 discusses the sample schedule for each of these types of samples.

Glass Redox Condition - Glass redox condition will be measured by the $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio.

Residence Time (dependent variable) - Residence time will be measured by a step change in a BaO tracer, which will be added to the feed. The BaO will be added in alternating tests to produce a change in the poured glass barium concentration, which can be used to determine the melter residence time. An addition of 0.25 wt% BaO on an oxide basis will produce a detectable change.

4.0 EXPECTED RESULTS

This section discusses the expected results of the RSM tests. The bases for the expected results are laboratory tests conducted at PNL and information that has been exchanged between the project, FRG researchers, and WSRC staff. The objective of RSM testing is to characterize noble metal characteristics, such as particle size, shape, the makeup of crystalline or metal agglomerations, and fraction of settling in the RSM. The data are meant to be compared between the various tests within the test matrix. The results will be compared qualitatively to other data obtained by KfK, WSRC, or PNL. The semi-quantitative data that are obtained will reveal the sensitivity of noble metal behavior to the process variables studied.

4.1 Noble Metal Concentration

Laboratory crucible studies conducted by Geldart, et al. (1987), provided results which showed the basic effect of increasing noble metal concentration was an increasing level of particle agglomeration. No new particles or alloys were found to occur. Laboratory studies of the behavior of ruthenium oxide particles in HWVP glass by Cobb and Hrma (1991) resulted in their proposing a mechanism for particle agglomeration. The mechanism is based on particle collisions, enhanced by mixing mechanisms, and provides an explanation for how particles are brought into such close proximity. It is possible then that a 2X increase in noble metals may result in a large population of particles above a single particle size. Subsequently, a greater fraction of the noble metals should settle in the melter based on the above data. Conversely Dr. Pentinghaus of KfK has supported the hypothesis that there is little particle interaction occurring in the glass

phase. If such is the case then larger particles would not be expected as a function of noble metal concentration. If this were the case the fraction of particles settling should not be affected by concentration. This is in possible agreement with the work performed by Geldart, et al. Work performed at WSRC has concentrated primarily on the relationships between noble metals and mercury (Nakaoka and Strachen 1990). There has been no similar work done at WSRC.

4.2 Oxide Concentration

Operating between the lower and upper limits of oxide loading will result in several changes. At the lower oxide concentration, the glass production rate will drop proportionately. This will increase the residence time of the glass in the RSM. A longer residence time provides the opportunity for a higher degree of particle settling. Longer hold times can also lead to additional spinel growth and particle agglomeration or alloying if a mechanism for particle collisions to occur exists. In discussions with Dr. Pentinghaus of KfK, (Sevigny 1990), he has the technical opinion that once the melt phase is reached there is little chance or time for particle growth. As already stated, Cobb and Hrma have developed at least one plausible mechanism for continued particle growth in the melt phase. Geldart, et al (1987) found additional particle settling and some spinel growth as a function of time. Tests conducted with higher oxide loadings should have the opposite effects. That is, lower residence time should result in lower particle settling and smaller particles.

Oxide concentration will also affect the cold cap melting history. That is, the time and temperature experience of the feed solids will be different. At the lower oxide concentration a thin cold cap is typical. Therefore, a high temperature profile will exist across the cold cap solids phase and quicker melting times will result. The effects on the cold cap kinetics are not known. Work being performed by the gradient furnace testing activity is intended to provide data and insight into this area.

4.3 Glass Redox Level

Noble metal oxides can be reduced to metal phases if a sufficiently strong reducing environment exists. The nominal redox level is near the detection level for the ferrous-to-ferric ratio analytical method used. At this value of 0.01 or less Geldart, et al. (1987) observed ruthenium oxide and palladium and rhodium oxides. Palladium and rhodium alloys with tellurium were also observed. Typically, the palladium and rhodium behaved as nucleating sights for spinel growth. As the redox level increased, ruthenium oxide concentrations were reduced and metallic ruthenium was observed. The upper ferrous-to-ferric

ratio level to be tested will be targeted at 0.3. To achieve this high level, sugar will be added. This is below the levels required to achieve gross reduction of noble metal oxides to metals experienced in past PNL tests and at WSRC (Nakaoka and Strachan 1990) in which redox levels greater than 0.5 existed. Based on the laboratory data at hand it is expected that little affect of the higher redox will be observed. However, the cold cap kinetics were not simulated in laboratory tests. The presence of sugar as a reductant in the cold cap may cause more metal reduction than has been observed to date due to its strong reducing potential.

