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SURVEY OF SOLIDIFICATION PROCESS TECHNOLOGIES

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ABSTRACT

This report provides a current status of the high-temperature solidification technologies that have been used or proposed in the United States and abroad. The technologies presented in this report can be broadly classified into the following categories: Inconel®-based, joule-heated melters; high-temperature, joule-heated melters; induction melters; cold-crucible induction melters; plasma melters; combustion melters; microwave melters; molten metal technology; and Synroc technology. The operating experience and safety issues associated with major solidification technologies are summarized.

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EXECUTIVE SUMMARY

The objective of this report is to provide the Nuclear Regulatory Commission (NRC) a current status of high-temperature solidification technologies that have been used or proposed throughout the world. The report includes a survey of technologies used or proposed in the waste management (chemical and nuclear materials) industries, and relevant information on commercial technologies used in the ceramic and glass industries. This report has been prepared to assist the NRC in:

- determining whether sufficient information exists to assess safety considerations regarding the Hanford Tank Waste Remediation System (TWRS)
- determining whether current regulatory guidelines are adequate for controlling implementation of the technology to solidify Hanford waste
- identifying the existence of technical uncertainties
- assessing where future guidance may be warranted
- evaluating a "first-of-a-kind" process that is being proposed or utilized

The survey of waste solidification processes used in the United States and abroad indicates that, although major accomplishments have occurred in the area of vitrification in the last 20 yr, developments are continuing in other solidification technologies such as glass-ceramics, Synroc (synthetic rock), and more recently, molten metal processes. The technologies reviewed in this survey can be broadly classified into the following categories: Inconel®-based, joule-heated melters; high-temperature, joule-heated melters; induction melters; cold-crucible induction melters; plasma melters; combustion melters; microwave melters; molten metal technology; and Synroc technology. The development of a successful solidification process requires a reasonable level of characterization of the wastes that need to be solidified before a technology can be selected. This selection should be based on the nature of the waste and the final waste form that will provide effective encapsulation.

In chapters 3 and 4, information from high-level waste (HLW) vitrification experience at existing facilities, such as those at the West Valley Demonstration Project (WVDP, West Valley, New York), Defense Waste Processing Facility [(DWPF), Savannah River Site (SRS), Aiken, South Carolina)], Tokai Vitrification Facility (Japan), Sellafield (United Kingdom), Mayak Vitrification Plant (Russia), Waste Vitrification Plant (WVP, India), and the Marcoule and La Hague vitrification facilities in France, is provided for use in the development of the regulatory framework for the privatized Hanford facility. In addition, information from other sources such as experience from commercial glass and ceramic industries (chapter 2), mixed low-level radioactive mixed and hazardous and nonradioactive waste vitrification plants (chapter 5 and 6), Hanford low-level waste vitrification program (chapter 7), mixed waste solidification technology development program (chapter 8), research-scale vitrification plants (chapter 9), pilot-scale vitrification plants (chapter 10), emerging solidification technologies (chapter 11), and non-vitrification technologies (chapter 12) is provided for use. The key elements of the solidification processes, including a description of feed preparation, melting, and offgas treatment systems for each technology/operating plant, and process upsets and events leading to incidents and accidents, are reviewed in each chapter.

In chapter 13, technological assessments, in terms of their strengths and weaknesses, are provided. The joule-heated Inconel® melter technology and induction melting technology are the two most widely accepted and mature technologies for vitrifying HLW. Both technologies provide extremely low volatility for alkalis, boron and radioactive components such as technetium and cesium, and homogeneous product due to long residence time in the melter. While the size of the joule-heated melter can be increased significantly (Mayak Vitrification Plant, Russia) to meet production rate requirements, the size of the induction melter cannot be increased due to the attenuation of induction frequencies in large-diameter crucibles. In addition, life of a joule-heated melter ranges from 3 to 5 yr, while the melting crucible for the induction melting is considered a disposable item with replacement time ranging from 1,500 to 4,000 hr. Due to the design of the induction melting system, only calcined feeds can be processed in the melter while a joule-heated melter can easily adopt to wet or dry feeding. Other technologies that are discussed in the report are either in the development stage or have never demonstrated solidification of radioactive wastes.

In chapter 14, a review of potential safety issues that could be encountered during processing of Hanford wastes is presented. Safety issues associated with the key elements of the solidification processes such as feed preparation, solidification, and offgas treatment systems are reviewed. Based on the review of the solidification technologies, technological assessments, and evaluation of the process and operational safety issues, a number of areas associated with the solidification options for TWRS activities that will require evaluation have been identified. These include:

- Explosion hazard due to flammable gas (hydrogen and ammonia) generation
- Criticality hazard from plugging and accumulation of radionuclides in transfer and offgas pipes
- Uncontrolled chemical reactions, leading to radionuclide release, due to mixing of incompatible wastes and chemicals
- Corrosion of melter components, leading to melter failure, due to processing of wastes containing corrosive chemicals
- Gap formation in the melter, due to thermal stresses and thermal shock during heatup and cool-down cycles
- Precipitation of metals, leading to electrical shorting of the melter, due to improper redox control methodology or settling of noble metals
- Failure of the process components, leading to radionuclide release, due to incompatibility of the materials-of-construction with waste and feed chemistry

1 INTRODUCTION

The U.S. Department of Energy (DOE) established the Tank Waste Remediation System (TWRS) program at the Hanford site in 1991 to manage the maintenance and cleanup of high-level radioactive waste contained in 177 aging underground storage tanks. The DOE has agreed to commitments and milestones for remediation of the waste tanks under the Hanford Federal Facilities Agreement and Consent Order of 1989 (Ecology, 1994), also known as the Tri-Party Agreement. To accomplish the TWRS requirements, the DOE plans to privatize the waste treatment and immobilization operations. The TWRS privatization is divided into two phases, a proof-of-concept or demonstration phase (Phase I) and a full-scale operations phase (Phase II). The Phase I program, scheduled for completion in 2012, is divided into Part A (feasibility study), which was completed in April 1998, and Part B (demonstration pilot plant study), which is scheduled for completion in June 2011. A Memorandum of Understanding has been signed between the DOE and the Nuclear Regulatory Commission (NRC)[1] for Phase I activities, which provides that the NRC acquire sufficient knowledge of the physical and operational situation at the Hanford waste tanks and processes involved in Phase I activities to (i) assist the DOE in performing reviews in a manner consistent with the NRC regulatory approach, and (ii) be prepared to develop an effective regulatory program for the possible licensing of DOE contractor-owned and contractor-operated facilities during Phase II.

The objective of this report is to provide NRC staff an overview and current status of high-temperature solidification technologies that have been used, tested, or proposed throughout the world. The report includes a survey of technologies used or proposed in the waste management (chemical and nuclear materials) industries, and includes a survey of commercial technologies in the ceramic and glass industries that are relevant to high-level radioactive waste (HLW). Information presented in this report is intended to assist the NRC in conducting safety assessments and developing regulatory requirements for the Hanford TWRS and subsequent solidification operations. This report supersedes the report titled "Survey of Solidification Process Technologies" CNWRA 97-005.

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[1] Memorandum of Understanding Between the Nuclear Regulatory Commission and the U.S. Department of Energy, January 29, 1997, Federal Register, V. 62, No. 52, 12861. March 18, 1997.

2 RELEVANT ASPECTS OF COMMERCIAL TECHNOLOGY

The glass, ceramic, and metals industries have been in existence for a long time. Consequently, the technologies used in these industries for manufacturing glass are well developed for manufacturing traditional products. There are thousands of operating plants around the world and a huge body of information is available in the literature. In fact, the development of the vitrification technology for HLW depended largely on input from the commercial glass industry. The total glass produced in a float glass plant in one day is equivalent to processing the entire HLW inventory at West Valley in 30 to 36 mo. While the ultimate purpose for the two products are dramatically different, there is a significant similarity in their conceptual design and processing behavior. In both traditional and nuclear waste applications, the process is designed around the melter/furnace/firing kilns, and in most cases, the performance of the melter or firing kilns determines the life of the process. Designing the melting systems to meet the process requirements and determining the operating limits for the process are the keys to a successful plant. The melter design and performance depend upon the melter operating temperatures, the selection of refractories to meet thermal expansion and thermal conductivity requirements, the compatibility of refractories with melter components and the melt, and glass properties such as corrosivity, electrical conductivity, and viscosity. In addition, supporting systems such as raw material (feed) preparation systems or offgas treatment systems also require compatibility evaluation for materials and processing requirements.

A survey of the traditional industries is beyond the scope of this report, but a brief overview of parameters that influence the process designs are discussed in the following. The melting chambers for glass or metals are designed to meet processing constraints. The contents of the melting chambers could either be heated by thermal energy such as burning fossil fuels, or by electrical energy that could be dissipated by joule heating, microwave heating, plasma heating, or induction heating. Commercial glass melters are typically air/fuel fired rectangular melters lined with a thick layer of corrosion resistant refractories. Electric glass melters are used in the production of several specialty glasses such as lead-glasses. The blast furnaces for the iron and steel industry have barrel shapes. The barrel shape provides for spalling resistance and improves integrity for the refractories by helping cracked refractories to be retained in their position. Cement kilns are also cylindrical in design.

A rectangular base for glass furnaces provides better conditioning of the glass. The depth of the glass furnaces depends upon the emissivity and thermal conductivity of the melt. If all parameters are fixed, dark glasses have a shorter depth compared to clear glasses, because of high absorption in dark glasses. Therefore, understanding product characteristics is important even before a process can be designed. The glass melting temperatures could range from 1,000 °C for certain glasses to 2,200 °C for fused silica. A key element of furnace design is the selection of refractories to withstand required operating temperatures. Additional parameters that are a part of refractory selection criteria are operating conditions and the nature of the glass melt.

The operating conditions include issues such as thermal cycling during production and thermal expansion of the melter during furnace start-up and cool-down. Generally, the refractories that exhibit excellent corrosion resistance are also excellent in terms of heat transfer, but poor in thermal shock resistance. The glass contact refractory is always the highest corrosion-resistance-material, but insulating refractories are used as a backup to minimize heat losses. Industry prefers to use a graded approach in their selection of refractories. The glass contact refractory, the most corrosion resistant and the least adequate in thermal insulation, is followed by a series of refractories with decreasing corrosion resistance and increasing thermal insulation. The last layer is composed of fiberboard, which does not have any corrosion resistance to glass melts, but its high porosity provides the best thermal insulation. There are two types of refractories that are widely used in the glass industry; alumina-zirconia-silicate (AZS) and high-chrome refractories. While high-chrome refractories have much better corrosion resistance than AZS refractories, glass manufacturers prefer to use AZS because corrosion of Cr_2O_3 from high-chrome refractories at times leaves a streak of coloration in products. Most of the melters designed for nuclear waste vitrification use high-chrome as a glass contact refractory.

The thickness of the refractory provided in a melter usually depends on the design life of the melter, which is a function of operating conditions such as temperature and the corrosive nature of glass melts. The thicker the refractory, the longer the life of the melter. But the melter has components other than the refractories, such as electrodes and penetrations for bubblers and drains, that could fail before the refractories. An optimum design focuses on selecting the components such that all parts corrode uniformly. The refractories in the melter are designed to provide uniform wear in the entire melter. In the area of higher wear, refractory blocks are made thicker, if possible, or made of better performing refractory. The selection of an inappropriate refractory will reduce the life of the melter. For example, the use of basic refractories such as MgO and dolomite for acidic melts will result in extensive degradation of the refractories. While MgO refractories are suitable for cement calciners, acidic refractories such as fused cast AZS are preferred for manufacturing float and container glass. The selection of roof refractories requires special consideration, because it depends upon the nature of offgases generated from the decomposition reactions and the burning of fuel/air or fuel/O_2 mixtures. Most of the melter roof also undergoes extensive temperature cycling. Therefore, the roof needs to be corrosion resistant to the offgas components as well as have a good thermal shock resistance. In all refractories, a better thermal shock resistance always compromises corrosion resistance or chemical attack, making selection of roof refractories a challenging task.

The selection of refractory materials by itself is not sufficient for designing the melter. A compatibility evaluation with other components present in the melter is required. If the melter is electrically heated, electrode materials and their compatibility with the refractory need to be evaluated. If the electrode material wears faster than the refractory, or if the refractory materials wear faster than the electrodes, the melter will have to be shut down prematurely. Other components that require further evaluation are the bubblers, thermocouples, and drains.

After the selection of refractories and a heating source such as an air/fuel mixture or electricity is made, the most important design criterion that determines the furnace longevity is the thermal expansion of different components during heat-up, cool-down, or normal operating thermal cycles. The presence of different types and shapes of refractory makes this a challenging task. The failure of pour-spout and alumina inserts in the nozzles of the West Valley Demonstration Project (WVDP) melter and failure of the roof or formation of gaps between the refractory blocks in some of the old melters are a result of thermal stresses that were not relieved during heat-up. The failure of the separation block between melting chambers in the Fernald melter was attributed to the use of a poor thermal shock resistant refractory in an area of extensive thermal cycling. While the blocks required a high corrosion resistance, the material selection failed to account for poor thermal shock characteristics. These safety problems will be reviewed in greater detail in chapter 4.

Finally, the melt properties determine whether the glass will process (i.e., melt and flow) as desired. In electric melters, the electrical conductivity of the melt is of prime concern. If the electrical conductivity is low, it will result in a high voltage drop between the electrodes causing conduction within the refractory material, which will heat the refractories rather than the melt. If the electrical conductivity is high, it may cause the current required to heat the glass to exceed the recommended maximum current density for the melter electrodes, which will eventually damage the electrodes. Therefore, the selection of electrode size and type depends on the electrical conductivity of the glass melt. For certain waste types containing excessive amounts of metals or small amounts of ionic conductors, electric melters may not be suitable.

The operating temperatures and corrosivity of the melt greatly influences the selection of electrodes. In the crystal glass industry (high-lead glass), molybdenum electrodes cannot be used for melting lead-glass because lead oxide reacts with molybdenum to form lead metal and molybdenum oxide, which is volatile. This reaction would result in the destruction of the electrodes as well as precipitation of lead metal on the melter floor, resulting in premature melter failure. In the crystal glass industry, tin oxide electrodes are preferred. The failure of the melter at Fernald, to be discussed in detail in section 6.1, was in fact a result of molydisilicide ($MoSi_2$) bubbler tubes reacting with the lead oxide in the waste glass. In most of the HLW plants, Inconel® alloy 690 is used as an electrode material because the melting temperatures required for HLW vitrification are within the operating range for Inconel® alloy 690. Lower operating temperatures allow minimizing volatilization of radioactive species.

Melt properties such as viscosity and liquidous temperature are important for processing. The liquidous temperature in glasses is defined as the lowest temperature below which crystal formation occurs in glass. Liquidous temperature is an important property of the melt. If the temperature of the melt in the melter is below the liquidous temperature, crystal formation occurs in the melt. If the crystalline phase is conductive, it may result in formation of an alternate path for the current in the melter, making joule-heating ineffective. Also, it may clog bottom drains and pour spouts making glass pouring impossible. The viscosity of glass is another important processing property. In glass manufacturing, if viscosity of the melt is off by a few percent, the entire process is shut down due to the problems in the forming processes. In addition, high viscosity will result not only in glass pouring problems but also in poor convective currents in the melter. Convective currents are essential to homogenize and completely dissolve the raw materials into glass. If viscosity is high, unmelted raw materials could be discharged into the forming process line. In nuclear waste vitrification, this may result in an inhomogeneous waste form and problems in glass pouring.

3 JOULE-HEATED, HIGH-LEVEL RADIOACTIVE WASTE PROCESSING PLANTS

Initial research on the development of the vitrification process for HLW started in the early 1960s. The first vitrification plant that was operational in the United States was commissioned for radioactive operations in December 1985 to produce 32 heat and radiation source canisters for the Federal Republic of Germany (FRG). This facility was shut down in March 1987. The melter was developed at the Pacific Northwest National Laboratories (PNNL) as part of a bilateral agreement between the Bundesminiterium fur Forschung und Technologie and the DOE. The first joule-heated melter plant, the Pamela vitrification facility in Mol, Belgium, was commissioned in 1985. In the United States, vitrification plants at the WVDP, West Valley, New York, and the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS), Aiken, South Carolina, were commissioned in 1996. The Tokai Vitrification Plant (TVP) in Japan was commissioned in 1995 and radioactive operations at the Mayak vitrification facility (S. Ural) in Russia were started in 1986. Except for the Pamela and Mayak vitrification plants, all plants are currently operational. The Pamela plant concluded its operation, after 6 yr of radioactive operations, in September 1991 and the Mayak plant was shut down in 1997. The process flowsheet, including process issues for each of the above plants, is discussed in the following sections.

3.1 WEST VALLEY DEMONSTRATION PROJECT VITRIFICATION FACILITY AT WEST VALLEY

In 1980, the United States Congress authorized establishment of the WVDP as a DOE HLW management project. Immobilization of the HLW into a stable and nondispersible form using vitrification was successfully initiated at the WVDP in July 1996. However, before the start of radioactive operations, one full-scale nonradioactive vitrification system and three scaled vitrification systems were operated to support the development of the radioactive vitrification process (Barnes and Jain, 1996). The full-scale vitrification system was operated for 5 yr, from December 1984 through December 1989, under the Functional and Checkout Testing of Systems (FACTS) campaign. In parallel, the scaled vitrification system was operated to develop redox control methodology. The second scale vitrification system, was operated at the end of the full-scale nonradioactive testing in 1989. The third scale vitrification system (SVS-III) was operated in 1995 to optimize and develop techniques to control radioactive operations. The SVS-III testing and operations are discussed in section 9.4.

The WVDP HLW vitrification facility is a remotely operated facility designed using canyon remote technology. All major components are designed for fully remote replacement by using only the impact wrench and crane hook. Master slave manipulators (MSMs) are provided to support activities such as sampling, canister closure, welding, and decontamination. As of August 15, 1997, 320-m^3 (84,500-gal.) of HLW has been vitrified into 130 stable canistered waste forms (Hamel et al., 1998). The HLW transferred from Tank 8D-2 is mixed with the glass-forming chemicals and fed to a joule-heated melter at 1,150 °C. The glass is then poured into stainless steel canisters. After the canisters have cooled, they are capped, welded, decontaminated, and stored on site for eventual disposal. The description of the HLW vitrification process provided in the following sections has been extracted from Ploetz and May (1996), Firstenberg et al. (1995), West Valley Nuclear Services (1996), Barnes and Jain (1996), Chapman and Drosjack (1988), Carl et al. (1990), Jain (1993), Jain and Barnes (1993, 1997), and Hamel et al. (1998).

3.1.1 Waste Pretreatment and Feed Preparation

The HLW at the WVDP was generated by the commercial reprocessing of 640 tons of spent reactor fuel. At the inception of the WVDP, two types of wastes were stored in underground tanks. The majority, 2,270-m^3 (600,000-gal.), was neutralized plutonium-uranium recovery extraction (PUREX) waste stored in the carbon-steel Tank 8D-2. Another 40 m^3 of partially processed thorium recovery extraction (THOREX) waste was stored in the stainless steel Tank 8D-4. The PUREX waste was washed to minimize the sodium and sulfate salts to be vitrified. The original supernatant and wash solutions were decontaminated using a zeolite ion-exchange process to remove the radioactive cesium (Cs-137). The process was conducted in Tank 8D-1. The effluent was encapsulated in cement. Prior to the start of vitrification operations, the THOREX was transferred to Tank 8D-2, mixed with washed PUREX waste and the combined PUREX and THOREX waste was washed one or more times. The washed PUREX/THOREX waste was then blended with Cs-137 loaded zeolite. The volume of the waste at the start of vitrification operations was approximately 1,000-m^3 (264,000-gal.). The vitrification process can be separated into four phases: (i) tailoring the waste slurry by adding glass-forming chemicals to achieve the desired glass composition, (ii) melting the waste slurry in a melter and casting the glass into canisters, (iii) closing the canistered waste-forms, and (iv) treating the offgas before releasing it to the stack. The overall vitrification process flowsheet is shown in figure 3-1, and each phase is discussed in the following.

The initial step in the vitrification process is the pumping of a batch of HLW slurry from Tank 8D-2 to the concentrator feed makeup tank (CFMT) in the Vitrification Facility (VF). The CFMT is a 3-m-diameter (10-ft) and 4.3-m-high (14.1-ft) Hastelloy® alloy C-22 tank with a nominal capacity of 20.8-m^3 (5,500-gal.). Half-pipe heat exchange jackets are included outside the tank on the sides and the bottom to provide both heating (steam) and cooling (water) to the tank. Since the CFMT undergoes much more thermal cycling and higher temperature excursions compared to other tanks, Hastelloy® alloy C-22 was selected to provide better corrosion resistance from the waste components. To homogenize slurry, the CFMT has an agitator equipped with dual high-efficiency impellers. The HLW is transferred from Tank 8D-2 to the CFMT through an underground shielded trench. Approximately 100 batch transfers may be required to process the HLW inventory in Tank 8D-2. The volume of waste required for each transfer is calculated based on the heel present in the CFMT, the volume of recycled solutions, and the maximum glass that could be made without exceeding tank volumes. Nominal HLW transfers have been from 7.6-m^3 (2,000-gal.) to 10-m^3 (2,650-gal.) of waste from Tank 8D-2. After the transfer is complete, the contents of the CFMT are sampled and analyzed for composition, density, total solids, nitrates, and nitrites. The samples are obtained at a slurry sample station. An air displacement slurry pump transfers the slurry from the CFMT to the sample station. At the sample station, samples are collected in 15-cm^3 (0.9-$in.^3$) glass vials and sent to the analytical laboratory by a pneumatic sample transfer system. While the samples are being analyzed, the contents of the CFMT are concentrated by evaporating water from the slurry. The amount of HLW that could be transferred or the maximum glass that could be produced from a waste transfer depends upon the concentration potential of the wastes in the CFMT. The concentration potential is enhanced in the CFMT by the addition of sodium metasilicate as a deflocculating agent (Firstenberg et al., 1995). Based on the chemical analysis of the CFMT contents, the total amount of glass-forming chemicals required to produce the WVDP target glass composition is calculated. The glass formers are prepared in a nonradioactive facility and transferred to the CFMT. The target borosilicate glass composition and its acceptable process limits for composition are shown in table 3-1. The waste-feed slurry is the final mix of the HLW and the glass-former slurries. The mix contains all chemical species needed to produce the target waste form. The chemical analysis of this slurry is the key hold point for approval to transform the final slurry mix into glass. The Waste Form Qualification Report (WQR) (West Valley Nuclear Services, 1996) requires that the feed batch, to be of acceptable

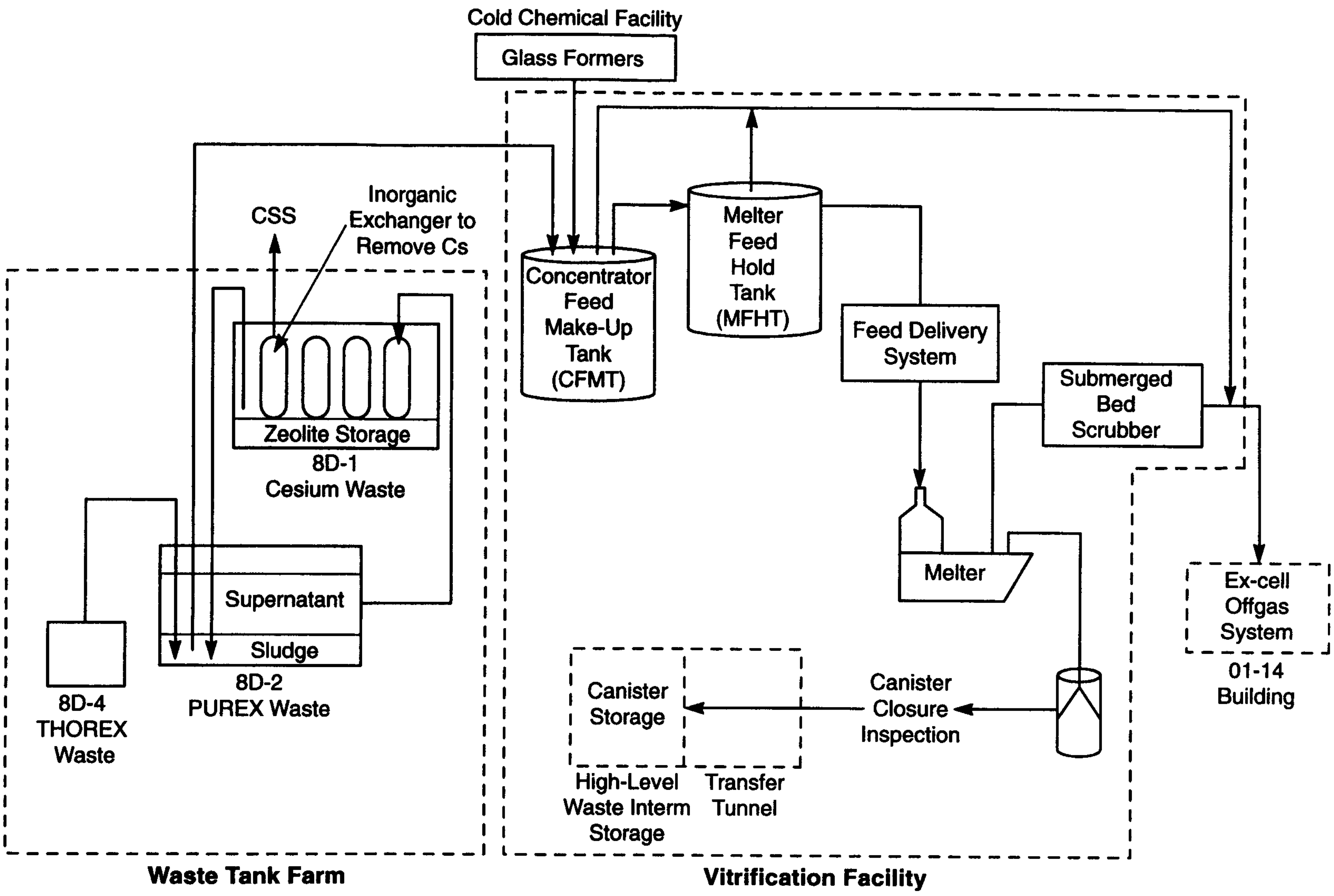

Figure 3-1. West Valley Demonstration Project vitrification process flowsheet (Jain and Barnes, 1997)

Table 3-1. West Valley Demonstration Project target glass composition (Jain and Barnes, 1997)

Oxide	Lower Process Limit (weight %)	Target Composition (weight %)	Upper Process Limit (weight %)
Al_2O_3	5.43	6.00	6.57
B_2O_3	11.00	12.90	14.80
CaO	0.36	0.48	0.55
Fe_2O_3	10.20	12.00	13.80
K_2O	4.37	5.00	5.63
Li_2O	3.25	3.71	4.17
MgO	0.76	0.89	1.02
MnO	0.70	0.82	0.94
Na_2O	7.00	8.00	9.00
P_2O_5	1.02	1.20	1.38
SiO_2	38.70	41.00	43.20
ThO_2	2.67	3.56	4.09
TiO_2	0.68	0.80	0.92
UO_3	0.47	0.63	0.72
ZrO_2	1.12	1.32	1.52
Others*	na	1.70	na

* Includes BaO 0.16%, Ce_2O_3 0.31%, CoO 0.02%, Cr_2O_3 0.14%, Cs_2O 0.08%, CuO 0.03%, La_2O_3 0.04, MoO_3 0.04%, Nd_2O_3 0.14%, NiO 0.25%, PdO 0.03%, Pr_6O_{21} 0.04%, Rh_2O_3 0.02%, RuO_2 0.08%, SO_3 0.23%, Sm_2O_3 0.03%, SrO 0.02%, Y_2O_3 0.02%, and ZnO 0.02%.

composition for making the waste form, should fall within the processing region shown in table 3-1. After the glass formers are transferred to the CFMT, the contents of the CFMT are sampled again and analyzed. If the composition of the feed falls outside the acceptance region, a new set of samples is taken and analyzed, and then the analyses are grouped with the previous set to redetermine the chemical composition of the

the contents resampled and reanalyzed. All the batches processed to date were within the processing region of the target glass composition (Jain and Barnes, 1997).

In addition, WQR requires that, before the final mix is approved for making glass, the mean of the normalized release rates for B, Na, and Li in the feed (as estimated by the prediction equations based on chemical analysis) (West Valley Nuclear Services, 1996) is at least two standard deviations below the mean normalized release rates for B, Na, and Li in the Environmental Assessment glass using the product consistency test (PCT) (Jantzen, 1992). The product consistency in a sample is measured by subjecting a known amount of a sample (particle size between 100 and 200 mesh), with 10 times its mass of deionized water at 90 °C for 7 days in a closed stainless steel vessel. After 7 days, the leachate is filtered and analyzed for B, Na, and Li.

The final step in feed preparation is to estimate the amount of reductant, usually sucrose, to be added to the feed. The reductant addition is necessary to provide proper redox conditions in the melter. The amount of sucrose needed is calculated from Total Organic Carbon (TOC) using the empirical relationship

where Index of Feed Oxidation (IFO) is the index of feed oxidation, NO_3 is the total nitrate concentration,

$$\mathbf{TOC = NO_3\,(1 - TS)/IFO} \tag{3-1}$$

TS is the fraction of total solids in the feed, and TOC is the total organic carbon concentration. A target IFO of 3.0 is used to estimate the amount of sucrose required to process the feed and ensure that the Fe^{2+}/Fe^{3+} ratio remains between 0.01 and 0.20. Uncontrolled redox excursions could lead to major process upsets. If the melt becomes too oxidizing ($Fe^{2+}/Fe^{3+} < 0.01$), a stable foam layer develops at the glass surface, diminishing the glass production rate. Alternatively, if the glass melt becomes overly reduced ($Fe^{2+}/Fe^{3+} > 1$), electrically conductive phases precipitate from the melt and interfere with the electrical current flow within the glass. The impacts of such process upsets have been further discussed in detail [Barnes and Jain (1996) and Jain (1997)].

The waste-feed slurry containing sucrose is transferred to the melter feed hold tank (MFHT) by a steamjet and mixed with the heel of the previous batch. The MFHT is a 3-m (10-ft) diameter and 3-m-high (10-ft) stainless steel tank with 22-m^3 (5,800-gal.) capacity, and the agitator is equipped with a dual high-efficiency impeller. The combined slurry is then fed to the melter. The feed rate depends on the melting characteristics of the feed. Higher total solids and sucrose concentrations allow higher feed rates, while higher water and nitrate concentrations decrease feed rates in the melter. An optimum balance is maintained between total solids, nitrates, and sucrose to maximize the feed rate while maintaining the Fe^{2+}/Fe^{3+} ratio within the specified range.

3.1.2 Vitrification

The second phase is initiated by pumping the slurry from the MFHT to the melter. In the melter, the remaining water is evaporated from the slurry forming a solid crusty layer on the surface (cold-cap) and the waste fuses with the glass-forming chemicals thereby producing the target waste-form composition. Figure 3-2 shows a sectional view of the slurry-fed ceramic melter (SFCM). The SFCM is encased inside a water-cooled jacketed box. The internal surface of the box is constructed from Inconel® alloy 690 to provide corrosion resistance to molten glass or condensed salts from the melting process. All penetrations for measurements and service are made from the top of the melter. The interior of the melter assembly is a

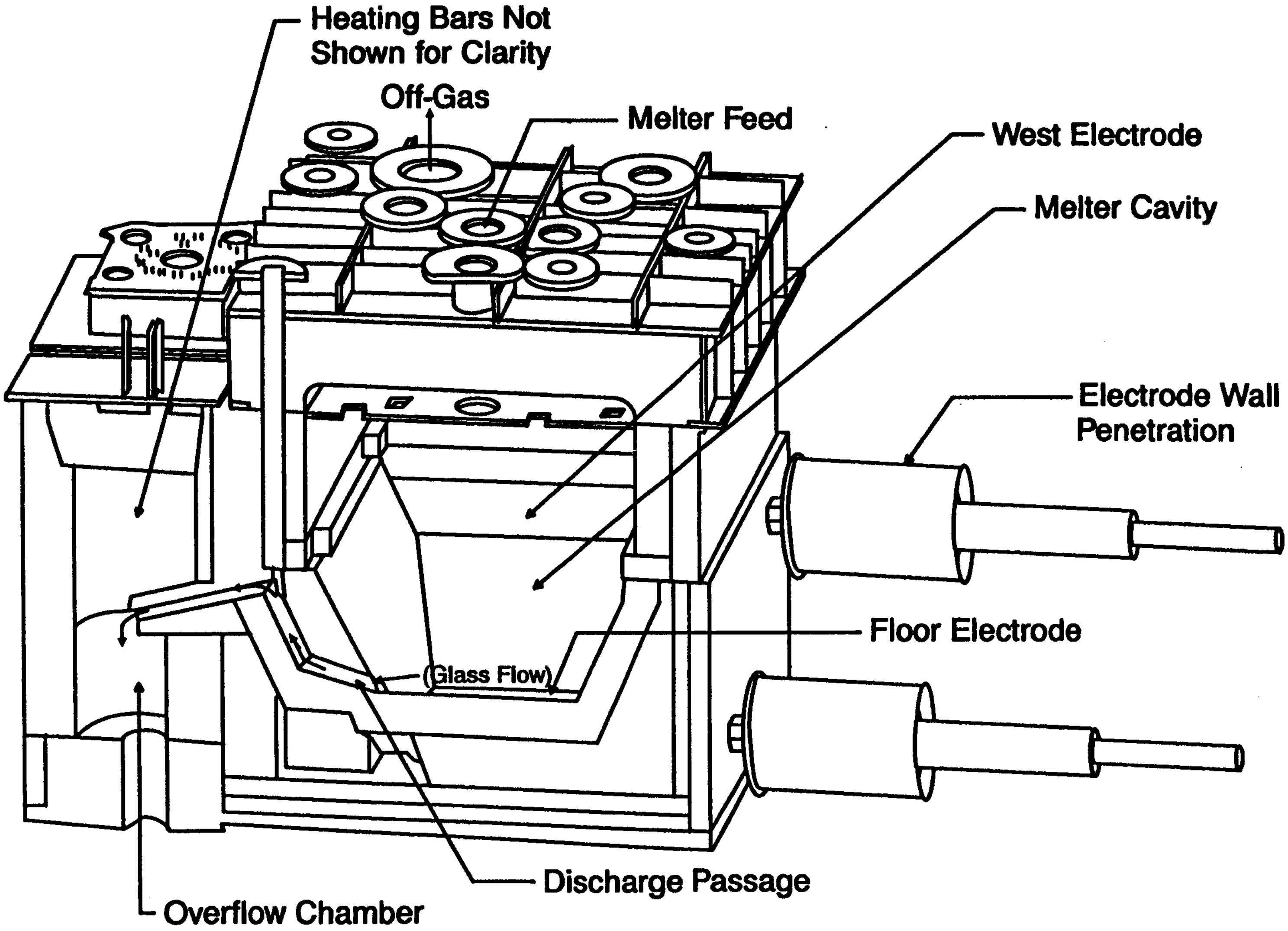

Figure 3-2. Sectional view of the West Valley Demonstration Project slurry-fed ceramic melter (Carl et al., 1990)

composite of various refractory materials. Like all joule-heated melters, high-chrome fused cast is used as a glass contact refractory to minimize corrosion from the molten glass. Between the glass contact refractory and the metal box, a series of refractories with increasing thermal insulation and decreasing corrosion resistance are used. The high-chrome refractory is backed up by Zirmul®, which is an alumina-zirconia silicate refractory. This, in turn, is backed up by castable bubble alumina and, finally, thermally insulated fiberboard is used. The fiberboard accommodates expansion from interior refractories on melter heat-up. The interior of the melter box is composed of three chambers: one melting and two discharge chambers. The two discharge chambers are provided for redundancy. The inner cavity of the melter is an irregular shaped prismoid similar to an inverted prism and contains three electrodes: two electrodes on the side and one at the bottom. The electrodes are made of Inconel® alloy 690 and air-cooled to keep the electrode temperature below 1,100 °C to minimize corrosion. The floor and the side walls slope toward the bottom electrode, as illustrated in figure 3-2. The melter has 2.15-m^2 (23.1-ft^2) of glass pool surface area and contains about 860-L (227-gal.) of glass. The molten glass is maintained at operating temperatures by adjusting the current between the three electrodes. The sloped side wall design for this melter was selected primarily because of concerns over noble metals or conductive sludges precipitating from the molten glass. Temperature and glass level control in the melter is accomplished by two thermowells (an Inconel® alloy 690 tube closed at one end) and a set of three Inconel® tubes acting as a bubbler set. Each thermowell contains nine thermocouples of various lengths, which are introduced in the melt chamber from the melter lid. These thermowells are replaced every 6 mo. The temperature profiles and the glass level obtained from these thermowells and bubbler tubes, along with power consumption and mass balances, are used to optimize the process and determine the need for adjusting feed rates and glass pour rates into canisters.

When the glass reaches a predetermined level in the melter, it is poured into the canister by activating an airlift mechanism. The glass is pushed out of the melter by introducing air in the melter discharge passage. Air is introduced via a platinum air-lift lance, called a riser tube, which is inserted from the melter lid into the discharge passage. Air bubbles reduce the density of glass in the riser tube, causing the glass to flow from the melter into the discharge trough. The glass flows from the trough into the canister. The glass flow is controlled by the airflow rate in the riser. The discharge or overflow chamber is heated by silicon carbide radiant heaters to maintain the temperature of the melt and prevent it from thickening before exiting the melter. Molten glass is periodically poured from the melter into a 3-m (10-ft) tall by 0.6-m (2-ft) diameter stainless steel canister located under the discharge chamber. During each airlift, 150- to 200-kg (330- to 440-lb) of glass is poured into the canister. Typically, it takes about 12 to 15 airlifts to fill one canister. A full canister contains between 1,800- to 2,000-kg (3,960- to 4,400-lb) of glass. The fill height is monitored using an infrared level detection system (ILDS). The ILDS consists of an Inframetrics® 760 imaging radiometer operating in the wavelength of 8–12 μm. The signal is displayed in the control room and tracks the fill level in the canister. In addition, load cells are used to monitor the weight of the canisters as the glass is poured. After a canister is full, the turntable on which the canister sits is rotated to bring a new empty canister under the discharge section and the turntable is sealed to the canister. The turntable structure is mostly made of 304L stainless steel. It consists of a stationary frame and a rotating frame. The rotating frame has positions for four canisters to move in a carousel fashion; the upper region of the turntable is sealed to the melter discharge section.

The full canister is allowed to cool under natural convection. Once the canister is cool, it is removed from the turntable and moved to a welding station. At the welding station, the canisters are closed by welding on a lid. The welding technique is an automated, autogenous, pulsed-gas tungsten-arc welding process (Kocialski and Dinsmore, 1994). Following a visual quality inspection of the closure weld, the canisters are decontaminated using an acidic, cerium-based, chemical oxidation procedure. After decontamination, a smear test is performed on the canisters to assure contamination levels are below the specification level (West Valley Nuclear Services, 1996). Finally, the canistered waste-forms are stored onsite until they can be shipped offsite to a federal repository for storage or disposal.

3.1.3 Offgas Treatment System

The WVDP offgas treatment system schematic is shown in figure 3-3. Basic components of the offgas treatment system located in-cell are a submerged bed scrubber (SBS), high-efficiency mist eliminator (HEME) and high-efficiency particulate air (HEPA) filter. The ex-cell components include another HEPA, a blower, and a NO_x abatement system.

The offgas first passes through a film-cooler, which is included as a component of the melter itself, and is located at the offgas nozzle on the melter lid. This device consists of a louvered insert that supplies cool airflow along the inner surface of the offgas line, thus minimizing buildup of carry-over glass and condensed salts on the pipe walls. The device also includes an offgas reamer, which consists of a brush that rotates as well as travels down the film cooler, discharging condensed salt deposits back into the melter. The offgas from the film cooler goes to an SBS. The SBS is designed for cooling and condensing melter vapor emissions. The SBS is also used as an interim storage for condensed fluids and spent canister decontamination solutions. The SBS has a double-tank configuration; the inner tank is a scrubber packed bed filled with ceramic spheres and water. The offgases are drawn from the bottom of the tank by vacuum and percolated through the packed bed. This results in condensation of water vapor and removal of particulates from the gas. As the water is condensed, the inner tank overflows into an outer receiver tank. The offgas is cooled from 300–400 °C to 30–40 °C. Both the sludge collected in the inner tank and condensate in the outer tank are recycled into the feed preparation process. The offgas from the SBS goes to a mist eliminator, which removes liquid entrained in the gas during scrubbing. After the mist eliminator, the offgas passes through the HEME, which removes more than 95 percent of the particulates. The gases are then heated and prefiltered through the HEPA, which captures small radioactive particulates. The HEPA prefilter contains two filter elements, each of which removes greater than 99 percent of 0.3 μm particulates. Upon exiting the HEPA prefilter, the offgas, primarily air, water vapor, NO_x, SO_2, and a minimal amount of particulates is sent to the ex-cell portion of the offgas system. The ex-cell provides further filtration of any radioactive particulates that may have eluded capture by the in-cell system and destruction of NO_x.

Offgas exiting from the in-cell portion of the system is sent to another building, the 01-14 building, through a pipe contained within an underground tunnel. Pipe insulation and an entrainment separator within the pipe are used to minimize or eliminate offgas condensation before it reaches the 01-14 building. At the 01-14 building, the offgas is preheated to ensure it reaches the HEPA filters at a temperature above the dew point. HEPA filters remove more than 99.999 percent (decontamination factor of 1×10^5) of all the remaining particles. The offgas is then sent to the NO_x abatement system. Three blowers are installed in parallel. One is used, and two are for backup. The blower maintains the vitrification system in negative pressure. The NO_x abatement system consists of a heater, a catalytic reactor, and an ammonia injection system. The NO_x is destroyed by heating the offgas and causing it to react with ammonia in the presence of a catalyst. The catalyst is NC-300®, a zeolite-based material proprietary to Norton Company. The reaction produces water vapor, nitrogen, and oxygen. The amount of NO and NO_x in the offgas is continuously monitored by separate analyzers before and after it is sent to the catalytic reactor. Following the NO_x destruction, the offgas is directed to the main plant stack for discharge.

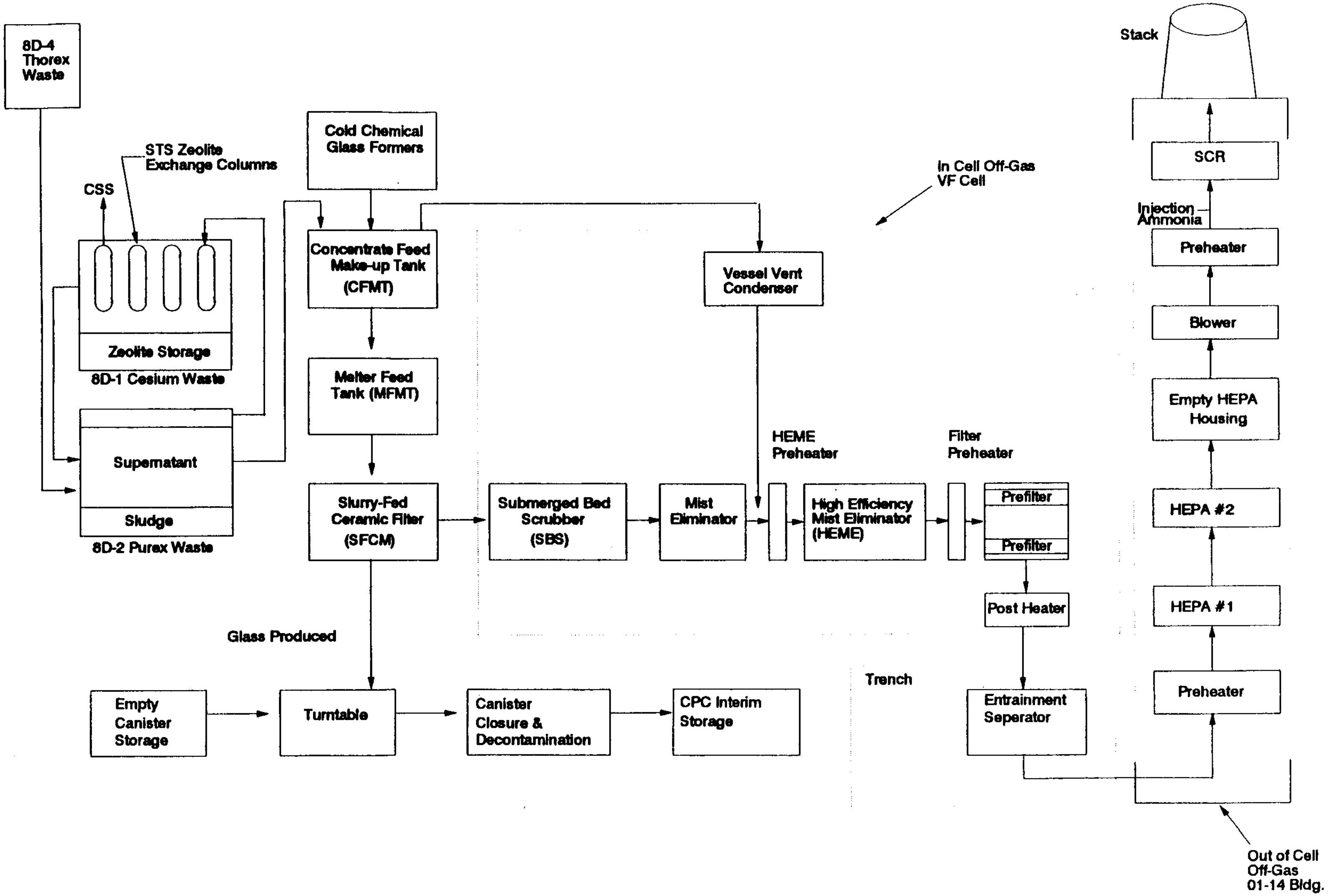

Figure 3-3. The West Valley Demonstration Project integrated offgas treatment system (Vance, 1991)

3.1.4 Process Issues and Upsets

3.1.4.1 Melter Nozzle Failure

During the non-radioactive operations from December 1984 to December 1989, it was observed that several cylindrical penetrations, lined with Inconel® alloy 690 tubes, in the lid were corroded due to high-temperature sulfur/halide attack. These penetrations are used for inserting instrumentation to measure temperature, density, pressure, and glass levels in the melter. The penetrations are also used for feeding and exhausting the offgas from the melter. After the conclusion of the non-radioactive testing, several materials were evaluated for improved corrosion resistance. Based on the evaluation, the cylindrical penetrations in the lid were replaced by alumina tubes. During the initial cold startup of the melter, several alumina pieces were found floating on the melt surface. This observation led to the shutdown of the melter. The alumina nozzles were removed and replaced by a single composite uniflange with replaceable Inconel® alloy 690 nozzle liners. Nozzle failure was attributed to insufficient thermal expansion allowance provided for the alumina nozzles during heatup of the melter.

3.1.4.2 Melter Pour Spout Failure

After nozzle repairs were completed, melter heatup was resumed. During September and October 1995, irregularities were noted with glass pours, including erratic flow and glass buildup at the bottom of the discharge cavity. Problems were also experienced with melter pressure fluctuation. The melter has two discharge sections: the west chamber is used for glass pouring, the east chamber is a backup. In November 1995, a large glass buildup was noticed in the west discharge chamber bottom as well as under the pour spout. Melter operations were suspended and the melter was allowed to cool. Initial examination revealed that the trough (pour spout) was displaced from its original location. A detailed examination revealed that the seal welds that held the pour spout to the dam (vertical Inconel® alloy 690 wall that separates the melting chamber and discharge chamber) had failed. The movement of the trough from its original location was attributed to the transposition of a weld symbol in the engineering drawing that resulted in a missing weld at the dam and trough interface. The corrective action plan included welding, reinforcement, and refractory modification in the discharge area. Weld repairs included three changes: increasing the weld size to provide additional reinforcement, adding a weld to the bottom of each trough, and using the weld procedure specifically developed to reduce distortion and stress during welding. Reinforcements were accomplished by providing additional gussets around the trough. Refractory modifications included use of six keystone shaped bricks placed on top of rectangular brick to provide greater structural support to the trough. The repairs were completed and melter heatup was resumed in February 1996.

3.1.4.3 Formation of Glass Fibers

During the early stages of the radioactive operations, formation of glass fibers in the discharge orifice led to the blockage of the discharge orifice. The incident was attributed to high airflow through the discharge orifice to the melter. The corrective action included installation of a flow-reducing orifice at the discharge orifice.