4.4 Glass Temperature

Geldart et al. (1987) observed higher spinel growth at lower glass temperatures than occurred at 1100°C. This may be due to spinels being present to a high degree as the cold cap melts. As temperatures progress to 1150°C the spinels go into solution. If temperatures are held below 1100°C, spinels will go into solution more slowly and be capable of reacting with noble metal oxides or metal particles which serve as nucleating sites. Conversely, the higher viscosity glass will also reduce convection currents and lead to a more stagnant tank. This effect may inhibit particle collisions and result in more plug flow and less mixing. The use of a tracer added to the feed slurry during these tests will indicate if any change occurs in tank mixing characteristics. Therefore, at this time it is not clear what the overall effect of lower glass temperature will be.

Higher glass temperatures will decrease glass viscosity which could increase tank mixing. If the hypothesis offered by Cobb and Hrma (1990) is applied there should result in a greater occurrence of particle interaction, leading to larger particle growth and settling rates will increase. These conditions should lead to a higher degree of settling. Conversely, higher convection currents, if present, may reduce somewhat the rate of settling through enhanced mixing. However, the net effect of convective mixing in a closed system will ultimately be complete settling of entrained particles. Unless mixing increases to a turbulent regime, as would be achieved with vigorous sparging (note: a clear distinction exists between vigorous sparging and using one or two bubblers in a glass tank), all particles would be expected to settle. This fact explains why complete drop out of noble metal particles occurs in a melter once feeding has been stopped and glass ceases to be poured. These conflicting effects make it unclear precisely how higher temperature will affect noble metal behavior.

4.5 Plenum Temperature

Plenum temperature changes will affect the boiling rate of water from the cold cap. As a result, lower plenum temperature will reduce feeding and glass production rates; and higher plenum temperature will increase feeding and glass production rates. Both will change the temperature history of the cold cap. As discussed earlier, the affect changing the cold cap history will have on noble metal behavior is not understood. Gradient furnace testing is expected to provide insight into this area and will be relied on heavily in drawing conclusions from this part of the RSM test.

5.0 TEMPEST Modeling

A simulation of the Research Scale Melter using the TEMPEST thermal/fluid analysis software package was performed by Loren Eyler of the Applied Physics Center. This simulation provided an indication of the electrode power and kiln temperatures required to achieve the desired bulk glass temperatures. The simulation also produced the convective circulation patterns in the melter. Measurements made during testing will be used to improve the post test simulations.

The model used was fully three dimensional and included the melter electrodes, thermowell and the discharge tube. Because of the asymmetry of the discharge section and the melter electrodes, the model used cartesian elements to represent the geometry. This simulation did not include the effect of pouring glass. It is currently planned to include this in the post test simulations. The model is shown in Figure 3.

The simulations were performed assuming that the kiln is maintaining the melter exterior at 500°C. The TEMPEST software then used its built in control algorithm to maintain a specified portion of the melt at an average temperature of 1150°C. The initial simulation used too large a portion of the melt as an average temperature to use as a control temperature. This resulted in the glass near the relatively cool walls and cold cap region being included in the average and forcing the electrode power up until the maximum temperature in the central core of the melt was at 1275°C. Once the averaging region was reduced to a smaller portion of the melt, near the center, the power required to maintain the 1150°C average decreased and the maximum temperature decreased to 1225°C.

The flow pattern in the melter is comprised of two roughly cylindrical roll cells which come together and generate a sheet of glass moving upward between the two electrodes. The velocity vectors are shown for planes cutting through the center of the melter in Figures 4 and 5. The cells are slightly asymmetrical due to the discharge tube. The maximum velocity in the convecting glass is approximately 3.2 mm/s. These low velocities result in little energy transfer through the melt as a result of

Figure 3 TEMPEST Model of RSM
Top - Plan View, Bottom - Cross Section

convection. Conduction is the predominant mode of heat transfer and is the reason why there is a large temperature gradient from the center of the melt to the walls.