3.1.4.4 Radiation Leak

In January 1997, during radioactive operations, radiation leaked in the operating aisle through an electrical jumper connecting the discharge heaters in the melter. This radiation leak was attributed to a slightly positive pressure existing in the discharge chamber at the time as a result of pressure fluctuations in the vitrification system.

3.1.4.5 Melter Level Probes

Melter level probes are considered consumable components and are designed for a 6 mo operating life. Continuous erosion and corrosion of the level probe tips by feed particles and glass melt, with time, provides a biased glass level reading in the melter. A weekly calibration of probes and adjustments were necessary to maintain proper glass level in the melter and to discharge required amounts of glass to the canister.

3.1.4.6 Slurry Backflow

In November 1996, during a backflushing operation of the slurry sample station, diluted HLW slurry exited the shielded cell through a water line and activated the area radiation alarm. The incident was attributed to the lack of an approved procedure for the backflush operation. Corrective actions included implementation of vigorous review of procedures.

3.2 DEFENSE WASTE PROCESSING FACILITY AT SAVANNAH RIVER SITE

The SRS has been storing radioactive residues from over 30 yr of reprocessing irradiated nuclear fuels for national defense. The inventory is approximately 130 million L (34.3 million gal.) stored in 51 underground carbon-steel tanks (Marra et al., 1996b). The DWPF was the first high-level radioactive waste plant in the United States to start radioactive operations. However, before the start of radioactive operations, four scaled vitrification systems were operated to support the development of the vitrification process (Iverson, 1993).

The first vitrification melter, S-1941, was operated from August 1980 to September 1981. The S-1941 melter was a refractory-lined, water-cooled, cylindrical melter with four 6-in. (15.2-cm) diameter Inconel® alloy 690, water-cooled electrodes installed through the top head. Glass was poured into a canister by tilting the melter (similar to a teakettle). The campaign produced 74-ton (162,800-lb) of glass from 54 dry runs and 20 slurry runs. Analysis of the Inconel® alloy 690 components concluded that the observed wear supported the premise of a 2-yr operating life. The next melter was a large slurry-fed melter (LSFM). The LSFM ran campaigns over a period of 749 days during which it was operated with slurry for 193 days producing a total of 234-ton (514,800-lb) of glass. The LSFM melter was octagonal in shape with four plate electrodes 90 degrees apart. The design of the electrodes was changed to provide more uniform temperature distribution in the melt. Glass was poured, similar to the S-1941 melter, by tilting the melter. The third scale melter, S-4234, was a modification to the original S-1941 melter. The modifications included side penetrations for the plate electrodes and incorporation of most of the subsequent DWPF melter equipment design features for electrodes, plenum heaters, riser/pour spout heater, pour spout bellows, thermowell, feed tube, level dip tube, TV cameras, bottom refractory and insulation, vacuum pouring, recirculating loop slurry feed system, and offgas system equipment. The S-4234 was used to verify operation of DWPF equipment design. The fourth melter, integrated DWPF melter system (IDMS), had a fully integrated one-fifth scale DWPF feed preparation system and a one-ninth scale DWPF melter and offgas system, and was used to develop process control strategy for radioactive vitrification operations. The IDMS testing and operations are discussed in section 9.5.

The DWPF was commissioned in March 1996 to vitrify 130-million L (34.3-million gal.) of HLW. The DWPF HLW vitrification facility is a remotely-operated facility designed using canyon remote technology. All major components are designed for fully remote replacement. The facility has two long canyons that adjoin each other. Remote cranes are used to remove failed components. The description provided in the following sections has been extracted from Pearson (1991); Weisman et al. (1988); Marra et al. (1996b); Schumacher and Ramsey (1994); Little et al. (1997); Carter et al. (1997, 1998); Kerley et al. (1997).

3.2.1 Waste Pretreatment and Feed Preparation

The radioactive wastes transferred to the tank farms at the SRS, initially consisted of a mixture of insoluble metal oxide sludge and soluble salt solutions. The wastes, after reprocessing, were aged for 1 yr to allow decay of short lived radioisotopes. After the initial cool-down period, the soluble salt solution was decanted from the insoluble sludge, concentrated by evaporation to concentrated salt solution and transferred to storage tanks as a salt cake, as shown in figure 3-4. The current inventory of salt cake is approximately 53.4-million L (14.1-million gal.), constituting 173-million Ci, in 22 tanks.

The sludge, consisting primarily of precipitates of the hydroxides of iron, aluminum, and manganese, contained most of the radioactivity in the waste except Cs-137. The current inventory of sludge is approximately 15.1-million L (4 million gal.), including residual soluble salts and aluminum, constituting 323 million Ci, in 23 tanks. This salt supernate constitutes 60.2-million L (15.9-million gal.). The total radionuclide inventory is 500-million Ci. Both sludge and salt cake undergo pretreatment before they are transferred to the vitrification facility. Pretreatment steps are shown in figure 3-5.

The sludge is washed and undergoes aluminum dissolution operation at the Extended Sludge Processing Facility. The main objective of this process step is to remove aluminum and soluble salts to reduce HLW glass volume and improve glass quality. The process dissolves and extracts soluble nonradioactive components such as aluminum and soluble salts, which are further processed with the salt solution into low-level radioactive waste (LLW). The sludges that contain high aluminum concentration undergo two processing steps. First, sludge is treated with 3 molar caustic at 90 °C to dissolve alumina and supernatant containing dissolved aluminum is decanted before sludge washing. The sludge washing is a water dilution process in which water is added to the waste tank and mixed. After mixing, the waste is allowed to settle and supernatant is decanted. The washed sludge is transferred to the vitrification facility.

The salt cake is subjected to an in-tank precipitation process (ITP) to remove Cs-137 along with residual Sr and Pu contained in the salt cake via sodium tetraphenyl borate (TPB) addition. The main objective is to remove soluble sodium salts from the salt cake so that it can meet compositional requirements for the vitrified glass product. The salt cake solution is pumped to a separate waste tank where sodium TPB along with minor additions of sodium titanate is added to precipitate insoluble salts of potassium, cesium, and NH^{4+}. Sodium titanate helps adsorption of residual strontium and plutonium. The treatment calls for addition of sodium TPB quantity in excess of stoichiometric quantity required to precipitate cesium as Cs TPB due to a significant amount of potassium present in the salt solution that is also precipitated as

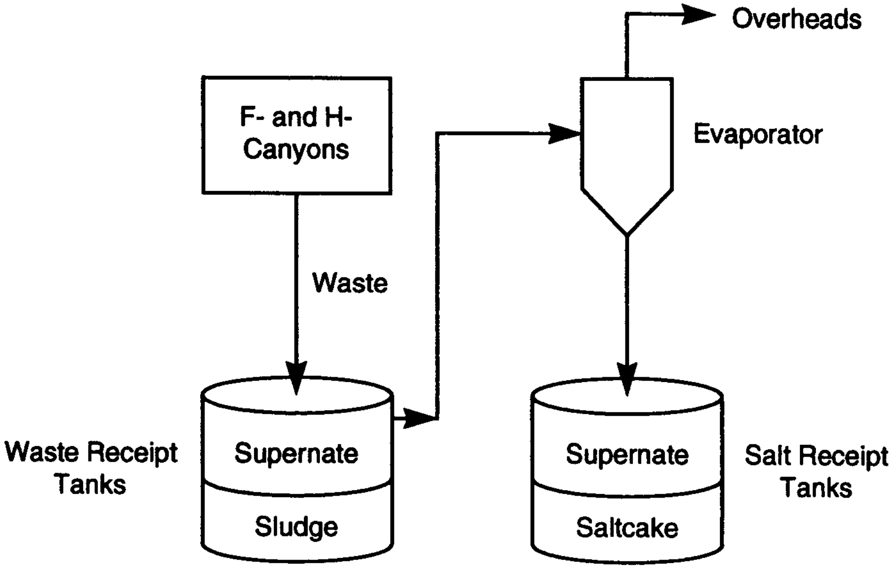

Figure 3-4. High-level waste evaporation process flowsheet

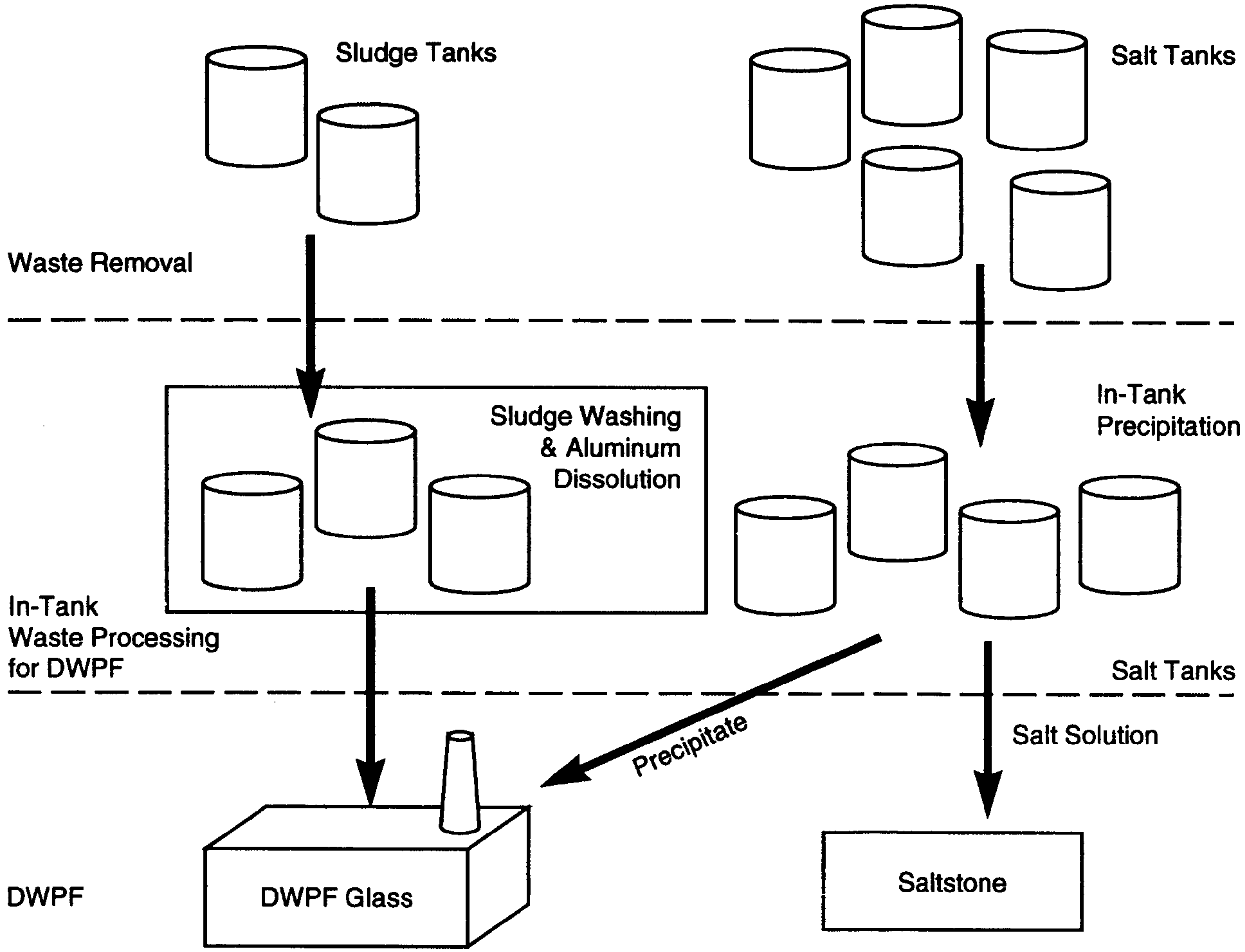

Figure 3-5. Sludge and salt pretreatment process flowsheet

potassium TPB. The excess sodium TPB also ensures complete precipitation of Cs-137. Next, the precipitate is concentrated by continuous filtration to 10 wt. % solids, washed to remove soluble salts, and transferred to the salt process cell. The processed soluble salt solution is mixed with cement, slag, and flash, and immobilized as a LLW at the Saltstone Facility.

The washed 10 wt. % precipitated slurry is transferred to the DWPF salt process cell to remove most of the organic materials. DWPF process flowsheet is shown in figure 3-6. About 90 percent of the phenyl groups are converted to an immiscible benzene phase by a formic acid hydrolysis process. The benzene is steam distilled, further decontaminated if necessary, and incinerated as LLW. The TPB compounds in the precipitate react with formic acid in the presence of copper (II) formate catalyst producing aromatic organic compounds (benzene, phenol, and minor amounts of higher boiling aromatics) and an aqueous phase known as precipitate hydrolysis aqueous (PHA). The PHA contains most of the radioactive Cs, soluble formate salts, boric acid, and excess formic acid.

The absorbed radiation doses from the Cs-137 in the precipitate required additional levels of copper formate catalyst than initially anticipated for the PHA formation. This increase in copper concentration in the melter feed increases the potential for precipitation of metallic copper phases in the melter. These metallic phases could accumulate over a period of time and interfere with the joule heating (Schumacher and Ramsey, 1994). Anticipated levels of elemental copper in glass are 0.4 to 0.5 wt.% The DWPF redox control studies have indicated that, in order to avoid precipitation of metallic copper phases in the melter and maintain elemental copper levels in glass at 0.5 wt.%, the Fe_2^+/Fe(total) ratio should be below 0.1. Since the

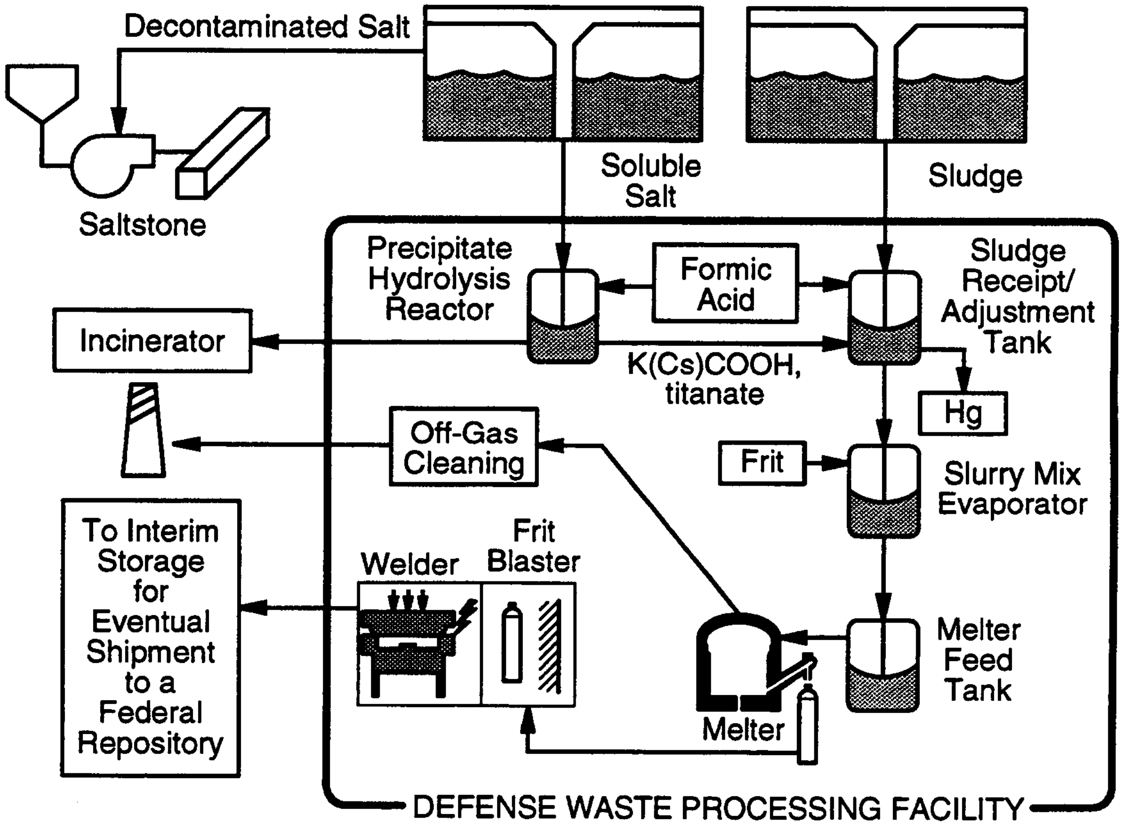

Figure 3-6. Defense Waste Processing Facility vitrification process flowsheet (Pearson, 1991)

redox ratio measurement at 0.1 or below is not accurate, an empirical model based on formate, nitrate, and percent total solids was developed to determine anticipated Fe_2^+/Fe(total) response in glass. In a feed containing nominal total solids of 45 wt.%, the molar difference between the formate and nitrate concentration should be maintained below 0.5. This provides an upper bound for operating the required redox control in the melter.

At the DWPF, the feed preparation begins with the transfer of the washed sludge directly to the sludge receipt and adjustment tank (SRAT). The SRAT is a 41-m^3 (10,800-gal.) alloy N10276 tank equipped with an agitation system, cooling/heating coils, and vertical cantilever centrifugal pumps for sampling and transfer. The washed sludge is first neutralized with nitric acid and then the PHA is added to the sludge (at boiling). The excess formic acid in the PHA reduces the mercuric oxide in the slurry mix to elemental mercury. The elemental mercury is then steam stripped from the SRAT into a holding tank from which it is later pumped and decontaminated. After the PHA and sludge are blended and processed in the SRAT, the mix is transferred to the slurry mix evaporator (SME). Note, that, due to benzene generation (discussed in detail in section 3.2.4.3) during the ITP process, Defense Nuclear Facilities Safety Board (DNFSB) has recommended that the ITP process should not be commenced until mechanisms involved in benzene generation are well understood. Therefore, the DWPF is only processing sludge along with simulated PHA. The SME is a 41-m^3 (10,800-gal.) alloy N10276 tank equipped with an agitation system, heating/cooling coils, and a vertical cantilever centrifugal pump for sampling and transfer. The wastes are then mixed with the borosilicate glass frit and concentrated to produce melter feed.

The ratios of PHA, sludge, and frit are determined by the product composition control system (PCCS). The PCCS is a computer program that uses glass property models and statistical algorithms to develop blending strategies and to determine the acceptability of the feed before it is transferred to the melter. PCCS input includes chemical analyses of the wastes, tank volumes, and tank heels. The sample analyses of the SME are used by the PCCS to determine acceptability of the melter feed.

3.2.2 Vitrification

Once the feed is approved for vitrification, the feed from the SME is transferred to the melter feed tank (MFT) and is fed to the melter. In the melter, the remaining water is evaporated from the slurry, forming a solid crusty layer on the surface (cold-cap) of the glass pool. The cold-cap prevents volatilization of radioactive components like Cs-137. The formates and the nitrates in the crusted slurry thermally decompose, forming a calcined oxide product. The calcined oxides fused to produce borosilicate glass melt.

The DWPF melter is the largest HLW vitrification melter operating in the world. The melter has a 2.6-m^2 (28-ft) glass pool surface area and contains about 2,200-L (581-gal.) of glass. It is designed to vitrify a continuous slurry stream of glass frit mixed with treated waste. The cross-section of the DWPF melter is shown in figure 3-7. The melter is cylindrical in shape; this geometry prevents the cave-in of the refractories. The glass contact refractory is high-chrome material to minimize corrosion by the waste glass. Two pairs of diametrically opposed Inconel® alloy 690 electrodes provide about 150 kW of power to the melt. In addition, plenum heaters provide additional heat to maintain a plenum temperature high enough to combust organics. Plenum heaters are resistance heated Inconel® alloy 690 tubes. The DWPF melter operates between 1,050 and 1,150 °C. A temperature higher than 1,150 °C could result in creeping and eventual damage to the Inconel® alloy 690 electrodes. In addition to meeting waste form disposal requirements, the glass composition is optimized to meet the viscosity and electrical resistivity requirements that would provide a maximum benefit of joule-heating and glass mixing by convective flows.

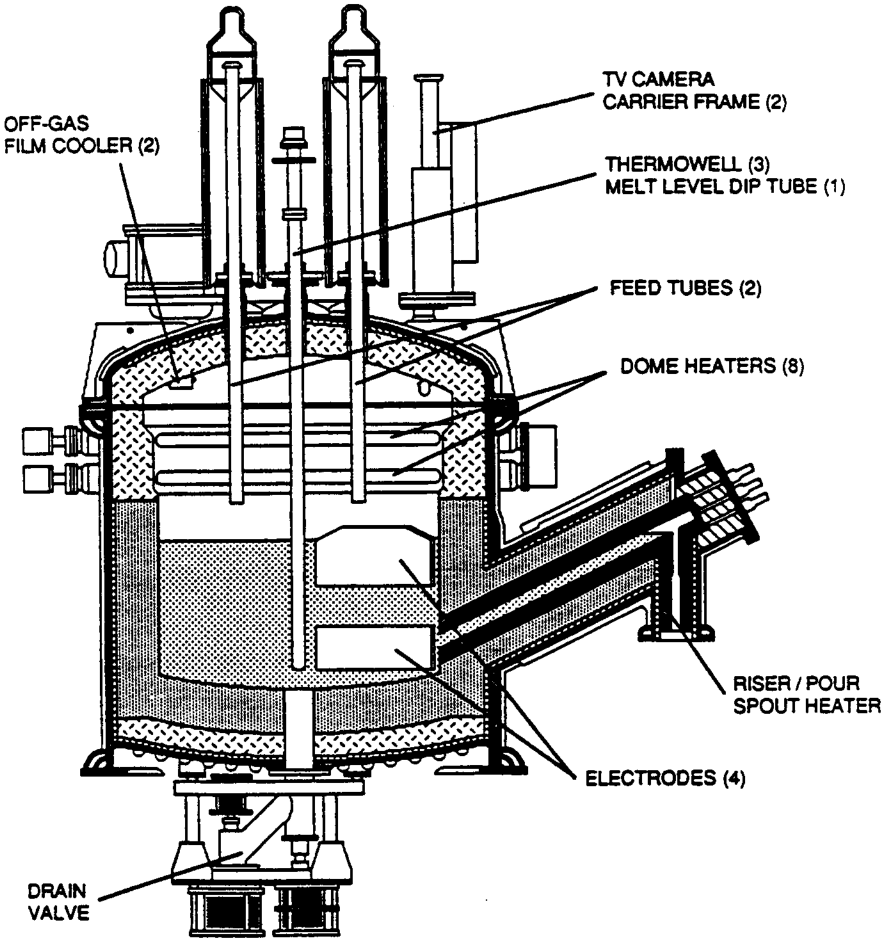

Figure 3-7. Sectional view of the Defense Waste Processing Facility vitrification melter (Weisman et al., 1988)

As the waste slurry is transformed into glass, the glass level in the melter rises. When the glass level reaches a predetermined level in the melter, glass is poured into a stainless steel canister. To pour glass, a differential pressure is introduced between the melting cavity and the pour spout. This is done by introducing a slight vacuum in the canister end. As the glass level increases in the riser, the glass overflows in the pour spout and travels vertically down into the canister. The melter is also provided with a bottom drain for complete draining.

The glass is intermittently poured into a 3-m (10-ft) tall and 61-cm (2-ft) diameter stainless steel canister. A full canister contains about 1,800- to 2,000-kg (3,960- to 4,400-lb) of glass. The fill height is monitored using an ILDS. In addition, load cells are used to monitor the weight of the canisters as they are filled. After a canister is full, the turntable on which the canister sits is rotated to bring a new empty canister under the discharge section.

After the canister is full, it is sealed using an inner canister closure (ICC) plug which provides a temporary water-tight seal to prevent ingress of water during the decontamination process. The ICC plug is tapered to facilitate installation into the canister throat while the canister is still hot and on the turntable. If the canister is not hot enough to form a shrink fit between the canister throat and the ICC plug, the canister is removed from the turntable and reheated. Next, the canister is moved to the ICC station where the ICC seal is leak tested. All canisters have to pass less than 2.0×10^{-4} atm-cc/sec He.

The ICC plugged canister is then moved to the canister decontamination cell and decontaminated prior to welding to remove the oxide layer from the outside surface of the canister. The canister is placed in a decontamination cell and the outside surface of the canister is blasted with an air-injected frit slurry. This technique uses an 8 percent slurry of glass frit driven by a 100-psig air stream that is sprayed in a helical pattern covering the entire surface. Each canister decontamination generates about 5,700-L (1,500-gal.) of frit slurry which is recycled to the SME. After blasting, the canister is water rinsed, air dried, and moved to a smear station. Canisters that fail the smear test are sent back for additional decontamination. Each canister is required to pass the smear testing acceptance criteria that is less than 220-dpm/100-cm^2 for alpha radiation and less than 2,200-dpm/cm^2 for beta/gamma radiation.

The canisters are welded before they are transferred for interim storage. Each canister is moved to the weld test cell and placed in the canister trolley. The trolley moves the canister to the ICC press where the ICC plug is pressed down by a 90,718 kgf (199,580-lb) hydraulic press into the canister neck to allow space for the weld plug. The weld plug is then installed into the canister throat and the trolley transfers the canister to the weld station. At the weld station, a combination of a 400,000 A DC capacity solid state resistance welder system and a ICC hydraulic press is used to pass current through the weld plug-canister flange interface. This generates enough heat to cause plastic flow of metal, and simultaneously allow the plug to be pushed into the canister throat. The canisters are smear tested again and transferred to an interim storage facility.

3.2.3 Offgas Treatment System

The offgas system is shown schematically in figure 3-8. The reaction products from the melter, along with the steam, pass through a film cooler, a quencher, an offgas condensate tank (OGCT), a two-stage steam atomizing scrubber (SAS), a HEME, and a HEPA filter. After required decontamination factors are obtained, the treated offgas is released to the stack. The offgas film cooler reduces the deposits at the entrance of the offgas system. A film cooler brush is used to clean any deposits that are formed. The quencher (venturi scrubber) cools the offgas and removes large particulates. The offgas condensate tank separates liquids and gases. The two SASs remove submicron particulates. The HEME removes the fine mist and particulates and the HEPA removes the trace particulates.

3.2.4 Process Issues and Upsets

3.2.4.1 Hydrogen Gas Generation

At the SRS, hydrogen is generated by wastes in all the tanks and constitutes a significant hazard. The hydrogen generation is mostly radiolytic. High nitrate concentration inhibits hydrogen generation. To prevent hydrogen accumulation in the tanks, considerable redundancy and independence is provided. This includes ventilation systems served by diesel backup power with alarms upon its failure. The ventilation systems are checked by operators every 12-hr shift. Hydrogen monitors, equipped with failure and low flow

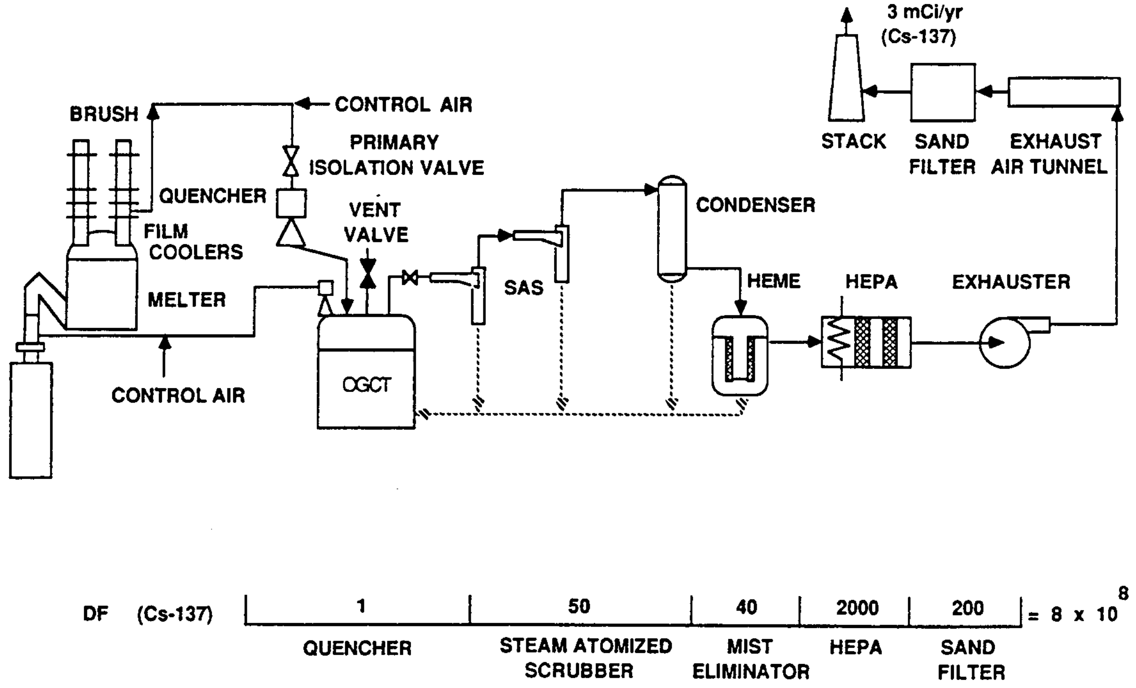

Figure 3-8. Defense Waste Processing Facility melter offgas treatment system (Weisman et al., 1988)

alarms, are provided for high-hydrogen generation tanks. The alarms are set at 10 percent of the lower flammability limit. In addition, tanks are continuously purged with nitrogen.

3.2.4.2 Corrosion of Tanks and Transfer Lines

In tanks and transfer lines, leaks due to corrosion are a significant hazard at the SRS site. Five of twelve tanks constructed in 1954 and all four tanks constructed in 1956 have leaked into their secondary containment vessels while two out of the eight tanks constructed in 1959 have penetration. All tanks have a secondary containment with leak detection devices. The waste chemistry is adjusted periodically to inhibit corrosion. All transfer lines are made of 304 L stainless steel and have a secondary containment. The secondary containment carries two transfer lines and drains to a leak detection box that is fitted with conductivity probes to detect leaks. All leaks go to a sump. In addition, secondary and primary containment integrity is verified biannually using a pneumatic pressure test, if possible. The test involves maintaining a 15 psig air pressure in the annulus for 20 min. Pressure drop of 1 psig indicates a leak.

3.2.4.3 Benzene Deflagration

The SRS uses sodium TPB and sodium titanate to separate Cs, Sr, and Pu from the salt cake solution in a ITP system. During batch 1 (first radioactive batch) processing, the benzene release was much greater than expected from historical tests conducted a decade ago, which postulated that the benzene is generated due to radiolytic destruction of TPB. In addition, when the ITP system pumps were restarted after several days or weeks of shutdown, the benzene release rate increased 2–3 orders of magnitude, indicating some sort of benzene retention phenomenon. The current opinion of the SRS staff, based on laboratory tests conducted since the batch 1 test, is that benzene is produced principally from the catalytic decomposition of TPB ions in solution. Catalytic decomposition is caused by palladium, which is present principally in the sludge and is carried along with the supernatent as an entrained solid during transfer. In 1996, the DNFSB issued recommendation 96-1, which stated that the ITP process cannot be resumed until a scientific understanding of the reactions leading to the generation of benzene, the mechanisms involved with the retention of benzene in the ITP system, and the mechanisms involved with the release of benzene in the ITP system are understood sufficiently well to ensure that the defense-in-depth measures taken to prevent deflagration are adequate. In addition, better understanding of chemistry issues related to ITP should be developed to determine the combination of controls and engineered systems necessary to prevent and mitigate benzene deflagration in process vessels. Engineered controls that are in place to avoid benzene deflagration in the sodium TPB tank and the filtrate hold tank include blanketing the tank plenum space with nitrogen, redundant nitrogen supply, and installation of instruments for monitoring tank pressure.

3.2.4.4 Moisture and Electrical Problems with Canister Manipulating Mechanism

The canister manipulating mechanism (CMM) is used for lifting and rotating the canister past the spray nozzles during decontamination. In 1996, standing water was found in CMM electrical jumpers and caused electrical faults between the lift and rotate motors. The source was determined to be water from in-cell washing that leaked into remote electrical connectors. Other problems with the CMM included pin-to-pin shorts on CMM electrical connector plates, a failed electrical connector on a transfer motor, a remote electrical connector for the recirculating pump electrical jumper that shorted and failed, limit switches for the CMM grapple and motors that failed, and a CMM rotational indicator that failed to operate during blasting operations.

3.2.4.5 Glass Pour Problems

Glass pouring problems have impacted the DWPF overall production performance. Glass pouring is accomplished by creating a slight vacuum at the pour spout end relative to the melter plenum space. The differential pressure forces glass to overflow into the pour spout and travel vertically 38-cm down the side wall of the pour spout where the wall is cut back to form a sharp knife edge to disengage glass. The glass then falls free about 360-cm through the bellows into the canister. Any wavering of the glass stream resulting from the pressure transients and airflow fluctuations through the discharge section during this free fall could result in the glass stream contacting the unheated bellows and adhering to the bellows surface, gradually leading to a buildup glass sufficient to clog the flow of glass. After the initial plugging of the discharge orifice, the DWPF designed a telerobotic manipulator (TRM) to clear the blockage. While the TRM was effective in removing the clogged glass from the discharge orifice, it did not resolve pouring problems. Pouring problems were significantly reduced after a removable insert was designed and installed at the end of the pour spout that lowered the knife edge from its existing location. Since the installation of the insert, pouring problems have been significantly reduced.

3.2.4.6 Foaming in the Melter

Foaming in the melter is related to the glass composition and redox conditions in the melt. Generation of foam in the DWPF melter is attributed to the presence of manganese dioxide and oxidizing conditions. If foaming is left uncontrolled, it can cause process upsets such as plugging of offgas lines, pressure transients, and unstable temperatures in the melter. The combination of these events can even lead to shortening of melter life. To date, generation of foam in the DWPF melter has not caused any significant process problems. The process is continuously monitored for foam.

3.2.4.7 Canister Turntable

A drive failure was observed in the canister turntable. The turntable sits under the pour spout and rotates to provide empty canisters under the discharge section. When the bellows or glass plug needs to be cleaned, the turntable is driven out from under the pour spout by an electric motor/gear box drive. The drive failure was attributed to overload in the drivetrain.

3.2.4.8 Process Component

The performance of all process equipment components was evaluated before the start of radioactive operations. The evaluation indicated that most of the equipment components except for the SME components met the design criteria. The examination of the SME agitator blades indicated severe erosion on the back side of the lower blades due to continuous impact of glass frit slurry particles. Similarly, severe localized erosion was observed in the SME coil assembly. The blades were overlayed with W73006 alloy coating and the damaged areas of the SME coils were repaired before the start of radioactive operations (Gee et al., 1996). Despite the coating, SME blade erosion recently caused temporary suspension of radioactive operations to repair the SME agitator blades again.

3.3 PAMELA VITRIFICATION PLANT, MOL, BELGIUM

The Pamela vitrification plant in Mol, Belgium, was the first vitrification plant to process HLW using joule-heated melter technology. The plant was constructed between 1981 and 1984. The Pamela vitrification plant is a remotely operated facility constructed from reinforced concrete with multiple shielded areas in which process and handling equipment are installed. After 1 yr of cold operations, hot operations were started on October 1, 1985. Radioactive processing was successfully completed in September 1991, vitrifying almost 900 m^3 (238,000 gal.) of high-level liquid waste (HLLW) into 500 tons of borosilicate glass in 2,201 canisters (National Research Council, 1996). During the process, two German designed flat-bottom, joule-heated, liquid-fed ceramic melters were used (Scott et al., 1988). The first melter was used for 3 yr and processed approximately 275 m^3 (72,650 gal.) of HLLW. This melter experienced noble metals buildup on the melter floor resulting in shorting of the melter electrical system and eventual failure. A second identical melter was installed and the campaign was successfully completed. Before and during radioactive operations, several vitrification systems (as shown in table 3-2) were developed and operated at the Kernforschungszentrum Karlsruhe site in Germany to support the development of vitrification processes at the Pamela vitrification facility in Mol, Belgium (Elliott et al., 1994). The HLW vitrification processing description provided in the following sections has been extracted from National Research Council (1996), Hohlein et al. (1986), Ewest and Wiese (1987), and Wiese et al. (1988).

3.3.1 Waste Pretreatment and Feed Preparation

There are two types of HLLW stored at the Pamela site. There is approximately 50-m^3 (13,120-gal.) of low-enriched waste concentrate (LEWC) from the reprocessing of spent fuel from commercial nuclear power stations with a low enrichment of U-235, and 800-m^3 (211,360-gal.) of high-enriched waste concentrate (HEWC) from the reprocessing of spent Materials Test Reactor fuel, with a high U-235

Table 3-2. History of vitrification melter development in Germany/Belgium, (Elliott, 1994)

Melter	Characteristics	Campaign/Run	Dates
K-1/VA-1	0.36 m^2 area, bottom drain, flat bottom	18 m^3 glass	1977–1979
K-2/VA-2	0.64 m^2 area, bottom drain, flat bottom	25 tons glass	1980–
K-3/VA-3	0.72 m^2 area, bottom and overflow drain, flat bottom	22 campaigns, 37 tons glass	1983–1985
K-4/Pamela*	0.72 m^2 area, bottom and overflow drain, 4° sloped bottom	LEWC campaign, 77.8 tons glass	1/85–12/86
K-4 Pamela*	0.72 m^2 area, bottom and overflow drain, 4° sloped bottom	HEWC campaign, 248.3 tons glass	1/86–1/89
K-5/Pamela	same as K-4	–	1987–
K-W1/V-W1	1.4 m^2 area, bottom drain, overflow, vacuum suction, flat bottom	–	1986–
K-W2	1.4 m^2 area, bottom drain, overflow, vacuum suction, 45° sloped floor	Campaign W4, 13.2 tons glass	4/88–5/88
K-W2	1.4 m^2 area, bottom drain, overflow, vacuum suction, 45° sloped floor, air bubblers	Campaign W5, 12.8 tons glass	1/89–3/89
K-6	0.88 m^2 area, bottom drain, 75°/60° sloped floor	8.5 tons glass	6/90–present
K-6	0.88 m^2 area, overflow system, 75°/60° sloped floor, air sparging	5.5 tons glass	6/90–present

*Radioactive melters.

enrichment. LEWC contains significant amounts of process chemicals such as sodium, in addition to actinides and fission products. The HEWC is mostly aluminum nitrate solution and has about 10 percent radioactivity of LEWC. LEWC also contains a significant amount of sulfur. The presence of sulfur limits the waste loading in glass to 11 percent (Wiese et al., 1988), attributed to low sulfur solubility in borosilicate glass.

The basic flowsheet of the vitrification process is shown in figure 3-9. The LEWC is transferred from the storage tanks at the EUROCHEMIC reprocessing plant via steam jets through a shielded overhead pipeline to the receiving tank at the Pamela vitrification facility. Each transfer is approximately 1.5-m^3 (400-gal.). After each transfer, the receiver tank contents are sampled for solids and activity. Next, the waste is batch transferred in 10-L (2.64-gal.) increments to the feed tank using a two-stage airlift transfer system. This waste is then continuously fed to the melter. Simultaneously, 5-kg (11-lb) bags of 1.5-mm glass frit beads are loaded in a solids handling system and are fed to the melter. The amount of frit added to the melter depends on the desired waste loading. Table 3-3 shows the composition of the glass frit and the LEWC waste glass.

3.3.2 Vitrification

The joule-heated ceramic melter is a major component of the Pamela process. Figure 3-10 shows major parts of the melter. Like all joule-heated melters, the high-chrome ceramic refractory is used as a glass contact refractory to minimize corrosion from the molten borosilicate glass. The melter has 0.77 m^2 (8.29 ft^2) of glass pool surface area and a normal glass pool operating depth of 0.4 m (1.3-ft) and contains approximately 0.31 m^3 (82 gal.) of glass.

The joule heating for melting is provided by four Inconel® alloy 690 plate electrodes. These electrodes are air cooled to keep the electrode temperatures below 1,120 °C to minimize electrode corrosion. The electrical input to the melter is controlled by fixing the current to the power supplied to the electrodes. The power consumption of the melter is about 55 kW for the upper electrodes and 20 kW for the lower pair of electrodes.

The slurry feeding to the melter results in water and free nitric acid evaporation. This leaves behind a crusty layer of salts (cold-cap) on the surface of the glass melt. The cold-cap formation reduces the volatilization of radioactive species like Cs-137. The solids between the crusty layer and the glass melt surface are calcined to their oxides and incorporated into the glass melt at about 1,150 °C. The melt chamber temperatures at various points in the melter are measured by thermocouples. Four thermocouples, placed in Inconel® alloy 690 tubes, are installed through the melter lid to various depths to measure the plenum, calcination, and molten glass zones temperatures. These temperature profiles, along with the power consumption and mass balances, are used to determine the need for changing feed rates or pouring glass into a canister.

In the production of glass blocks, glass is drained to a canister batch-wise by using a bottom drain. When the glass in the melter (based on temperature readings) reaches a predetermined level, approximately 150-kg (330-lb) or about 60 L (15.8 gal.) of glass is removed from the melter. The glass flow is accomplished by providing induction heat to the bottom drain valve from a water-cooled, medium-frequency induction heating coil. Additional heat is provided by passing current from the bottom drain tube to the bottom electrodes. The initial fill rate is about 150-kg/hr (330-lb) and averages about 120-kg/hr (204-lb/hr). The total time from start of heating to filling the canister to the required level is about 2 hr. The weight of glass in the canister is determined by a strain gauge balance located on the canister lifting carriage, and these readings are integrated periodically to determine the fill rate. Two gamma detectors are installed to measure the glass level in the canister to confirm the present weighing system. The upper detector is set for the maximum fill level and the lower detector is 10-cm (4-in.) below the maximum fill.

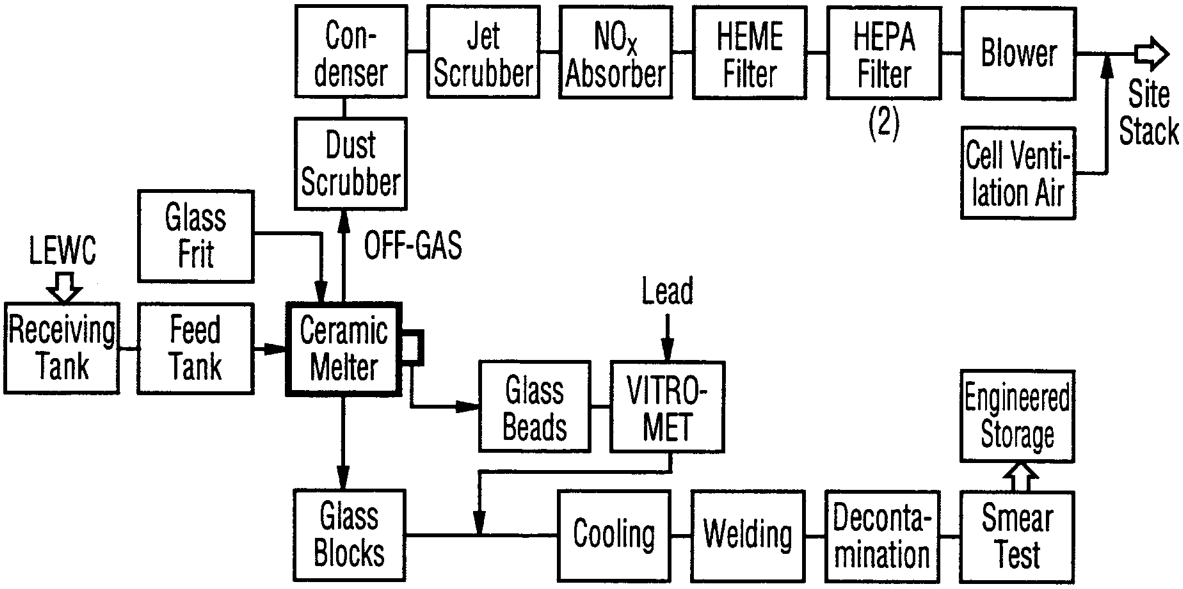

Figure 3-9. Pamela vitrification process flowsheet (Hohlein et al., 1986)

Table 3-3. Composition of the glass frit and the low-enriched waste concentrate glass produced in the Pamela plant (Hohlein, et al., 1986)

Constituent	Glass Frit, wt%	Waste Glass, wt%
SiO_2	58.6	52.2
B_2O_3	14.7	13.1
Al_2O_3	3.0	2.7
Li_2O	4.7	4.2
Na_2O	6.5	5.8
MgO	2.3	2.0
CaO	5.1	4.5
TiO_2	5.1	4.5
LEWC-oxides	—	11.0

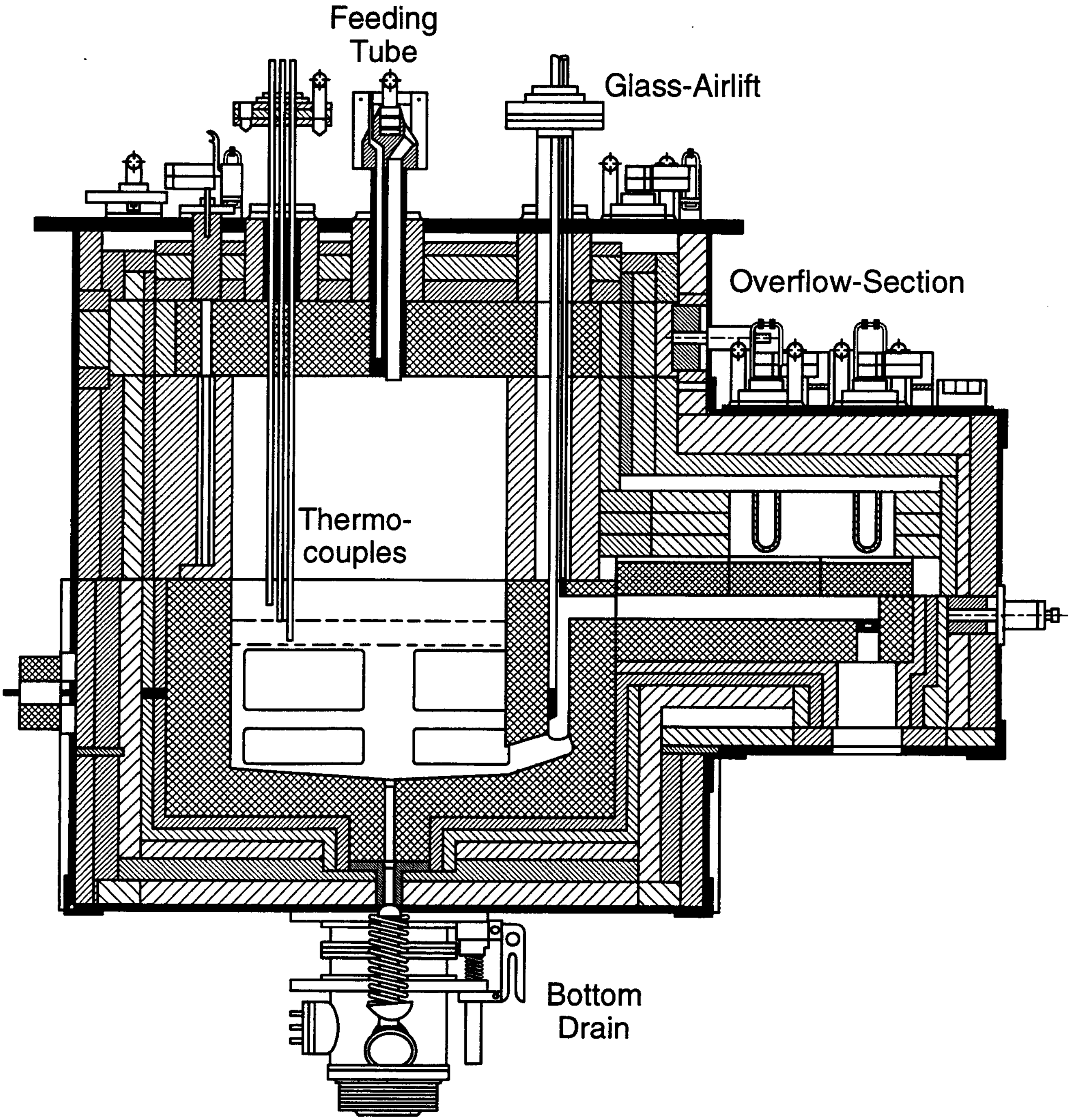

Figure 3-10. Sectional view of the joule-heated melter at the Pamela facility (Hohlein et al., 1986)

The bead production unit consists of an Inconel® alloy 690 pot, heated by a resistance furnace to 1,100 °C, that breaks the continuous glass stream from the melter into droplets. These droplets of glass fall onto a rotating turntable where they solidify. A scraper transports the beads to a hole in the center of the turntable where they fall into a container. During the time when the container is changed, the continuous stream of glass beads is temporarily collected in a buffer. After cooling down, the void volume between beads is filled with lead by induction heating the container to about 400 °C. These filled containers are called VITROMET.