The predicted flow patterns in the melter would tend to sweep any heavy particles settling out of the melt into a line between the two electrodes. This makes this a good location for the sampling of melter sludges along with another location which is less likely to accumulate settled particles for a comparison of the two.

6.0 Equipment Description

The RSM/Noble Metal Test Run will be conducted in the Engineering Development Laboratory in the 324 building. The major pieces of equipment used in feed storage, vitrification, and off-gas treatment are described in this section.

The RSM System consists of an electrically joule heated melter, placed within an electrically heated firebrick kiln, and the equipment associated with the delivery of feed and discharge of glass.

6.1 RSM MELTER

The research scale melter is 10¹/₄ inch OD (by 15 1/2 inch high) and possesses an Inconel¹ 601 shell. Ceramic paper and Alfrax² 66 line the melter tank refractory as principle insulators.

The glass melt cavity refractory is an 8 inch OD x 6 inch high cylinder of K-3 block. The melt cavity is a 6 inch ID x 4³/₄ inch deep cylindrical volume with a nominal capacity of 1.33 L (with a plenum vacuum of 2 inches H₂O). The configuration of the RSM's refractories and insulation are shown in Figure 6.

Both electrodes for the RSM are fabricated from 1/4 inch Inconel 690 plate. The electrodes have a square face with dimensions measuring 3 inch x 3 inch. The arms of the electrodes extend 17³/₄ inches and measures 1 inch in width. Detailed dimensions are presented in Figure 7.

The electrodes are allowed to rest on the bottom surface of the K-3 refractory melt cavity. They are located 4³/₈ apart. The arms of the electrodes extend out of the melt region, through the plenum space, penetrate through the lid, and terminate in direct connection to the electrode power supply wiring. Isolation of the electrodes from the lid is achieved by providing oversized lid penetrations through which the electrodes protrude and filling the unoccupied space with Alfrax 66. This provides sufficient electrical isolation in addition to stabilizing the

¹ Inconel is a registered trademark of Inco Alloys International.

² Alfrax is a registered trademark of Carborundum Corporation.

VELOCITY VECTORS

Approx Cyl model: full 3d w/spout/

Figure 4 TEMPEST Velocity Vector Plot
Plane Perpendicular to Electrode Faces

VELOCITY VECTORS

Approx Cyl model: full 3d w/spout/

Figure 5 TEMPEST Velocity Vector Plot
Plane Parallel to Electrode Faces

Figure 6 Research Scale Melter

electrodes.

Another significant heat contribution is the presence of a plenum heater. The heater is a 1 inch diameter, 15 inches long silicon carbide bayonet style heater with an effective heating length of 5 inches. The element is supported off the lid through a 9 inch length of 2 inch schedule 80 pipe. A ceramic sleeve is utilized to isolate the heating element from the pipe. The end of the heater length sits 2 inches above the melt level.

The RSM sits inside an electrically heated firebrick kiln. The inner geometry of the kiln is an octagon with a diameter of $16\frac{1}{2}$ inches and a height of 18 inches. This kiln will be operated and maintained at approximately 500°C. The melter will sit on 2 firebricks. This configuration is presented in Figure 8.

The melter lid is a one piece unit which covers the melt cavity. It is 12 inches in diameter, $\frac{1}{4}$ inch Inconel 601 plate. All services to the RSM run through the lid. The locations of specific services for the test are indicated in Figure 9. The feed port is located in the center of the lid.

To monitor the glass and plenum temperatures $\frac{1}{8}$ inch type K Inconel 601 sheathed thermocouples will be used to measure the glass temperature in the melter. Two thermocouples will be in an

Figure 7 RSM Electrode Details

Inconel 690 thermowell. This thermowell is welded to the back side of one of the electrodes. The thermocouples will be $\frac{1}{2}$ inch and $2\frac{1}{4}$ inch from the floor of the melt cavity. Bulk glass temperatures will be correlated to the thermowell measurements. One Inconel 601 sheathed thermocouple will be fixed in the plenum space at $6\frac{1}{4}$ inches from the lid. An additional Inconel 601 sheathed thermocouple will be used to periodically determine temperature profiles in the melt region. This thermocouple will be inserted through an opening in the off-gas port or through the viewport.

Pressure in the melter will be maintained at 2 inches w.c. through the use of a vacuum regulating valve attached to the EDL 102 Vessel Vent System.

6.2 Feed Delivery System

During the test the feed slurry will be stored in a stainless steel, agitated tank located on 2nd floor EDL-102 in Module 18. The tank has an ID of 24 inches, a height of $36\frac{3}{4}$ inches and a nominal capacity of 250-270 liters. Primary delivery of the feed is gravity induced head. Feed levels in the tank will be monitored via weight factor/specific gravity

Figure 8 RSM Located in Kiln

instrumentation. A peristaltic pump will regulate the feed rate to the feed nozzle. The rate of feed to the melter will be established by maintaining a 50 - 70% cold-cap coverage of the melt surface. The actual feed rate will be measured by the rate of drop in the feed tank.

A $\frac{3}{8}$ inch x 0.035 wall stainless steel tube runs down from the feed tank on the second floor to the peristaltic pump, located on a shelf above the RSM. At this point, the $\frac{3}{8}$ inch stainless steel tube terminates and connects to $\frac{3}{8}$ inch Norprene flexible tubing which runs through the pump. The Norprene tube then connects to $\frac{1}{4}$ inch stainless steel tube which, in turn, connects to the feed nozzle. The feed nozzle extends $6\frac{1}{2}$ inches into the plenum from the top. During the operation of the melter the feed nozzle will be water cooled to prevent premature drying of the feed while still in the nozzle. Water flushing and nozzle cleanout capabilities are designed into the feeding system. The feed nozzle is shown in Figure 10.

Figure 9 RSM Lid Detail

6.3 Glass Discharge System

A continuous gravity controlled overflow is used for simplicity, and because the discharge rate is small. The design is intended to provide a gas-tight transfer line between the melter and the discharge. No consideration for enhancing of inhibiting particulate transfer was intended.

The discharge trough (see Figure 11) is constructed entirely of Inconel 690 1/2 inch schedule 160 pipe. It has an overall length of 4³/₈ inches and has a 15° slope. The vertical portion of the discharge trough is submerged in the glass. Once the level of glass rises to the point which corresponds to the highest point of the trough slope then glass discharge will occur. The exterior face of the discharge trough is chamfered at a 15° angle to prevent molten glass from clinging to the trough.

The discharge trough is presented in Figure 11. The trough protrudes from the melter body by $1\frac{1}{4}$ inches. The glass flows from the end and falls $10\frac{1}{4}$ inches into a 4 liter stainless steel canister. To prevent the glass from solidifying in the pour tube it falls through an Inconel 690 1" tube which is surrounded by a $2\frac{1}{2}$ inch x 8 inch electrical clam shell style heater. The heater will be operated at approximately 1000 C. A type K thermocouple will be placed inside the heater to monitor the temperature of the discharge region. To determine glass pour

Figure 10 RSM Feed Nozzle Detail

rate the 4 liter stainless steel canister will be located on a small platform scale to measure the weight of glass being poured.

6.4 Power Control System

The electrode, plenum heater, and discharge tube heater power are all controlled by silicon controlled rectifiers (SCR's). The SCR's act as a switch to turn the line voltage on and off to the load at an extremely fast rate. The longer fraction of time they are turned on, the more power is going to the load. The power output is controlled by a signal from an external process controller. This controller can operate in a manual mode or automatic mode. In the automatic mode the temperature of the specific point which that heater is controlling is fed back to the process controller and it adjusts the output of the SCR accordingly. It is anticipated that the melter power and heaters will be operated in an automatic temperature controlled mode for the majority of the testing.

Figure 11 RSM Discharge Tube Detail

6.5 Off-Gas Treatment System

The gases and airborne effluent generated by the RSM vitrification process are exhausted through and treated by an off-gas system. An insulated 1 inch stainless steel tube is extended from the melter and is routed through a venturi scrubber to provide initial cooling and remove the majority of the condensable and particulate material. The liquid for the scrubber is recirculated in a continuous loop which passes through a small shell and tube heat exchanger to remove the heat from the melter off-gas. As condensate accumulates, it will be drained down into Tank 20 in the Tank Pit below EDL 102. From the scrubber, the off-gas is run through a High Efficiency Mist Eliminator (HEME). The HEME will remove condensed phase aerosols. All accumulated waste liquids will be drained to Tank 20.