Pamela canisters are 1.2-m (4-ft) in height and 0.3-m (1-ft) in diameter. The canister can hold 150-kg (330-lb) of glass [about 60-L (15.8-gal.)]. In-cell, these canisters are put in a heat insulating overpack and moved to a canister lifting carriage. The carriage is driven along a rail to position the canister directly underneath the bottom of the fill valve. It then lifts the canister up to the bottom valve bellows for filling. After filling, the canister and the overpack are returned to the handling cell for cooling. After the canister is cooled for 60 hr to about 60 °C, it is removed from the overpack and moved to the welding station. A cover is welded using a gas tungsten arc welder (GTAW).

The welded canister is decontaminated in an ultrasonic bath containing 1 molar nitric acid. It is then moved to a separate chamber where it is rinsed with water. A smear test is performed on the canisters to assure contamination levels are below 10^{-7} Ci/m^2. Finally, the canisters are moved to the engineered storage building.

3.3.3 Offgas Treatment System

The offgas treatment system schematic is shown in figure 3-11. First, the offgas passes through a dust collector where large particulates are removed. The dust scrubber consists of a pot with a 204-mm-diameter column containing nine plates at a 175-mm (6.9-in.) spacing. The scrubber solution is held at 80–85 °C by an electric heater and is circulated counter-current to the offgas flow. The temperature is maintained to prevent steam condensation. The solids are periodically removed and recycled back to the process. A mechanical system is used to push back the solids that are deposited between the dust scrubber and the melter.

The offgas from the dust scrubber goes to a condenser where cooling water at 30 °C is used as a condensing media. The upper part of the condenser is a set of tubes and a lower section has a vapor disengaging and collection vessel. The condenser contact surface is enough to produce an offgas exit temperature of 40 °C. The condensate, which is usually a nitric acid solution, is periodically transferred to the secondary waste evaporation system.

The offgas leaving the condenser is mostly NO_x, small particulates, and aerosols, and it is combined with the offgas from vents of the other radioactive tanks. The mixture is fed to a jet scrubber where it is contacted by a recirculating fluid stream at a pressure of 5 bar. The recirculating scrub-solution energy is provided by a pump. Routine analyses of the scrub solution are made and, when the activity reaches 0.5 Ci/L, used scrub solution is sent to the secondary waste evaporation system.

The scrubbed offgas is next sent to the NO_x absorber. In this case, the scrubbing medium is 5 to 6 molar nitric acid. The scrubber solution also contains 0.2 molar hydrogen peroxide to oxidize NO to NO_2. The solution is maintained at 15 °C by a cooling water coil to cool the offgas and remove the heat of solution.

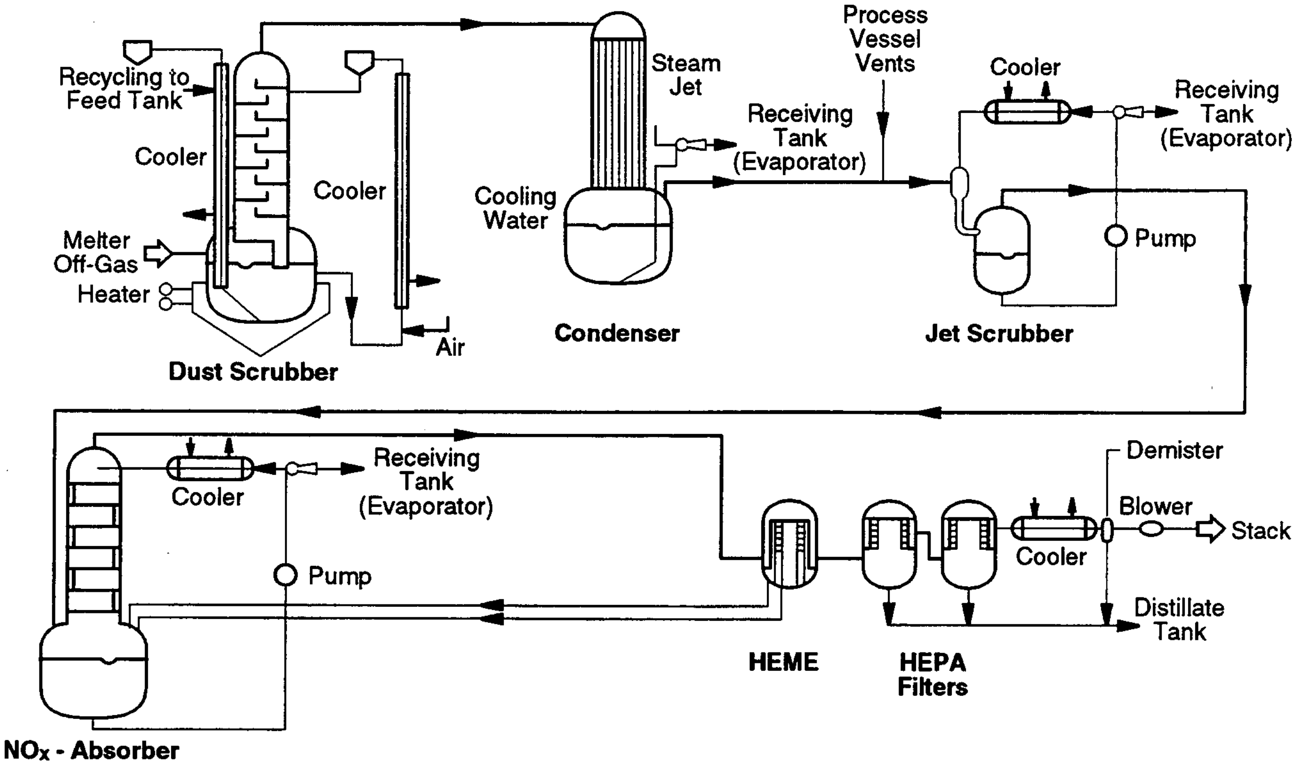

Figure 3-11. Offgas treatment system at the Pamela facility (Hohlein et al., 1986)

The offgas exiting from the NO_x scrubber is essentially air, nitric acid aerosols, and fine particulates. The offgas is next treated in a fiberglass filter where the nitric acid aerosols are removed and then heated to 70 °C to ensure that it is above the dew point before passing through two HEPA filters in series to minimize radioactive discharge. The gas is cooled to 30 °C, sent through an impingement, and discharged to the stack by an offgas blower.

3.3.4 Process Issues and Upsets

3.3.4.1 Noble Metal Issues in the Melter

During the initial processing of 47-m^3 (12,400-gal.) LEWC, approximately 90-kg (198-lb) of noble metals (Pd, Rh, Ru) were fed into the melter; Ru accounted for 64.4-kg (141.7-lb). In addition, during idling (time during which the melter is not fed), the melter temperature was lowered to around 800 °C by decreasing the voltage between the electrodes. On restart of the feeding to the melter, the system showed a glass production rate decrease from 30-kg/hr (66-lb/hr) to 20-kg/hr (44-lb/hr), and a loss in energy consumption. A glass sample taken from the melter bottom indicated an 80 times higher Ru concentration in the glass. This implies 27–61-kg (59.4–134.2-lb) of noble metals accumulation in a layer approximately 5-cm (2-in.) thick on the melter floor. Investigations with simulated bottom glass indicated that the electrical resistance was three times lower and the viscosity about five times higher than those of the normal LEWC glass at 1,150 °C. The decrease in the glass production rate from 30-kg/hr (66-lb/hr) to 20-kg/hr (44-lb/hr) or a loss of energy consumption in the melt could be explained because a significant portion of the current was passing through the highly electrically conductive bottom glass containing noble metals. Noble metals accumulated on the melter floor, because of their limited solubility in glass melt and their decrease in solubility with decreasing temperature. To eliminate this bottom glass, the melter was successfully rinsed with inactive glass and then sparged with nitrogen. Fortunately, the HEWC solution which was vitrified after this incident in the plant had 10 percent lower noble metal than LEWC. It was assumed that the situation would improve with time by washing out the layer.

Premature failure of the Pamela plant melter occurred in 1987, caused by rapid accumulation of noble-metal-enriched conductive sludges. The conductive sludge caused bottom drain plugging and resulted in electrode failure caused by shorting through the sludge (Scott et al., 1988).

3.3.4.2 Electrode Damage

At the beginning of the HEWC campaigns in October 1986, a hole in an Inconel® alloy 690 electrode next to the bottom of the melter was discovered when electrode cooling air was leaking into the melt. It was attributed to the layer of noble metals which contacted the lower side of the electrodes, resulting in a spot attack from the current. Since the bottom electrodes are not used for normal operation, the vitrification process continued.

3.3.4.3 Failure of the Bottom Draining System

In November 1986, cooling air from the bottom draining flange, which contacts the refractory, was leaking into the glass melt. Because of the limited capacity of the induction coil, the glass was kept running with direct heating. A much higher heat dissipation was maintained in the circuit outlet channel of the bottom draining system causing the region to overheat. This overheating resulted in glass flow beside the metallic outlet channel of this system. Because of the loss of the cooling circuit at this outlet, it was decided to fill the containers with the overflow system. Stopping and starting the glass stream was managed by the nitrogen fed glass airlift inserted in the riser of the overflow channel. Within three days, the lifting device for the containers was remotely adapted for the overflow operation in order to be able to produce glass blocks.

3.3.4.4 Blockage of the Outlet of the Overflow Channel

In January/February 1987, the outlet of the overflow channel was blocked several times with solidified glass. The blockage was remotely removed by inserting Kanthal heaters into the outlet to melt the solidified glass. The viscosity of the glass was too high for the glass to flow through the outlet nozzle, particularly during starts and stops of the glass stream. Blockage problems were resolved by changing the viscosity (at 1,150 °C) of the glass by reducing the waste oxide content from 22.5 to 21 wt.% and by increasing the temperature in the outlet region by 40 °C. In addition, it was observed during these incidents that the glass was partly crystalized in the outlet channel as a result of the long residence time involved. The crystals were identified as being predominantly rutile needles (TiO_2). As a consequence, a glass frit without TiO_2 was developed for HEWC.

3.4 TOKAI VITRIFICATION PLANT, JAPAN

The Power Reactor and Nuclear Fuel Development Corporation (PNC) of Japan started development of vitrification technology in 1975 in cooperation with universities, national research institutes, and private companies. The TVP was designed to vitrify HLLW from the Tokai Reprocessing Plant (TRP). The radioactive operations were started in December 1995, employing a joule-heating melter system similar to the Pamela, WVDP, and DWPF vitrification systems. TVP is a remotely operated facility with two main cells. The vitrification cell has most of the vitrification process equipment such as the receiving vessel, evaporator, melter, welding system, and offgas treatment equipment. For maintenance, overhead systems such as two-armed servo-manipulators, in-cell cranes, and a "rack system" that mounts the process equipment on modular frames, are disposed in one cell. The other cell is a transfer cell with storage pits where the canisters are inspected and stored. The glass production rate is 9-kg/hr (19.8-lb/hr), and the glass is poured from the bottom of the melter into a 304-L stainless steel canister. The waste form is produced as borosilicate glass with approximately 25 percent waste loading. However, before the start of radioactive operations, several vitrification systems, as shown in table 3-4, were developed and operated to support the development of the vitrification process. The HLLW vitrification processing description provided in the following sections has been extracted from Senba et al. (1997), Tomikawa and Yoshioka (1996), National Research Council (1996), Uematsu (1986), and Tsuboya and Tsunoda (1988).

3.4.1 Waste Pretreatment and Feed Preparation

The TRP was the first reprocessing facility in Japan, and it is capable of reprocessing 0.7 ton/day (1,540-lb/day) of fuel. The plant has been operational since 1977. As of 1988, the TRP has processed 350 ton (770,000-lb) of light-water reactor fuels and has generated, as a result, 300-m^3 of HLLW. The reprocessed fuels also include 5 ton from the prototype "Fugen" Advanced Test Reactor (Tsuboya and Tsunoda, 1988). The process is accomplished through four major systems: the waste retrieval and feed preparation system, vitrification, the offgas treatment system, and the canister closure and storage system. The schematic of the vitrification process is shown in figure 3-12.

The HLLW is transferred from the reprocessing plant to a receiving tank in the TVP through an underground trench system once a week. The composition of the HLLW is analyzed and adjusted by the addition of chemicals such as sodium. The waste is concentrated using an evaporator to a target concentration 500 L/metric ton uranium (132-gal./MTU). The pretreated HLLW is transferred to the feed tank by a steam jet. Before HLLW is fed to the melter, it is soaked into cylindrical glass fibers. The size of the cylinder is approximately 70-mm (2.75-in.) in diameter and 70-mm (2.75-in.) in length. The diameter of the glass fiber is about 10 μm. The soaking capacity is 4 ml-HLLW glass fiber. This keeps the glass melting stable without rapid evaporation.

3.4.2 Vitrification

Figure 3-13 shows a schematic of the TVP melter. The PNC melter is square in cross-section with a 45 degree sloped floor sloped; sloped walls facilitate discharge of noble metals with glass. The melt surface area is approximately 0.53-m^2 (5.7-ft^2) and the volume capacity is 300-L (79.3-gal.). The melter utilizes a composite refractory design. Four layers of refractory are used in the melter tank wall and three in the lid; this design is similar to the West Valley concept. The glass contact refractory is fused-cast high-chrome-alumina, backed up by successive layers of mullite, alumina castable, and a ceramic fiberboard. The containment vessel is cooled by natural air convection. The joule heating is provided by two main plate

Table 3-4. History of vitrification melter development in Japan (Elliott, 1994)

Melter	Characteristics	Campaigns	Dates
ETP A	0.3 m^2 area, overflow drain, flat bottom	–	1978–1984
ETP B	0.59 m^2 area, overflow drain, flat bottom	–	1980–1983
ETP C	0.3 m^2 area, bottom drain, flat bottom	–	1978–1984
MTP Mock-up	160 L volume, overflow and bottom drain, flat bottom	5 campaigns	1982–1983
Advanced-B	45° floor, 0.53 m^2 area, bottom drain	3 campaigns	11/85–8/86
CPF	bottom drain	11 runs	12/82–1987
Small Scale	30° floor, 0.054 m^2 area bottom drain	8 batches	estimated 1983–1984
Small Scale	45° floor, 0.054 m^2 area, bottom drain	13 batches	estimated 1983–1984
Pilot Scale IHI	0.25 m^2 area, 45°/53° floor, bottom drain	2.3 tons glass	1987
Mock-up II	data not available	–	1984–1986
Mock-up III	0.66 m^2 area, 45° floor, bottom drain	14.5 tons glass	2/88–1/89
Large Scale	2.2 m^2 area, 49.6°/53.3° sloped floor, bottom drain	30.3 tons glass	1991

electrodes and another set of smaller plates that acts as auxiliary electrodes below the main electrodes. The electrodes are made of Inconel® alloy 690. The melt temperature is maintained between 1,100 and 1,250 °C. The electrodes are cooled by forced air through the channels incorporated inside the electrodes. Current density is restricted to avoid excessive electrode corrosion.

The molten glass is discharged periodically, through a metallic nozzle located at the bottom of the melter, into a canister. A bottom freeze valve is heated by two-zone induction coils. This provides a higher degree of control over the starting and terminating of the glass draining into the canister.

Electroconductive deposits such as ruthenium oxide that have the potential to cause electrical shorting in the melter are also discharged along with the glass. This eliminates their accumulation on the floor. An estimated design life of the melter is 5 yr.

After the canisters are cooled, the cap is welded using a GTAW, and the canister surfaces are decontaminated by high-pressure water jet spray with wire brushing. Decontamination is verified using smears. The canisters are further inspected for appearance, length, and diameter before they are stored.

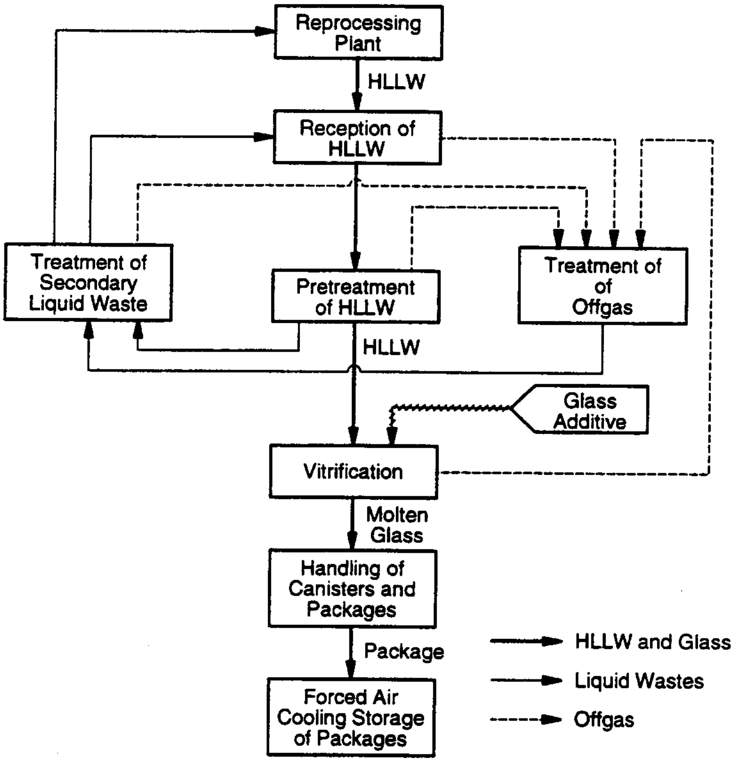

Figure 3-12. Tokai Vitrification Plant process flowsheet (Uematsu, 1986)

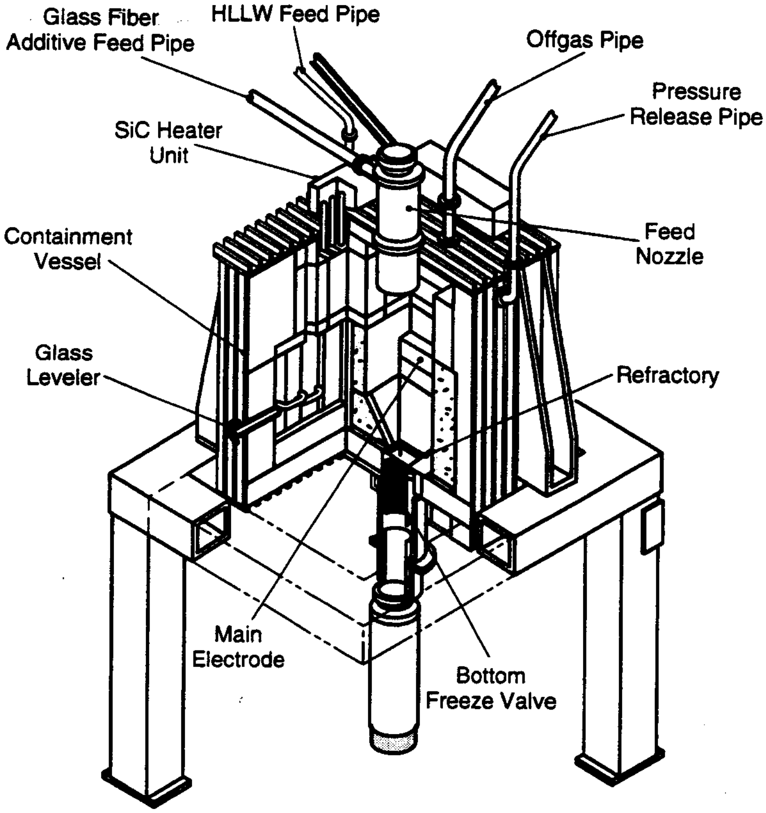

Figure 3-13. Three-dimensional view of the Tokai Vitrification Plant joule-heated melter (Uematsu, 1986)

3.4.3 Offgas Treatment System

Figure 3-14 shows the melter offgas treatment system. After release from the melter, the offgas goes through the air-film cooler, dust scrubber, venturi scrubber, perforated plate water scrubber, HEME, a ruthenium adsorber (silica gel), an iodine adsorber, and HEPA filters.

3.4.4 Process Issues and Upsets

3.4.4.1 Remote Operations

Two yr before the start of the radioactive operations, maintenance tests were conducted on all remote-type process equipment. During these tests, several problems related to hardware as well as software were identified (Senba et al., 1997). The majority of the problems were related to interference in making remote handling equipment access to process equipment. Most of the software problems were solved by changing operational procedures; hardware problems were solved by demonstration tests conducted using simulated objects. For example, equipment with electrical cables was improved by shortening and rearranging cable routes, cameras were moved to achieve better viewing, and easy access to objects was enhanced by improving the electric drive system; higher clearance was provided to impact wrenches to prevent fracture of impact wrench sockets and bolt heads.

3.4.4.2 Glass Accumulation in the Melter

During the radioactive operations, radioactive glass accumulated in the coupling device between the melter and canister (Tomikawa and Yoshioka, 1996). This was attributed to extremely low temperatures at the discharge orifice region due to the lack of proper temperature control in the region. The discharge orifice was remotely modified and the location of the thermocouples was changed to provide better temperature control near the discharge section.

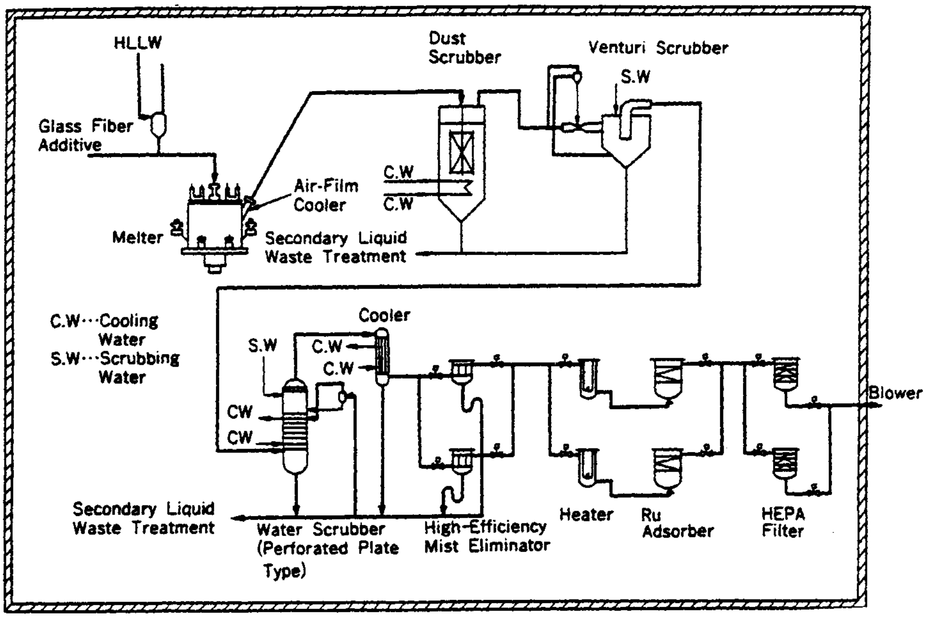

Figure 3-14. The Tokai Vitrification Plant offgas treatment system (Uematsu, 1986)

3.4.4.3 Offgas Plugging

A high-pressure differential in the melter offgas line leading to the SBS was encountered during cold testing, and was determined to be caused by the formation of deposits in this line. The problem was rectified by the repositioning and modification of the exhaust gas coupling device in this line assembly.

3.5 HLW VITRIFICATION PLANT, MAYAK, RUSSIA

3.5.1 Waste Pretreatment and Feed Preparation

No information available.

3.5.2 Vitrification

Research on HLW vitrification was initiated in Russia in the 1950s. Several pilot-scale vitrification plants were designed and operated using nonradioactive simulated wastes as well as radioactive wastes between 1967 and 1987. The first large-scale, liquid-fed melter at Chelyabinsk-65 in Kyshtym started operation in 1986 and was commissioned in February 1987. The melter is lined with a high-alumina zirconia refractory and is fired using top entering molybdenum electrodes. The melting surface area is 10.7-m^2 (115.2-ft^2) with a nominal glass depth of 0.4-m (1.3-ft). The outside dimensions of the melter are 9.48-m (28.9-ft) × 4.2-m (12.8-ft) × 3.2-m (9.7-ft) and it uses 56 electrodes (4 groups of 14). The melter suffered an electrode failure after 12 mo in operation due to a very high current load (2,000 A) that caused accelerated corrosion and eventual failure. Between 1987 and 1988, the HLW vitrification facility produced 160 MT (352,000-lb) of phosphate glass containing 3.9 million Ci of radioactivity (Bradley and Schneider, 1990).