6.6 Data Acquisition

Data acquisition and melter control are performed with a Computer Data Acquisition and Control System capable of acquiring data, computing values based on the data and controlling the

melter including all alarm functions associated with the melter. In addition, some critical data (glass temperatures, melter power) will be sent to chart recorders.

7.0 Feed Description

The composition of the simulated NCAW waste is shown in Table 3 below. This composition is based on the latest information communicated to PNL from WHC (Letter, R.A. Smith to J.M. Creer). Table 3 shows the deletions and substitutions of constituents which will not be included in the simulated waste either due to the small amount of the constituent which is present or to avoid a radioactive element. The composition after deletions and substitutions is normalized to 100%.

Based on this composition, a chemical form for each of the cations was determined to use in the melter feed makeup. This is shown for each of the oxides in Table 4. Table 4 also shows the weight percent on an oxide basis for each of the simulated waste components and the grams/liter of each of the feed makeup chemicals in the melter feed.

Some of the chemicals are added in multiple forms to meet the anion specifications (F, Cl, NO₃...) called for in the NCAW feed specifications. Sodium is primarily used for this function due to the availability of these sodium salts and the relatively high sodium concentration in the feed.

The noble metal chemicals will be supplied as nitrates as listed in Table 4, but will be neutralized along with the other minor constituents and less soluble components using NaOH. These are the components in Table 4 other than aluminum, iron, manganese, nickel and zirconium. This is done to more accurately simulate the chemical processes taking place in the waste tanks. When the hydroxide forms of these chemicals have precipitated, the solution will be washed to remove most of the Na and NO₃ and the minor constituents will be added in their hydroxide forms. Feed preparation and formatting requirements will be based on work yet-to-be conducted under the 1.2.2.03.02 subtask.

8.0 Data Acquisition and Sample Schedule

8.1 M & TE

The Research Scale Melter Measurement and Test Equipment List is shown below. Accuracy of the M&TE is as follows:

Temperature:	+/- 20°C
Pressures	: +/- 2 in.WC
Voltage	: +/- 5 volts
Current	: +/- 5 amps
Power	: +/- 200 watts

Table 2

Waste Composition on an Oxide Basis

Oxide	Reference Wt % Oxide	Substituted Wt % Oxide	Normalized Wt % Oxide
Ag2O	1.2E-01	1.2E-01	1.2E-01
Al2O3	9.0E+00	9.0E+00	9.3E+00
B2O3	5.7E-03	5.7E-03	5.9E-03
BaO	1.8E-01	1.8E-01	1.8E-01
BeO	1.0E-01	Sub Mg	
CaO	7.9E-01	7.9E-01	8.2E-01
CdO	3.0E+00	3.0E+00	3.1E+00
CeO2	6.0E-01	6.4E-01	6.6E-01
Cr2O3	2.6E-01	2.6E-01	2.7E-01
Cs2O	6.0E-01	6.0E-01	6.2E-01
CuO	2.5E-01	2.5E-01	2.5E-01
Dy2O3	1.0E-04	Sub Nd	
Er2O3	3.1E-06	Sub Nd	
Eu2O3	2.0E-02	Sub Nd	
F	9.7E-02	9.7E-02	1.0E-01
Fe2O3	2.8E+01	2.8E+01	2.9E+01
Gd2O3	3.7E-03	Sub Nd	
GeO2	1.6E-04	1.6E-04	1.6E-04
Ho2O3	5.3E-06	Sub Nd	
I	4.5E-06	4.5E-06	4.6E-06
K2O	2.0E-01	2.0E-01	2.0E-01
La2O3	6.5E-01	6.5E-01	6.7E-01
Li2O	1.8E-04	1.8E-04	1.9E-04
MgO	2.0E-01	3.6E-01	3.8E-01
MnO2	2.1E+00	2.1E+00	2.2E+00
MoO3	5.6E-01	5.6E-01	5.8E-01
Nb2O	2.1E+01	2.1E+01	2.2E+01
Nb2O3	1.0E-02	1.0E-02	1.0E-02
Nd2O3	5.8E-01	2.5E+00	2.6E+00
NiO	2.3E+00	2.3E+00	2.4E+00
P2O5	8.7E-01	8.7E-01	9.0E-01
PbO2	7.0E-01	7.0E-01	7.2E-01
PdO	1.2E-01	1.2E-01	1.2E-01
Pm2O3	4.6E-02	Sub Nd	
Pr2O3	1.5E-01	1.5E-01	1.6E-01
PuO2	6.0E-02	Sub Ce	
Rb2O3	5.7E-02	5.7E-02	5.9E-02
Rh2O3	1.0E-01	1.0E-01	1.1E-01
Ru2O3	3.8E-01	3.8E-01	3.9E-01
SO3	6.5E-01	6.5E-01	6.8E-01
Sb2O3	5.9E-03	5.9E-03	6.1E-03
SeO2	1.6E-02	1.6E-02	1.6E-02
SiO2	4.0E+00	4.0E+00	4.2E+00
Sm2O3	7.5E-02	7.5E-02	7.7E-02
SnO	1.1E-02	1.1E-02	1.1E-02
SnO	1.2E-01	1.2E-01	1.2E-01
Ta2O5	3.3E-03	3.3E-03	3.4E-03
Tb2O3	2.3E-04	Sub Nd	
Tc2O7	1.5E-01	DEL	
TeO2	1.0E-01	1.0E-01	1.0E-01
TiO2	6.5E-01	6.5E-01	6.7E-01
Tm2O3	1.7E-10	Sub Nd	
U3O8	4.7E+00	Sub Nd	
Y2O3	8.0E-02	8.0E-02	8.3E-02
ZnO	3.3E-01	3.3E-01	3.4E-01
ZrO2	1.5E+01	1.5E+01	1.6E+01
Totals	100.0	97.0	100.0

Table 3

Chemical Form Used in Simulated NCAW

oxide	oxide conc (wt %)	feed compound	comp'd conc (g/L feed)
Ag ₂ O	0.03	AgNO ₃	0.25
Al ₂ O ₃	2.61	Al(OH) ₃	19.97
B ₂ O ₃	0.00	H ₃ BO ₃	1.47E-02
BaO	0.05	Ba(OH) ₂ + 8H ₂ O	0.52
CaO	0.23	Ca(OH) ₂	1.51
CdO	0.87	Cd(OH) ₂	4.98
CeO ₂	0.19	Ce(OH) ₃	1.03
Cr ₂ O ₃	0.08	Cr(NO ₃) ₃ + 9H ₂ O	1.99
Cs ₂ O	0.17	CsNO ₃	1.21
CuO	0.07	Cu(SO ₄) ₁ + 5H ₂ O	1.11
Fe ₂ O ₃	8.15	Fe(OH) ₃	54.51
GeO ₂	0.00	GeO ₂	2.27E-04
K ₂ O	0.06	KOH	0.34
La ₂ O ₃	0.19	LaF ₃	0.10
		La(OH) ₃	1.00
Li ₂ O	0.00	Li ₂ O	0.00
MgO	0.11	Mg(NO ₃) ₂ +6H ₂ O	3.36
MnO ₂	0.62	MnO ₂	3.09
MoO ₃	0.16	MoO ₃	0.81
Na ₂ O	6.18	NaCl	0.69
		Na ₂ CO ₃	14.84
		Na ₂ CO ₃	1.05
		NaI	0.03
		NaN ₂ O ₂	33.60
		NaN ₂ O ₃	4.10
		Na ₃ PO ₄	2.91
		Na ₂ SO ₄	1.04
		NaOH	3.46
Nb ₂ O ₃	0.00	Nb ₂ O ₅	1.65E-02
Nd ₂ O ₃	0.73	NdF ₃	0.39
		Nd(OH) ₃	3.88
NiO	0.66	Ni(OH) ₂	4.12
PbO ₂	0.20	Pb(NO ₃) ₂	1.40
PdO	0.03	Pd(NO ₃) ₂	0.33
Pr ₂ O ₃	0.04	Pr(OH) ₃	0.26
Rb ₂ O ₃	0.02	RbNO ₃	0.11
Rh ₂ O ₃	0.03	Rh(NO ₃) ₂ +2H ₂ O	0.38
Ru ₂ O ₃	0.11	Ru(NO) ₃ (NO ₃) ₃	1.39
Sb ₂ O ₃	0.00	Sb ₂ O ₃	3.00E-02
SeO ₂	0.00	SeO ₂	2.30E-02
SiO ₂	1.16	SiO ₂	5.82
Sm ₂ O ₃	0.02	Sm(NO ₃) ₃ +6H ₂ O	0.28
SnO	0.00	Sn(NO ₃) ₂	2.81E-02
SrO	0.03	Sr(NO ₃) ₂	0.35
Ta ₂ O ₅	0.00	Ta ₂ O ₅	4.81E-03
TeO ₂	0.03	TeO ₂	0.15
TiO ₂	0.19	TiO ₂	0.94
Y ₂ O ₃	0.02	Y(OH) ₃	0.14
ZnO	0.10	Zn(OH) ₂	0.59
ZrO ₂	4.36	Zr(OH) ₄	28.19