A second melter, similar in design, started testing operations in December 1990 and was commissioned for radioactive operations on June 25, 1991. This melter has produced more than 2,010 tons of glass containing 235 million Ci of radioactivity. The glass production rate was between 400- and 450-L/hr (105.7 and 118.9-gal./hr). The facility was shut down in January 1997, 2.5 yr past its operational design life of 3 yr (Nuclear Waste News, 1997).

Each mild steel pour container was filled with 200-L (52.8-gal.) of phosphate glass in a batch process with a pour time of 1–2 min. A mechanical valve was used to open and close the melter side-drain. After lids were welded, three containers were placed in a stainless steel overpack. The pour canisters were not decontaminated prior to placement in the overpack. The overpacks were welded using a tungsten inert gas weld fixture attached to the cell floor, and rotating the canister by the weld head to obtain the fusion seal. No filler material was used during welding. Except for the visual inspection, there were no leak checks or other quality checks of the welds. The overpacks were placed in a storage building that is designed to cool canister heat loads of up to 5,000 W by a forced-air circulation.

The liquid HLW used as a feed was based on reprocessing fuel of both the BM-type and from VVER-440 reactor fuel. Unlike the rest of the world, the Soviets use phosphate glass as their high-level wasteform.

Phosphate glasses, unlike borosilicate glasses, offer lower melting temperatures (approximately 900 °C) coupled with higher sulphate solubility but have poor chemical durability and thermal stability. Furthermore, the melts are highly corrosive (Donald et al., 1997). Even though phosphate glasses are melted at a lower temperature, the corrosive nature of the melt limits the operating life of the melter. While significant improvements have been made in improving chemical durability and thermal stability of phosphate glass wasteform, their performance is still well below borosilicate glass wasteforms, and they still remain highly corrosive. Significant process characteristics are:

- Molasses is used in the feed to trap the volatile radionuclides.
- Frit is not used, but the feed is spiked with additives to get the proper phosphate glass composition.
- The melter does not have any problems with noble metals because they alternate HLW solutions with solutions that contain no noble metals (such as intermediate-level waste streams). In addition, the large melter volume, 12 m^3, helps dilution/dispersion of noble metals.
- Electrode and refractory corrosion is a problem but they expect that the electrodes will last as long as the refractories.

3.5.3 Offgas Treatment System

No information is available.

3.5.4 Process Issues and Upsets

The first HLW melter suffered an electrode failure due to excessive current load that caused accelerated corrosion and eventual failure of the molybdenum electrodes (Bradley, 1992). The electrode failure was attributed to failure of the cooling system that resulted in overheating of the electrodes and, hence, increased corrosion of electrode material. The facility was shut down and the damaged melter was replaced by a similar melter with an improved electrode cooling system.

4 INDUCTION MELTING HIGH-LEVEL WASTE PROCESSING PLANTS

Induction melting technology using calcined wastes for encapsulating HLWs was first developed in France. The Atelier de Vitrification de Marcoule (AVM), also known as the Marcoule Vitrification Facility, was commissioned in 1978 to vitrify fission product solutions from the UP1 reprocessing plant in France. The success of the AVM led to the startup of two similar facilities, R7 and T7. The R7 and T7 facilities were commissioned in 1989 and 1992, respectively, at La Hague reprocessing plant. R7 and T7 are identical plants, each having three vitrification lines. Each vitrification line is designed for a production rate of 30-kg/hr (66-lb/hr). R7 and T7 are being used for vitrifying wastes generated from reprocessing 800 MTU at the UP2 and UP3 reprocessing facilities, respectively. Each plant has an interim glass storage facility of 4,500 canisters. Table 4-1 shows the operating data at the end of August 1997 for the three vitrification facilities in France. Furthermore, in 1981, the United Kingdom adopted this technology at Sellafield. The Waste Vitrification Plant at the Sellafield site was commissioned in 1991. In addition, similar technology was adopted in India to process HLW.

4.1 MARCOULE AND LA HAGUE R7/T7 VITRIFICATION PLANTS, FRANCE

The HLW vitrification processing description provided in the following sections has been extracted from the National Research Council (1996), Merlin (1986), Maillet and Sombert (1988), Desvaux and Delahaye (1994), Jouan et al., (1997), Pierson (1997)[1], and Jain (1997)[2]. Since all French facilities are similar in operations, a combined description is provided for Marcoule and La Hague facilities.

Table 4-1. Operational summary as of August 1997 for high-level liquid waste vitrification plants in France (Jouan et al., 1997)

	Marcoule	La Hague R7	La Hague T7
Commissioned	1978	1989	1992
Waste treated (m^3)	2,114	3,366	1,872
Curies Processed (million)	435	1,254	832
Glass Produced (tons)	955	1,287	777
Canisters	2,652	3,218	1,943

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[1] Pierson, R.C. 1997. *Visit to Regulators and Facilities in France and England.* Trip Report December 1, 1997. Washington, DC: Nuclear Regulatory Commission.

[2] Jain, V. 1997. *Technical Exchange with the Regulators and Site Operators of the High-Level Waste (HLW) Vitrification Facilities at La Hague, France and Sellafield, UK.* Trip Report. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.

The remotely operated vitrification facility layout consists of several cells organized as workshops at different levels which are separated based on process functions. This was done to reduce cross-contamination risks, especially for the glass containers. The cells are stainless-steel lined, with viewing windows and manipulators along one side. Equipment in the plant is modular to facilitate remote replacement. The facility design takes into consideration accidents such as failure of high activity liquid waste cooling system, loss of air for the dilution of radiolytic hydrogen, loss of cooling for the vitrified waste storage, fall of a heavy load (container) in the vitrified waste storage, flooding of the building from an external origin, extreme weather conditions, an aircraft crash, a fire, or an earthquake.

4.1.1 Waste Pretreatment and Feed Preparation

The characteristics of the waste solutions that constitute the blend feed for the melter are the following.

- Fission product solutions—These are the concentrates from the fission product evaporators, including raffinates from the first extraction cycle and from other extraction cycles after preconcentration in acid recovery units.

- Clarification fines—The fines are made of zircaloy and undissolved fission products such as platinoids and molybdenum and are separated by centrifugation.

- Alkaline waste—These solutions come from the solvent regeneration of the first extraction cycle and the Pu purification cycles and contain mostly sodium nitrate and sodium carbonate. They also come from alkaline rinsing of fission-product concentration evaporators; in this case, they contain mostly sodium hydroxides.

A vitrification process flowsheet is shown in figure 4-1. Fission product solutions, alkaline waste, and clarification fines are transferred from the reprocessing plant to the vitrification plant and stored in separate stainless steel tanks. The tanks are water-cooled and equipped with mechanical stirrers. Alkaline solutions are neutralized using nitric acid. Both fission product solutions and neutralized alkaline wastes, in required proportions, are blended in an adjustment feed tank. The batch is analyzed and additives are included. The additives, nitric acid and aluminum nitrate, are intentionally combined with the waste to produce the desired glass composition. These solutions are separately metered in required proportions in a tank and blended with adjustment additives. Separate feeding lines are provided for the blend of fission products, alkaline waste and additives, and for the clarification fines. The two lines feed directly to the calciner through a metering wheel. The metering wheel outlet is connected to a hydraulic gauge that collects the solution from the recycle stream of the offgas treatment system. The hydraulic gauge is then connected to a small pot where the solution is mixed with sugar before flowing into the calciner.

In this process, the liquid waste along with scrubbing solutions and sugar is converted to the oxide form by heating above the decomposition temperature of the waste components. The calciner is an inclined (3 degree) tube heated by electrical resistance, that rotates at a speed of 20 rpm, and is operated at about 400 °C. Sugar is added upstream of the calciner to reduce ruthenium oxide to ruthenium metal. The heat decomposes nitrates to oxides. The offgas generated during calcination is sent to the offgas treatment system while the calcined waste is delivered directly to the melter crucible.

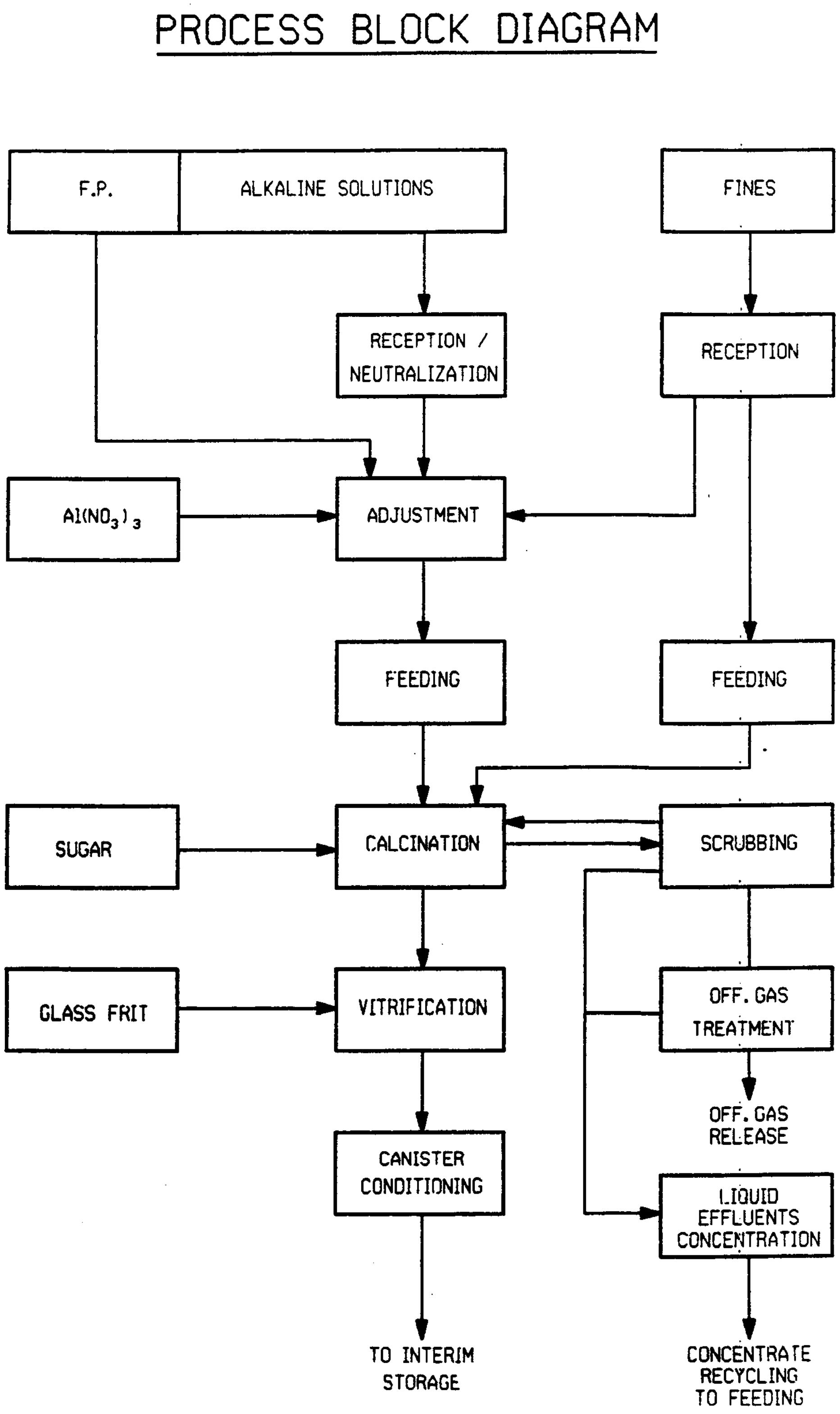

Figure 4-1. La Hague/Marcoule vitrification process flowsheet (SGN, 1987)

4.1.2 Vitrification

The waste exiting the calciner, as shown in figure 4-2, is mixed with the required amount of glass frit and fed to the inductively heated, oval-shaped, melting crucible. The melting crucible sits in an induction furnace that has four induction coils around the crucible and operates at 4,000 Hz frequency. The melting crucible, as shown in figure 4-3, is 1-m (3-ft) long, 0.25-m (0.82-ft) wide and is 1.38 m (4.5 ft) tall and is made of 10-mm (0.4-in.) thick Inconel® alloy 601. The air space between the melting pot and furnace is under a slight vacuum, and exhausts separately from the melter offgas. Unlike joule-heated melters in the United States and elsewhere that have an average operating life span of 3 or more yr, the melting crucible in induction melting technology is considered a disposable component. It takes about 2 wk to replace the failed melting pot. The failed components are sent to a breakdown cell where they are cut into pieces and disposed. A major achievement has been made in the operating life of the melting pot. The operating life has increased from 500 to 7,000 hr. The crucible material is still Inconel® alloy 601 but better heat control and distribution to reduce thermal, chemical and electrical stresses has resulted in improved life. Other factors contributing to improved pot life include changes in pot fabricating technology, and preheating of the pot to 900 °C before the first glass pour. A typical failure mode of the melting pot is a leak in the melting pot due to vapor phase corrosion. Leaks occurs above the glass melt line. The operators run the melter to its failure. The failure is predicted by the changes reflected in pressure drop or increase in the offgas flow rates.

Recently, the T7 vitrification plant added stirring by mechanical stirrers and argon bubbling to homogenize the melt. The melting pot has two mechanical stirrers that were introduced from the top. Additional stirring is accomplished by introducing argon under the melt. Since the introduction of the mechanical stirrers, the T7 facility has seen a 10-percent increase in production rate. The glass is poured every 8 hr, with pouring triggered by heating the bottom nozzle. Heating is stopped as soon as pouring begins, and the pouring stops by itself when the glass level reaches the siphon level and a glass plug forms in the nozzle. The melter crucible has another glass plug at the bottom, which is used to completely drain the melter crucible.

Each canister is 1.335 m (4 ft) tall and 0.43-m (1.3-ft) in diameter, can hold about 0.15-m^3 (5.3-ft^3) of glass, and requires two pours to fill. Before the first pour, the canister is pre-heated and, after filling, is transferred to the cooling and welding cell by means of a crane. After 24 hr of cooling, the canisters are transferred to a welding machine. Tacking and welding are performed without any filler metal by rotation of the plasma torch around the canister lid. Next the canister is transferred to the contamination monitoring unit. If the canisters are contaminated, they are transferred back to the decontamination cell and decontaminated using a high-pressure (250 bar) water jet. After decontamination, the canisters are first transferred to the contamination monitoring unit and then to the vitrified product store (VPS)[3]. The VPS is an array of 500 stainless tubes that can hold nine containers in each tube for a total of 4,500 containers. The VPS is forced-air-cooled to keep the temperature of the walls below 90 °C and the glass temperature below 510 °C. In case of power failure, the containers are cooled by natural convection. The change from normal ventilation to natural draft is automatic. The average heat generation rate is about 2 kW per canister. The sequence of these operations is illustrated in figure 4-2.

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[3] The vitrified product resulting from reprocessing fuel for foreign clients is sent back to the clients.

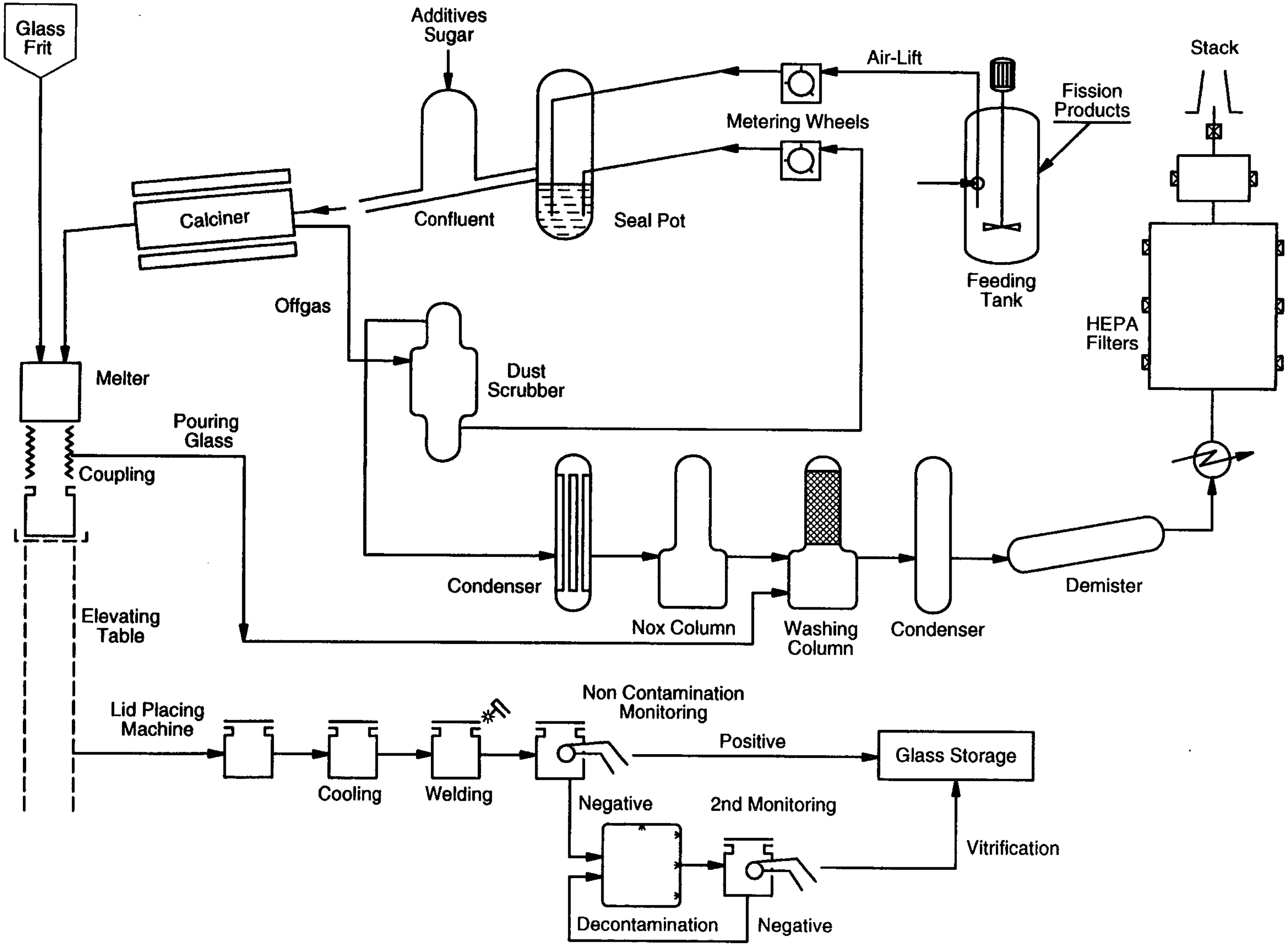

Figure 4-2. La Hague/Marcoule offgas treatment system (SGN, 1987)

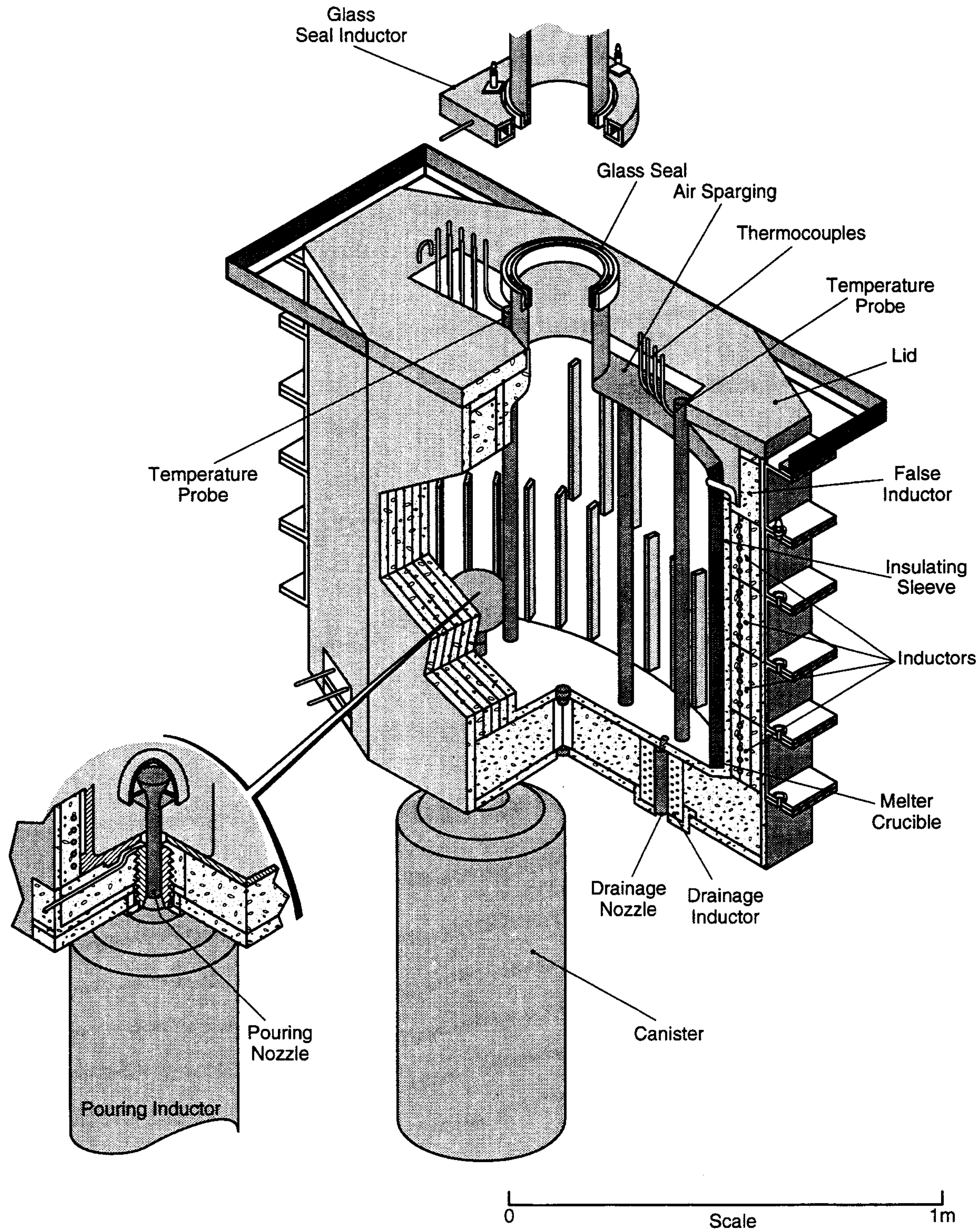

Figure 4-3. LaHague/Marcoule vitrification induction melter (SGN, 1987)

4.1.3 Offgas Treatment System

The function of the offgas treatment system is to scrub offgas from the calciner, recycle scrubber solution from the calciner, condense the steam at the scrubber outlet, absorb NO_x vapors, transfer liquid effluents to collecting tanks, ensure proper negative pressure in the equipment, wash offgas, and release offgas to the atmosphere. A schematic of the offgas treatment system is shown in figure 4-3. Dusts and offgases from the calciner are first passed through a dust scrubber. The dust scrubber is a cylindrical vessel, with the upper portion equipped with inclined plates, and the lower portion containing boiling nitric acid. The inclined plates trap the dust and are washed down by nitric acid sprays. The used nitric acid feeds back to the calciner with the recycling solution. The offgas at the scrubber outlet is passed through a condenser. Condensate is collected in a buffer tank located below the condenser and the offgas goes to the NO_x absorption column. In the washing column, the offgas is mixed with other offgases coming from various units of the plant. The offgas then passes through a cold trap, demister, heater to limit droplet carryover, two shielded HEPA filters, and one nonshielded HEPA filter. Two pumps ensure negative pressure in the washing column and all the other equipment. The pumps also ensure that the offgas is exhausted from the plant stack.

4.1.4 Process Issues and Upsets

No information is available.