8.2 Sample Schedule and Required Analyses

Sampling during RSM testing will be required during feed preparation and testing. Slurry and glass samples will be obtained to support mass balance calculations and compare the compositions to the target values. In addition, post test inspection of the RSM will potentially retrieve sludge samples from the melter which will also be analyzed. Table 5 identifies the type and minimum number of samples and analyses that will be performed.

Minimum sample requirements require that at least one slurry and two glass samples be obtained each day. A typical slurry analysis requires less than 25 ml of slurry. To assure an adequate archive of samples will exist, all of the glass that is produced will be retained. In addition, two 100-ml slurry samples will be taken each day. Samples will be stored in the 3718G warehouse located behind the 324 bldg. Additional 125-ml samples will be obtained specifically for slurry redox measurements. The final glass and slurry samples will be taken at the end of each test. At the start of each test and immediately following cold cap melting at the end of each test, the melter tank glass and sludge samples will be obtained.

9.0 Schedule

The dates for the major events in the Research Scale Melter subtask are shown below.

<u>Date</u>	<u>Event</u>
5/31	Start up Melter
5/31	Approve Test Plan
6/24	Start Feed Makeup
7/24	Finish Feed Makeup
8/5	Start Testing
9/27	Conclude Testing & Decide Whether to Destructively Examine the RSM

10.0 Test Procedures/Requirements

All of the preparation for testing and testing associated with the Research Scale Melter will be done in accordance with the plans and procedures listed below.

Table 4

Minimum Sample and Analytical Requirements

Sample Type	ICP ^{*1000}	AA ^{*1000}	IC ^{*1000}	XRD ^{*1000}	SEM ^{*1000}	REDOX ^{*1500}
<u>Feed Preparation</u>						
Noble Metal Stocks	3					
Minor Constituents						
Feed Makeup	1		3	2	2	
Initial Feed Prep.	2	2	2			
Feed + Frit	2	2	5			2
Subtotal =	8	4	10	2	2	2
<u>Test Samples</u>						
Feed Samples/Test	3	1	1			
Glass Samples/Test	3	1		0-1	0-1	1
Tank Glass Spl/Test	2			0-1	0-1	
Tank Sludge Spl/Test					0-1	
Condensate Spl/Test	1		1			
Subtotal*11 Tests =	99	22	22	0-22	0-33	11
<u>Post-Test Samples</u>						
Sludge Samples	5			5	5	
TOTAL =	112	26	33	38	40	13

Plan or Procedure

Research Scale Melter Test Plan
 Prerun Activities Checklist
 Equipment Readiness Checklist
 Staff Training Documentation
 Chemical Makeup and Handling - SOP 1 Latest Rev.
 RSM Ceramic Melter - SOP TBD
 Feed Preparation Makeup Instructions - WTC-006-9
 RSM Feed & Glass Sampling Procedure - RSM-1
 Hazardous Chemical Handling Protocols

11.0 QA Requirements, Training, Safety and Waste Handling

11.1 QA Requirements

The RSM tests are being conducted as a QA Impact Level II activity. It is important that all data records, calculations, and analyses reported from this test be documented in a sufficient manner to be traceable from the primary data and the methods and equipment used, through the assumptions and/or interpretations made, to the corresponding results reported in the summary report. Where applicable, error analyses will be performed to support data reporting.