4.2 WASTE VITRIFICATION PLANT, SELLAFIELD, UNITED KINGDOM

The Waste Vitrification Plant (WVP) at Sellafield, United Kingdom, is an adaptation of the French AVM process. The construction of the WVP at Sellafield began in 1981 to vitrify HLLW from the Magnox reprocessing plant and the Thermal Oxide reprocessing plant, in addition to processing the backlog of the stored HLLW. The WVP consists of two vitrification lines, vit line 1 and vit line 2, and has a higher throughput than the AVM. The active operation of the plant started in 1991. Vit line 3 is currently being constructed and incorporates lessons learned from vit lines 1 and 2 operations. These changes include improved layout of cells, an improved dust scrubbing system, a dual melter on the turntable to reduce downtime from 2 wks to a few hours, improved decontamination systems, and improved saws in the breakdown cell. The description provided in the following sections has been extracted from Elsden and Woodall (1988), the National Research Council (1996), Pierson (1997)[4], and Jain (1997)[5]. The main steps of the process are similar to the Marcoule and La Hague facilities as discussed in detail in the earlier section. Specific aspects of the WVP process are described in the following.

4.2.1 Waste Pretreatment and Feed Preparation

Reprocessing at the British Nuclear Fuels Limited (BNFL) started in 1952 but no waste was treated until 1990. Currently, there are 21 storage tanks; tanks 1–6 contain old waste and tanks 7–21 contain active

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[4] Pierson, R.C. 1997. *Visit to Regulators and Facilities in France and England.* Trip Report December 1, 1997. Washington, DC: Nuclear Regulatory Commission.

[5] Jain, V. 1997. *Technical Exchange with the Regulators and Site Operators of the High-Level Waste (HLW) Vitrification Facilities at La Hague, France and Sellafield, UK.* Trip Report. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses.

solutions. There are about 180 different waste streams. Characteristics of waste include well-defined composition and high heat load, mostly fission products. Criticality issues are minimal.

Figure 4-4 shows a schematic diagram of the WVP process. The feed preparation takes place in two tanks. HLLW is transferred from the reprocessing facility to the tank in WVP. Lithium nitrate solution is added to the HLLW to ensure adequate reactivity of the calcined HLLW. The prepared feed is characterized by sampling and analysis before being fed forward for vitrification. A constant-flow meter is used to control the flow of feed to the calciner. In addition to HLLW, other feeds that go to the calciner include effluent recycle from the dust scrubber, sugar solution, additional lithium nitrate, and dilution waste. The calciner consists of an inclined stainless steel tube rotated inside an electrical inductance furnace. As the feeds flow down the calciner, they are evaporated, dried, and heated to decompose nitrates. The dried calcine is directed to the melter.

4.2.2 Vitrification

The melter furnace is inductively heated and controlled at 1,100 °C. Glass frit is fed along with calcined HLLW in controlled batches. As the level of the vitrified waste reaches a predetermined height in the melter, a freeze valve at the base of the melter is activated and molten glass is cast into the product container under the melter. The pouring takes place every 8 hr, and each container takes about two pours to fill. The glass container is 1.3-m (4-ft) tall and 0.42-m (1.3-ft) diameter and holds about 150-L of vitrified

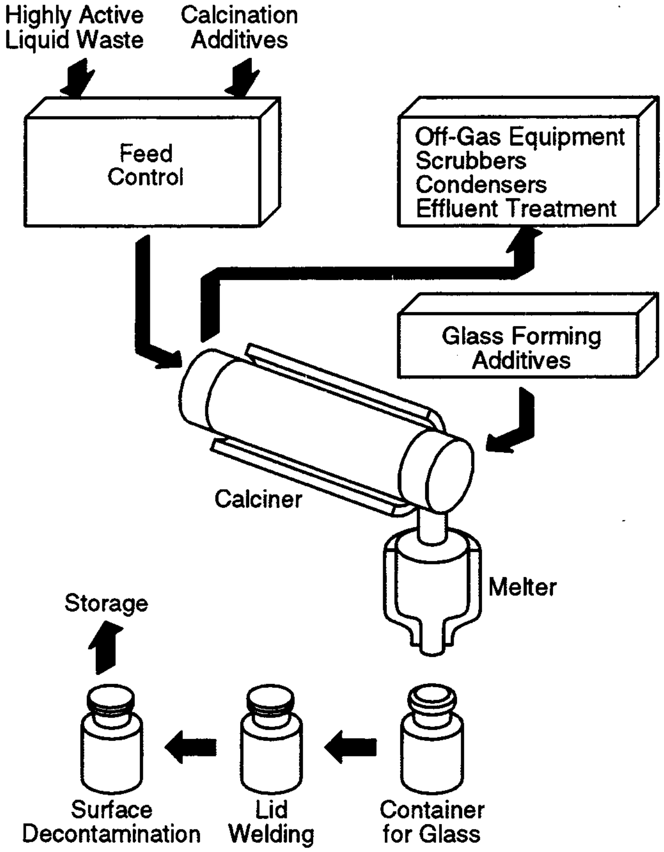


Figure 4-4. Process diagram for the Sellafield Waste Vitrification Plant in the United Kingdom (Elsden and Woodall, 1988)

HLLW glass. The glass container is held in a preheated furnace at 500 °C before and during pouring. This minimizes thermal shock on the glass. After filling, the container is lowered from the preheat furnace and allowed to cool. A lid is then loosely fitted, and the container and lid are completely sealed by an automatic fusion welding technique. The container is then placed in a decontamination vessel where high-pressure water or nitric acid is used to remove loose contamination from the external surfaces. After decontamination, the canister is checked and, if acceptable, it is transferred to the VPS. The VPS has a capacity to store 8,000 containers. The safety rule requires the temperature of the air not to exceed 110 °C. In addition, the centerline temperature of the glass cannot exceed 510 °C. The VPS is cooled by natural convection. The typical heat generation rate is 1.2 kW per container, which is well below the maximum allowable heat generation rate of 2.4 kW.

4.2.3 Offgas Treatment System

The offgas system consists of a dust scrubber, a tube condenser, a NO_x scrubber, an electrostatic precipitator, a scrubber column, and high-efficiency filters.

4.2.4 Process Issues and Upsets

In the 1980s, the induction melting technology was purchased from the French. While the technology was adopted from the French, the waste processed at Sellafield was significantly different compared to French waste. Major process problems resulted during the initial operations. Even though fundamentals of the technology were good, one of the lessons learned very early in the process was that success is embedded in knowing the fine levels of detail. Some specific problems that have a severe impact on vitrification operations are discussed in the following.

4.2.4.1 Melter Failures

Melting pot life is of significant concern. The best performance of the ovoidal 1-cm (0.40-in.) thick Inconel® alloy 601 melting pot has been 2,000 hr. Typically, melting pot life has ranged from 900 to 2,000 hr (this is in contrast to the La Hague facility where melting pot life of more than 4,000 hr is normally achieved). Routinely observed failures in the melting pot are:

- Leaks in the melting pot due to vapor phase corrosion followed by a vertical crack through the melting pot within 10 min. Due to the catastrophic failure of the melting pots, BNFL never runs melting pots to failure. The axial power profile and temperature gradients are monitored to estimate thinning of the Inconel® melting pot, which have been quite successful for replacing melting pots prior to failure. The improved life of the melting pots has been attributed to reducing thermal stresses by controlled heating and providing an even balance of temperature around the melting pots. In addition, an insulating fiber wool blanket is placed around the melting pot to ensure uniform distribution of heat.

- Failure of pour nozzles was the most frequent mode of melting pot failure. With melting pots, glass pouring is accomplished by inductively heating the pour nozzle to melt the solidified glass plug in the nozzle. When the glass has been poured, the induction heater is switched off and the glass is allowed to solidify in the nozzle to stop further glass pouring. Wavering of the glass pour stream due to pressure fluctuations in the melting pot results in an imperfect seal, allowing the glass to drip and form an external coating around the pour nozzle. The external corrosion of the pour nozzle by the glass is responsible for its failure. This type of failure has been minimized by controlling offgas flow characteristics and, in fact, in the last 18 mo pour nozzle failure has not occurred.

Early failure is attributed to pour nozzle failure, midlife failure is attributed to the splitting of external and internal reinforcing ribs at the ends, and general failure occurs around 1,300 to 1,400 hr due to vapor phase corrosion.

4.2.4.2 Failures of Cranes and Manipulators

The WVP requires significant usage of MSMs and in-cell cranes during normal operating conditions. There are five in-cell cranes and 80 positions for MSMs, of which 56 are regarded as key MSMs (Millington, 1995). A low reliability of the in-cell cranes and the MSMs was a major process issue. The main problem encountered with the in-cell cranes was the degradation of electrical cables, connectors, and electronic components at a rate greater than anticipated during design, and high failure rates of MSMs were coupled with inadequacies in the workshop and backup facilities needed for repairs. A secondary issue was the slow rate at which used contaminated crucibles were sectioned and disposed from the breakdown cell to allow room for a new crucible. In one instance, a portable grinder in the breakdown cell caught fire. Since the start of the operation in the cell, cranes, MSMs, and cutting equipment in the breakdown cell have been upgraded. These changes have resulted in a significant reduction in process downtime.

4.2.4.3 Shield Door Interlock Failure

Shield door interlock failure was a major finding. Dual shield doors are provided to ensure that while the equipment from the in-cell is moved for decontamination into the buffer zone, the ex-cell door is closed. During one incident, the operator opened the ex-cell door while the in-cell door was also open. This exposed the worker to a radiation dose. In addition, recurring contamination is a continual problem at the plant.

4.3 WASTE IMMOBILIZATION PLANT, TARAPUR INDIA

Solidification research on HLW was initiated at the Bhabha Atomic Research Center in India during the early 1960s. A remotely operating HLW Waste Immobilization Plant (WIP) was constructed in 1981 and commissioning tests were completed in 1985–86 at Tarapur to convert HLW to borosilicate glass. Information provided in this section has been extracted from the U.S. Department of Energy (1994).

Unlike the French induction melting process, the WIP is designed around a "pot-glass" process where HLW is first calcined at 600 °C in an Inconel® alloy 690 melter vessel. The HLW mix is transferred until the vessel is about 75 percent full; it is then calcined at 600 °C, and finally melted in the same vessel at 950–1,000 °C using a three-zone induction furnace. The melting vessel is 0.325-m (1-ft.) outside diameter and 1.8-m (5.5-ft) long. The contents of the melter are poured through a drain pipe into an insulated 304-L stainless steel canister which is 0.325-m (1-ft) outside diameter and 0.775-m (2.4-ft) tall with a 10-mm wall thickness, that can hold up to 45-L (11.9-gal.) of glass. A fully loaded canister has a heat generation rate of up to 1.75 kW and contains approximately 94,000 Ci. The HLW processing rate is 25-L/hr (6.6-gal./hr), and by using two vitrification lines, one canister/day is produced. The filled canisters are sealed by welding a lid. Two welded canisters are inserted into a carbon-steel overpack, which is sealed by welding a lid and placed in an interim storage facility designed with stack-induced natural draft air cooling. The current plans call for interim storage of vitrified wastes for 20–25 yr to cool and ensure integrity of the waste package before disposal in a repository.

5 JOULE-HEATED, MIXED LOW-LEVEL RADIOACTIVE AND HAZARDOUS WASTE PLANT

5.1 M-AREA VITRIFICATION PLANT AT SAVANNAH RIVER SITE, SOUTH CAROLINA

The SRS stores approximately 2,500-m^3 (660,000-gal.) of mixed low-level radioactive and hazardous waste at the M-Area. In November 1993, GTS Duratek was awarded the contract to construct a facility to vitrify the M-Area low-level radioactive mixed waste. The construction of the vitrification plant was completed in January 1996, and it was commissioned to process low-level radioactive mixed wastes in October 1996. The Duratek melter, Duramelter® 5000, is currently the largest low-level radioactive melter system operating in the world, and is also a one-third size prototype of the melter system to be built and operated by BNFL under the Hanford TWRS Program (Duratek, 1996).

The process description provided in the following sections has been extracted from Bowan and Brandys (1994, 1995). Since all the published information on this melter precedes the construction of the plant at the SRS, it is likely that the current design and operating process may be different.

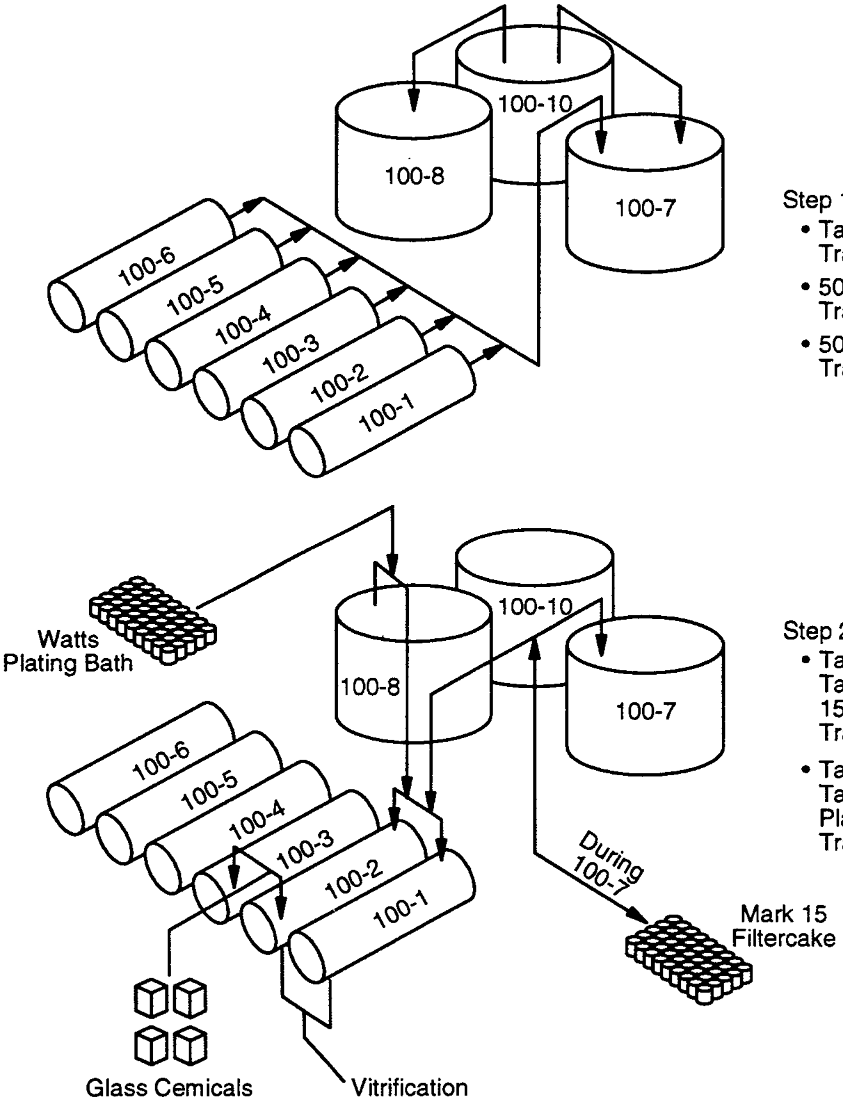
5.1.1 Waste Pretreatment and Feed Preparation

The M-Area waste at SRS is stored in three partially filled 2,900-m^3 (766,000-gal.) tanks, six 132-m^3 (35,000-gal.) tanks, and about 125 drums containing 0.21-m^3 (55-gal.) each. The 0.21-m^3 (55-gal.) waste drums contain Watts Plating Solution and Mark 15 Filtercake. Prior to vitrification, the wastes are blended to provide two large batches of similar compositions. Due to the limited free volume in the tanks, one-step mixing is not possible. The mixing strategy is shown in figure 5-1. It is planned to transfer the entire contents of the 132-m^3 (35,000-gal) tanks (tanks 100-1 to 100-6) to Tank 100-7. The contents of Tank 100-10 will be evenly split between Tanks 100-7 and 100-8. Since Mark 15 drums contain a substantial quantity of uranium, they are added to the Tank 100-7 mixture, which has a deficit in uranium concentration. The Watts Plating solution is added to the Tank 100-8 wastes. The estimated composition of the blended wastes is shown in table 5-1.

The vitrification process flowsheet is shown in figure 5-2. The waste mixed with glass-forming chemicals is transferred to the M-Area plant for vitrification. The waste slurry mixed with glass-forming chemicals is pumped to a single-stage vitrification melter. The slurry enters the melter through water-cooled entrance ports and is deposited on the surface of a molten-glass bath. In the melter, the remaining water is evaporated from the slurry, and nitrate salts are dried into a solid crusty layer (cold-cap) on the surface. The salts under the cold-cap calcine and fuse with the glass-forming chemicals, thereby producing glass melt of the target composition.

5.1.2 Vitrification

The Duramelter® 5000 is a joule-heated electric melter with a glass holding capacity of 1,950-kg (4,280-lb) and a glass pool surface area of 5-m^2 (54-ft^2). The glass pool is powered by three parallel submerged electrodes. The power supply to the electrodes controls the melt temperature at 1,150 °C. The melter has two discharge ports for the molten glass. One pour spout is dedicated to filling 0.27-m^3 (71-gal.) square drums while the second pour spout is coupled to a gem-machine to produce glass gems. Glass



Step 1:

- Tanks 100-1 Thru 100-6 Transferred to 100-7
- 50% Tank 100-10 Transferred to 100-7
- 50% Tank 100-10 Transferred to 100-8

Step 2:

- Tanks 100-7 Transferred to Tanks 100-1/100-2 with Mark 15, Chemicals Added, Transferred to Vitrification
- Tanks 100-8 Transferred to Tanks 100-1/100-2 with Watts Plating, Chemicals Added, Transferred to Vitrification

Figure 5-1. Mixing strategy for the M-Area mixed waste at the Savannah River Site (Bowan and Brandys, 1995)

Table 5-1. Composition of the Savannah River Site M-area blended waste batches (Bowan and Brandys, 1995)

Species	Tank 100-7 Blend Dry Wt (kg)	Tank 100-8 Blend Dry Wt (kg)	Species	Tank 100-7 Blend Dry Wt (kg)	Tank 100-8 Blend Dry Wt (kg)
Al	26,468	39,986	Zr	24	29
Ca	1,404	1,235	Ti	90	109
Fe	2,212	2,030	K	3,881	2,963
Mg	446	473	P	6,185	6,828
Mn	504	1,252	Ba	13	152
Na	44,170	30,859	Pb	454	431
Li	4	7	Mo	18	30
Ni	4,528	3,262	Zn	1,374	2,459
Si	70,470	69,946	Cu	195	66
Cr	20	54	F	198	118
B	99	33	Cl	1,939	515
U	11,596	14,834	SO_4	1,232	1,721
Sr	2	16	NO_3	66,874	64,405

gems are flattened marbles about 1.5 cm in diameter. Each pour spout is activated by an airlift for controlled glass discharge into the canister or gem-making machine. Additional lid heaters are provided in the melter plenum for startup and operations. In addition, the melter is equipped with a patented air-bubbling stirring system. This system accelerates melter production and oxidizes organics and metallic inclusions in the waste stream. The melter is designed to produce a minimum of 5 tons of glass per day and a maximum of 15 tons of glass per day.

5.1.3 Offgas Treatment System

The offgas treatment system maintains the melter at a constant but slightly negative pressure, traps particulate radionuclides, and treats the offgas emissions for release to the atmosphere. The offgas from the melter goes to a water spray quencher followed by two aqueous-based, packed-bed scrubbers connected in series, charged with NaOH and H_2O_2 to provide 90–95 percent removal of NO_x. Following the packed-bed scrubbers, a dry filtration process retains most of the particulates. These filtration units are baghouses and HEPA filters. The final exhaust contains steam, carbon dioxide, and a small fraction (less than 10 percent) of untreated NO_x.

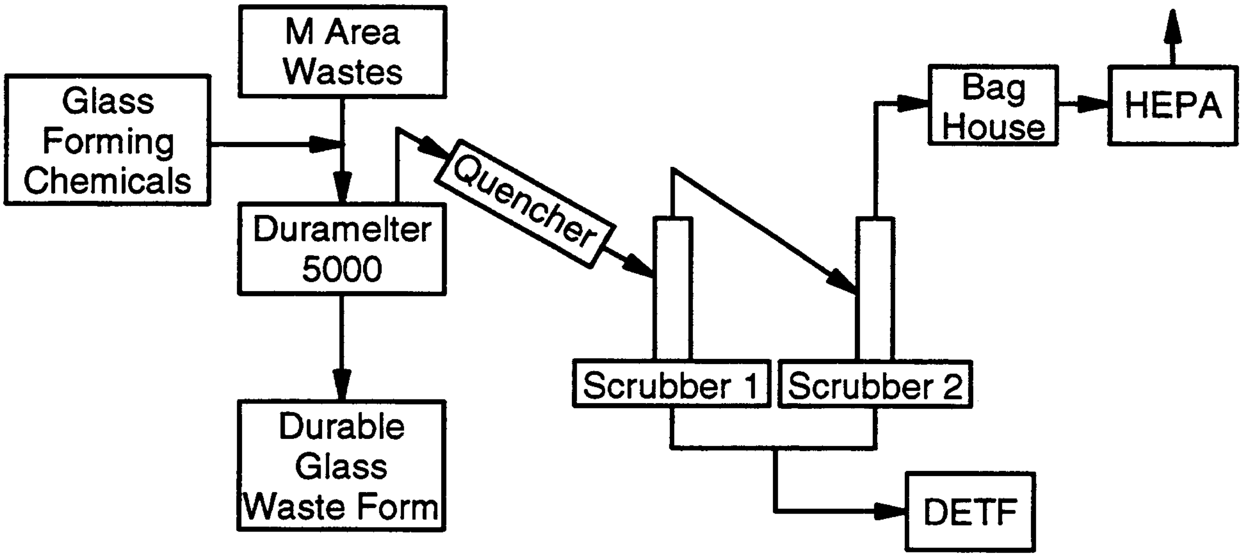


Figure 5-2. The Savannah River Site M-Area mixed waste process flowsheet (Bowan and Brandys, 1995)

5.1.4 Process Issues and Upsets

Since the startup of the plant, there have been numerous problems associated with the performance of the melter and other components. Except for the recent shutdown of the plant to evaluate melter components and the decision to replace the melter, the author is not aware of any published documents that detail these issues.

On March 31, 1997, the waste processing was temporarily suspended after observing possible signs of wear on melter components. Visual inspections indicated that hot spots formed in the melter were a result of refractory corrosion by molten glass, especially near the refractory joints, that were attributed to chemicals used in the melter startup. On April 16, a decision was made by GTS Duratek to replace the existing melter with a new melter. On December 11, 1997, a new melter was installed, and the operations were restarted.

6 HIGH-TEMPERATURE, JOULE-HEATED LOW-LEVEL RADIOACTIVE MIXED WASTE PLANTS

Several high-temperature, joule-heated melters designed to vitrify low-level mixed waste are operational around the world. In this section, discussion will be focused on the Fernald Vitrification Pilot Plant System (VPPS) and the Transportable Vitrification System (TVS). Even though both systems were shut down for major repairs because of glass leaks from the melter, they provide insight into the issues relevant to the safety of the vitrification operations. The TVS melter was redesigned and demonstrated vitrification of low-level radioactive mixed wastes; the VPPS is still shut down.