Samples and analytical work will be tracked using the Analytical Request Form (ARF) provided in PNL MA-70/PAP-404 as Exhibit 3 and a sample log. Calibrated measuring and test equipment (M&TE) will be used during testing and data reported to support TEMPEST to assure the accuracy and reliability of the reported data can be substantiated. Data obtained for preliminary study or to assist in the melter operation may include data obtain by uncalibrated instrumentation. This data and instrumentation will be clearly identified in any reporting of the data. The M&TE that will be used during this test will be recorded per PNL MA-70/PAP-70-1201.

The majority of data will be collected on data and status log sheets and test instructions. Additional observations, data, and remarks will be placed in a PNL laboratory record book (LRB). The RSM operations LRB is BNW 50265.

11.2 Records

Project records (e.g., test data, LRB copy, etc.) pertaining to this work will be maintained in the FY 1991 records inventory and disposition schedule (RIDS) file T.5 - Research-Scale Melter, for WBS 1.2.2.04.01.

11.3 Change Control

The desk copy of the run plan will be the controlled document copy in which notations and changes in the run will be recorded. Changes may be entered only by the shift leader, responsible engineer (M.F. Cooper), and 1.2.2.04.01 subtask leader (J. M. Perez). Any changes will be countersigned by the responsible engineer (can be after the fact) to indicate cognizance of the change. Any change to run activities which will affect the primary test objective must be approved additionally by G.A. Jensen, and the cognizant WHC HWVP staff prior to the change. Test modification forms will also be available at the operations desk for initiating and recording changes.

11.4 Operator Training

Training will be accomplished through the implementation of PNL MA-70 PAP 201. Staff responsible for operating test equipment, recording data, and making process changes will be required read and understand the following as a minimum: 1) this RSM test plan, 2) the RSM safe operating procedure, 3) the chemical handling SOP, 4) material safety data sheets contained in the run book, and 5) applicable PNL-MA-70 PAP's and activity procedures also copied and placed in the run book. Training will be documented by sign-off of reading and training instruction record sheets.

11.5 Safety

The operation of the RSM system will comply with all of the normal safety rules for operating in EDL 102. In addition there are specific burn and electrical hazards associated with the operation of the melter. These specific hazards are addressed in the Research Scale Melter Safety Operating Procedure (Waste Treatment Technology Department SOP # TED).

11.6 Waste Handling

All wastes generated during the course of this test will be disposed of per PNL's safety manual, PNL-MA-8. A PNL waste management specialist will review the quantities and types of waste expected to be generated during this study to verify that proper storage and disposal methods are known and can be implemented.

12.0 References

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Sevigny, G. J. 1990. "Foreign Trip Report." Trip taken June 21-June 29, 1990 to KfK Center, FRG.

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Appendix D

Sample Test Plan Outline for Pilot-Scale Melter Studies:

Liquid-Fed Ceramic Melter Run 9 Test Plan,
PNL HWVP Technology Development Project,
Pacific Northwest Laboratory, 1992

PNL HWVP TECHNOLOGY DEVELOPMENT PROJECT

Process Development Task: Vitrification Testing Cost Account

LIQUID-FED CERAMIC MELTER RUN 9 TEST PLAN

Approvals:

C. J. Freeman, Responsible Engineer

8/17/92
Date

J. M. Perez, Jr., Vitrification Testing
Manager

8/17/92
Date

G. R. Wyatt, Off-Gas System Performance
Evaluation Manager

8/17/92
Date

D. E. Larson, Process Development Manager

8-17-92
Date

B. D. Stonecker, Quality Engineer

8-28-92
Date

Concurrences:

G. R. Hoenes, Laboratory Safety Dept. Mgr.

8/20/92
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