6.1 FERNALD SILO WASTE VITRIFICATION SYSTEM, FERNALD, OHIO

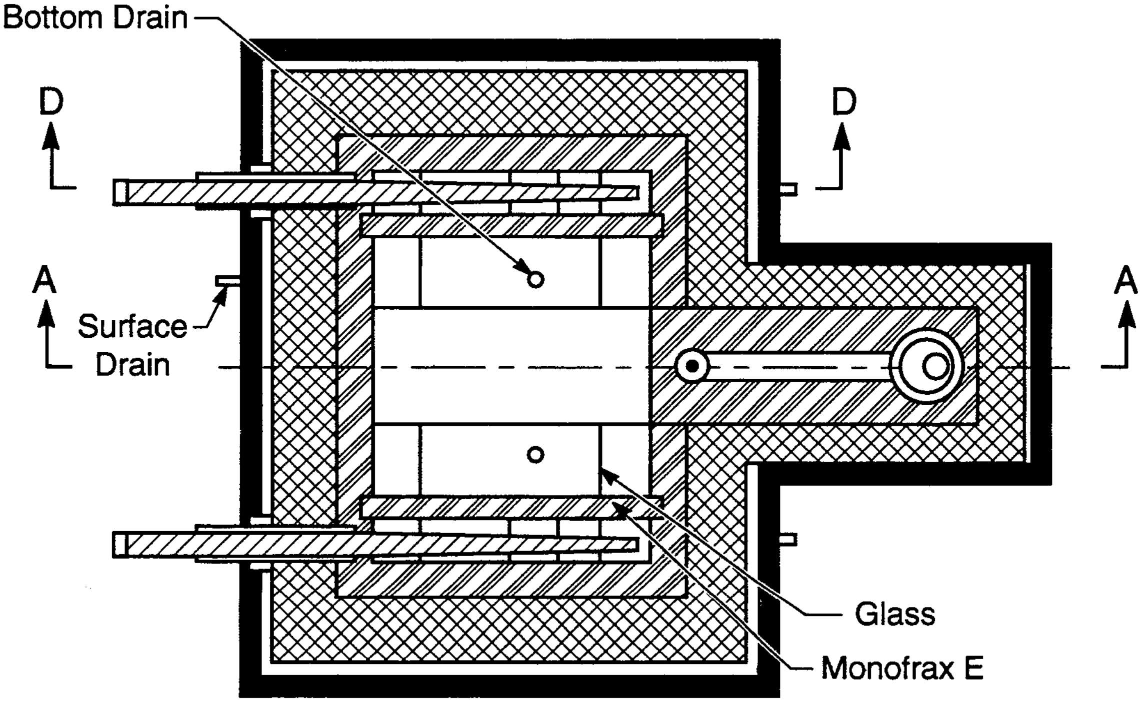
The Fernald Vitrification plant was designed to vitrify K-65 (Silos 1 and 2) and Silo 3 residues stored onsite in Fernald, Ohio. The Fernald vitrification melter, a Duramelter® 1000-HT, was designed, constructed, and delivered by GTS Duratek for vitrification operations. The Duramelter® 1000-HT is a high-temperature melter with a production capacity of 1,000-kg of glass/day (2,200-lb/day).

6.1.1 Waste Pretreatment and Feed Preparation

The three silos in Operable Unit 4 (OU-4) at the Fernald Environmental Restoration Management Project in Fernald, Ohio, contain residues from the processing of pitchblende (mineral-containing uraninite) ores (Merrill and Janke, 1994). Silos 1 and 2, designated jointly as K-65, contain the depleted ore with Bento Grout® cap over the materials. Bento Grout® is a synthetic mineral used to reduce radon emanation. Silo 3 contains calcined residue from processing solutions. The residues from the three silos contain radium, uranium, uranium daughters, and heavy metals (primarily lead).

6.1.2 Vitrification

The Duramelter® 1000-HT melter is unique in its design. The melter is designed to operate at 1,400 °C. Unlike traditional waste glass melters, it has three melting chambers. A top view of the melter is shown in figure 6-1. The two side chambers contain benign borosilicate glass while the central chamber contains waste glass melt. Since the waste glass melt contains almost 10 percent lead oxide, the presence of benign glass in the side chambers was designed to protect the molybdenum electrodes from corrosion and by lead oxide in molten waste glass. The three chambers are separated by high-chrome, high-electrical conductivity refractory Monofrax®-E blocks. The two side chambers contain five molybdenum tapered rod electrodes. The glass contact refractory, as for all waste melters, is high-chrome Monofrax® K-3. The Monofrax® K-3 is backed up by bonded Zirmul® and castable aluminum oxide. The glass containment refractory is housed in an Inconel® alloy 690 inner shell, whereas the entire melter is housed in a stainless steel outer shell. The space between the inner shell and the outer shell is filled with insulating fiberboard. The outer shell of this melter is not water cooled. Other unique features include the presence of several bottom and side penetrations in the melter. There are five bottom penetrations for the bubblers, one for the airlift lance, and three for the bottom drains. These are shown in figures 6-2 and 6-3. The bubbler tubes are placed uniformly through the floor of the melter down the middle of the center chamber. These tubes are made of molydisilicide and are used to provide agitation by blowing air into the center chamber glass melt. Additionally, air would provide an oxidizing environment to promote oxidation of metals in the feed. The airlift lance is also made of molydisilicide and is used to discharge glass down the pour spout and out into the canister. Four bottom drains are provided to empty the melter. There are two drains for the center



TOP VIEW (SECTION C-C)

Figure 6-1. Top view of the Durameltert® 1000-HT melter at the Fernald site (FERMCO, 1997)

chamber and one each for the side chambers. The bottom penetrations are provided to reduce corrosion of the tubes from sulfur and halide emissions at temperatures greater than 1,150 °C when exposed from the top of the melter. The melter heatup was started on May 16, 1996, and was shut down on December 26 when 6,000-kg (13,200-lb) glass drained out of the melter in 15 min from one of the corroded air bubbler tubes.

6.1.3 Offgas Treatment System

No information is available.

6.1.4 Process Issues and Upsets

The information provided in this section has been extracted from a single report (FERMCO, 1997). The process issues related to feed preparation and offgas system operations are not published anywhere. The melter incidents leading to its failure are presented in detail in the following. Other minor incidents included coolant leaks in bottom drains and electrical shorts to ground.

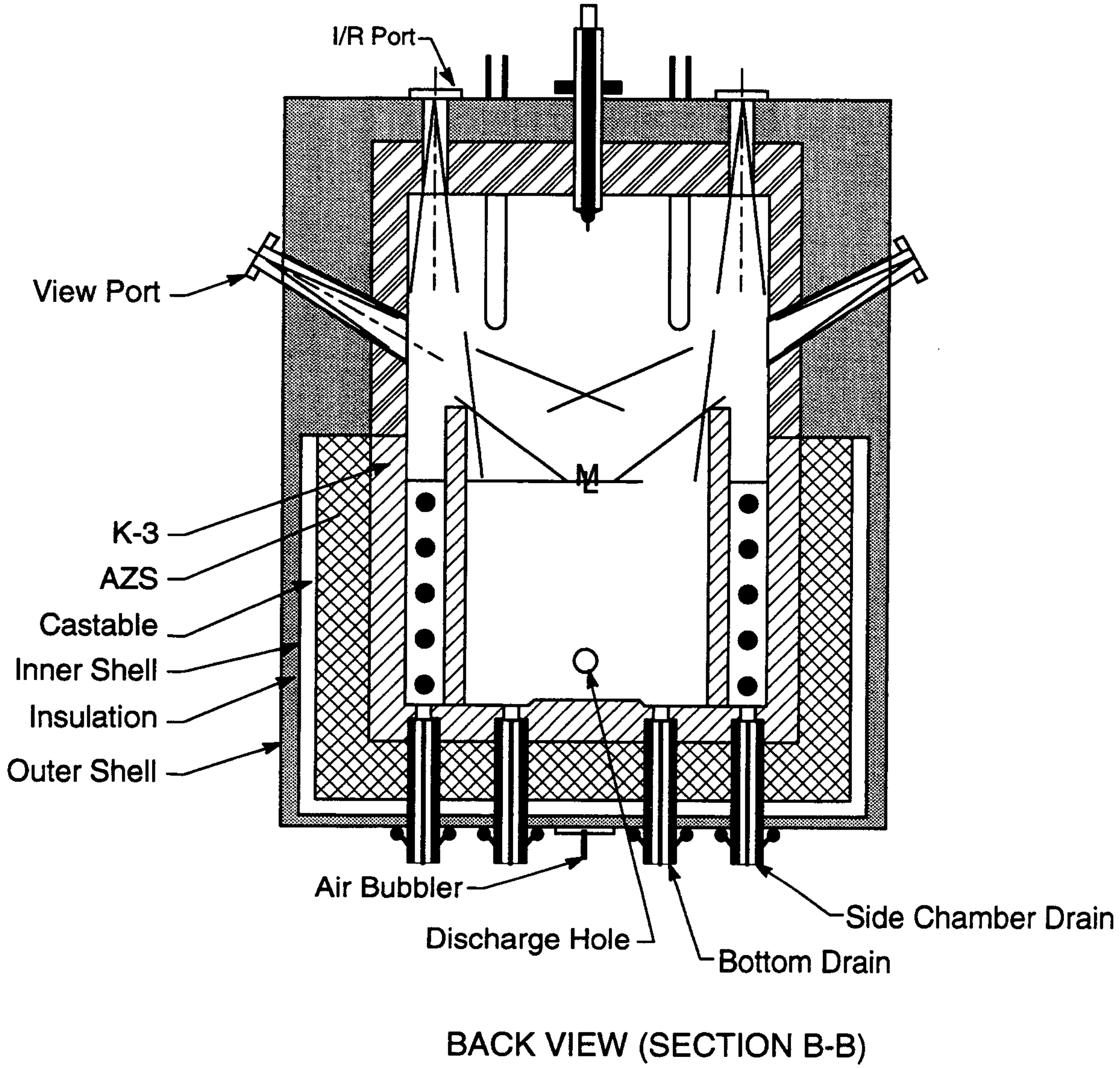


Figure 6-2. Back view of the Duramelter® 1000-HT melter showing bottom drain tubes (FERMCO, 1997)

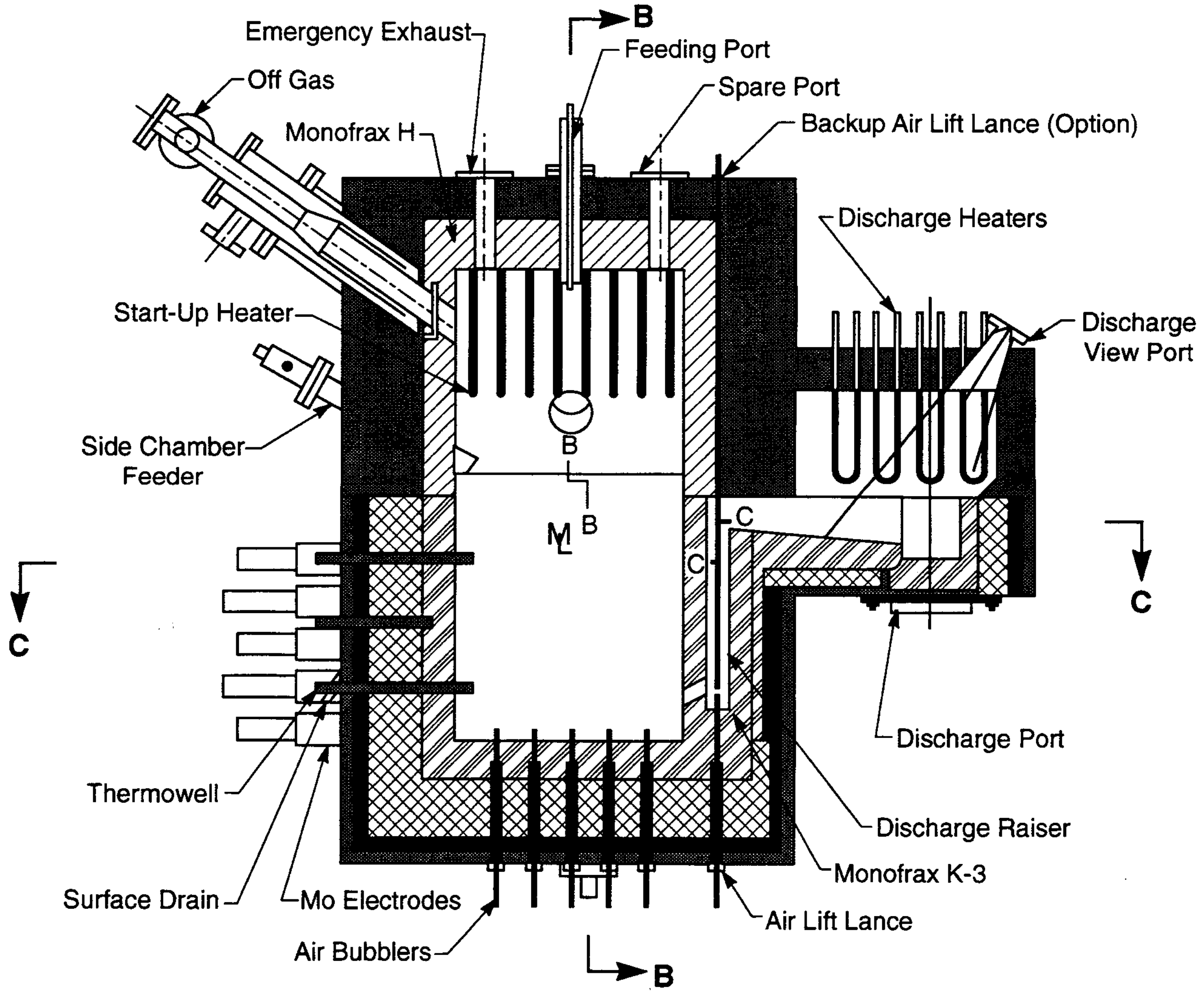


Figure 6-3. Side view of Duramelter® 1000-HT melter showing bottom bubblers (FERMCO, 1997)

6.1.4.1 Separation Wall Between the Chambers

The separation wall between the chambers was designed to avoid any mixing between the waste glass and the inert glass. Soon after the melter was heated up, cracks were observed in the separation walls. These cracks allowed migration of glass from one chamber to the other. The refractory was also used as a secondary electrode that allowed current to flow from molybdenum electrodes to the center chamber. However, the presence of electrical currents in the separation wall and inhomogeneous distribution of crystalline phase resulted in the formation of hot spots on the wall. These hot spots, when combined with the poor thermal shock resistance of the Monofrax® E refractory, caused the wall to crack, which allowed easy migration of lead into the side chambers.

6.1.4.2 Auto Discharging of Glass from the Melter

Auto discharging was a frequent event. On July 12, 1996, a large chunk of glass was removed from the discharge section. Investigations indicated that the discharge orifice brick had a large crack. During campaign 1, a torch was used to melt the glass from the discharge chamber. A cooling jacket was placed around the pour spout to solidify the glass and stop the migration into the discharge section. The failure of the brick could be due to thermal stresses in the melter generated during heatup.

6.1.4.3 Corrosion of $MoSi_2$ Components

The $MoSi_2$ tubes were used to determine the glass level in the side chambers. Inspection of the level probes during campaign 1 indicated corrosion of the tips. Corrosion of the $MoSi_2$ bubbler tubes was a major contributing factor to the failure of the melter. The $MoSi_2$ tubes in the presence of PbO in the waste glass caused formation of lead metal in the melter. As $MoSi_2$ tubes corroded in the presence of PbO in the melt, low-corrosion-resistant bonded Zirmul® bricks were exposed to the lead attack. Metal drilling of bonded Zirmul® bricks by metallic lead resulted in dissolution of more than 50 percent of the Zirmul® brick layer under the glass contact refractory Monofrax® K-3. The post-incident evaluation of the melter indicated that the K-3 bricks were still in good condition, while the Zirmul® brick layer was completely destroyed. Corrosion was further enhanced by abrasion, oxidation, and molten glass circulation via compressed air from the bubblers. The lead formation, in addition to corroding the $MoSi_2$, led to the formation of hot spots that disrupted electrical current paths and short circuited normal current paths in the melt. This accelerated Zirmul® dissolution and corrosion. Finally, the integrity of the melter was breached causing glass to flow out from the melt cavity.

6.1.4.4 Foaming Events in the Melter

Foaming was frequently observed in the melter. Foaming is the generation of stable gas bubbles in the glass that forms a stable froth on the surface. This froth is usually very insulating and disrupts the temperature profile in the glass. The disruption of the temperature profiles results in erratic power supply to the melter. Another event similar to foaming is the formation of an immiscible sulfate layer on the melt surface. In the Fernald melter, urea was used as a reducing agent to control redox and enhance destruction of sulfates in the melt. While reducing the melt, foaming excursions are minimized, but uncontrolled addition of urea could result in reduction of transition metal oxides to their metallic states. In one instance, the sulfate foam boiled over into the side chambers. No redox control strategy was implemented in Fernald. These incidents can be attributed to the lack of understanding of control of foaming, urea reactions, redox conditions, and sulfate chemistry.

6.2 TRANSPORTABLE VITRIFICATION SYSTEM

The TVS is designed to treat low-level radioactive and mixed wastes. The unit is a transportable large-scale, fully integrated vitrification system. The equipment is housed in modules that can be disassembled and sealed for shipment on standard trailers. Major modules include feed preparation, melter, offgas, process control and services, and a process laboratory. Each of these modules is discussed in the following (Jantzen et al., 1995). TVS started its operations at the Oak Ridge National Laboratory (ORNL). A glass leak was observed in the TVS melter in November 1996 and the melter was shutdown. The leak was attributed to the movement of the refractories during repeated heatup and cool-down cycles. Figure 6-4 shows the equipment layout for the TVS. The design of the TVS melter was modified and it was rebuilt and on October 17, 1997, the demonstration of the TVS with mixed waste was completed. A total of 7,330-kg (16,159-lb) of sludge was processed producing 7,866-kg (17,338-lb) of glass. The system is currently shut down due to a lack of funding.

6.2.1 Feed Preparation Module

The waste is introduced in the feed module where it is characterized and blended with the glass-forming chemicals. Pumps are used to feed the waste plus glass-former slurry to the melter. Both dry or liquid waste could be used in the module to make the slurry.

6.2.2 Vitrification Module

As the slurry falls on the glass-melt surface, water evaporates leaving behind a crusty layer of salts (cold-cap) on the surface of the glass melt. The cold-cap formation reduces the volatilization. The solids between the crusty layer and the glass-melt surface are calcined to their oxides and incorporated into the glass melt.

The melter module consists of a joule-heated melter and auxiliary equipment. The melter, which was manufactured by Envitco, Inc., Toledo, Ohio, is capable of operating between 1,100 and 1,400 °C. Since the melter operates at temperatures greater than 1,150 °C, molybdenum electrodes are used for glass melting. Anticipated glass production rates for this melter are between 50-kg/hr (110-lb/hr) and 150-kg/hr (330-lb/hr). The melter has three chambers, a center chamber and two side chambers. The center chamber is a melting chamber where waste and glass formers are vitrified; one side discharge chamber is used to pour glass into 610-mm stainless steel cubes, and the other side chamber is used to remove molten salts such as chlorides and sulfates from the molten-glass surface. Separate heaters are provided in side chambers to keep the glass molten while pouring or removing salts from the surface. A gas burner is placed at the top to start the melter system from cold conditions.

6.2.3 Offgas Treatment System

The offgas from the melter is sent through a refractory-lined pipe with an inside diameter of 200-mm (7.8-in.). Offgas is drawn from all three melter chambers, and the entire melter is maintained at a pressure of 0.25- to 1.25-kPa (18-psi) below atmospheric pressure. The blowers maintain a proper flow through the pipes. The other components of the offgas module are the quencher, packed bed cooler, variable throat venturi, mist eliminator, reheater, HEPA filter, and stack.

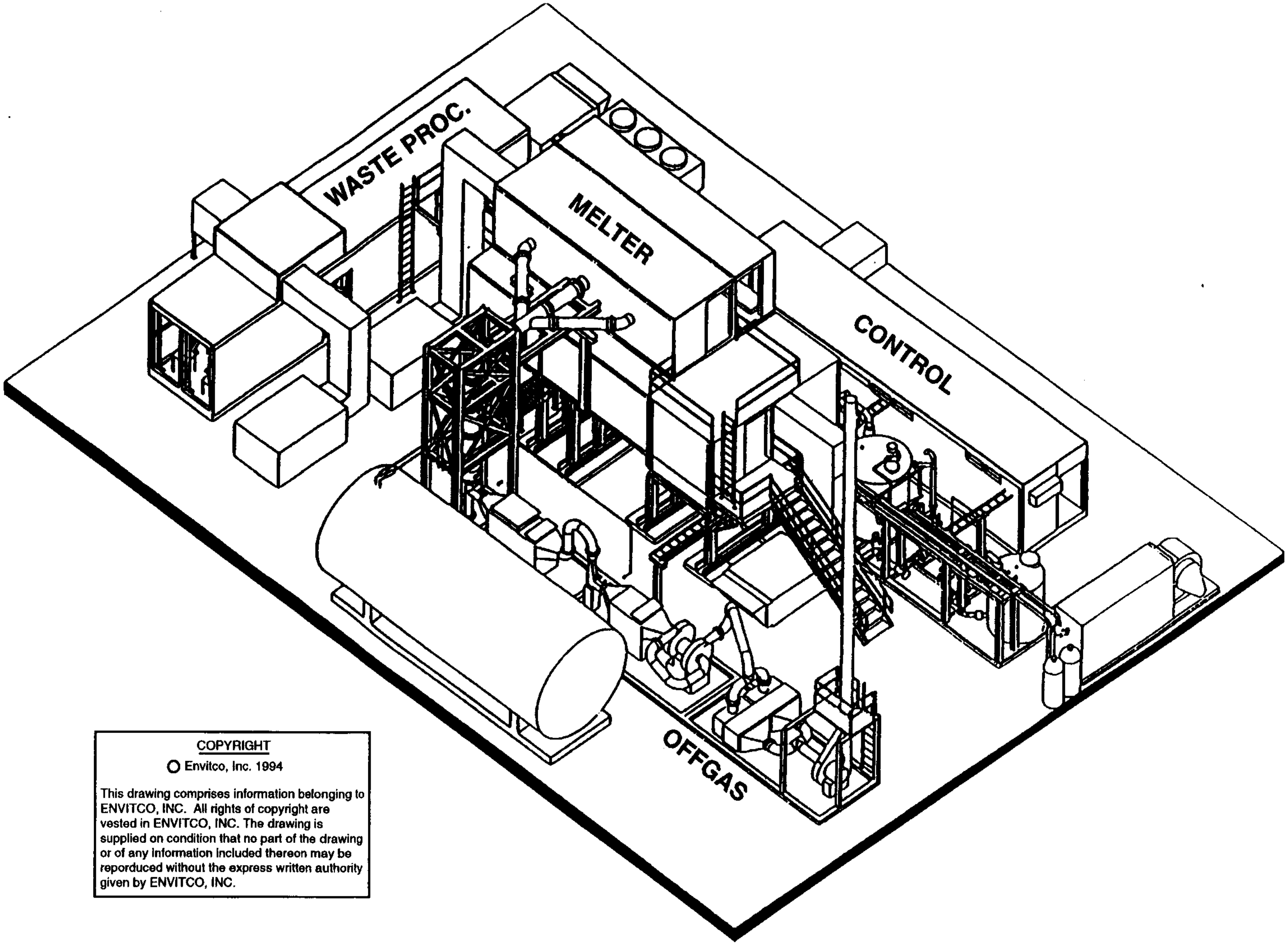


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Figure 6-4. Layout of the Transportable Vitrification System (U.S. Patent #5,611,766) (Jantzen et al., 1995)

The quencher cools the offgas and removes some coarse particles. The packed bed cooler further cools the gas and removes some moisture. The variable throat venturi removes most of the particulates. Downstream of the venturi is a mist eliminator to remove most of the moisture from the venturi. Offgas is then sent to a reheater to ensure that the temperature of the offgas is above the dewpoint before it enters a HEPA filter. The offgas exiting from the HEPA filter goes to the stack.

6.2.4 Process Issues and Upsets

During the shutdown of the TVS at the Oak Ridge K-25 site on November 5, 1996, the melter was flushed by adding bottle glass composition. During this addition, approximately one ton of glass leaked from the melter at a vertical joint between ceramic refractory blocks and flowed between the steel floor and subfloor of the melter module, burning cooling hoses, power cables, and instrument wiring routed between the floor and subfloor (Lockheed Martin Energy Systems, 1996). Visual observations during disassembly of the melter verified that the leak was caused by failure to maintain adequate compression of joints between refractory blocks in the melter chamber, which allowed vertical joints between refractory blocks to open on cooling. This may have occurred progressively over the four heat-up and cool-down cycles that the melter had experienced during its operating life. Once the glass entered and froze in the refractory joints, it would be extremely difficult to close it when heating, due to thermal expansion or external compression. In order to mitigate the risk of future glass losses, jack bolts were added to maintain refractory compression during cooling, and coolers were installed along the vertical joints to solidify any glass that may penetrate through the melting chamber.

7 HANFORD LOW-LEVEL WASTE VITRIFICATION TEST PROGRAM (TRI-PARTY AGREEMENT) EXPERIENCE

The 1994 revision of the Tri-party Agreement (Wilson, 1996a) between the DOE, the U.S. Environmental Protection Agency (EPA), and the Washington State Department of Ecology, specified vitrification as the treatment method for LLW streams derived from retrieval and pretreatment of single-shell tank (SST) and double-shell tank wastes at Hanford. The main objective of Phase 1 of the program was to test and evaluate promising commercial vitrification technologies to support selection of reference technologies for the Hanford site LLW vitrification. The technical objectives included evaluation of feed preparation systems, melter operations, melter offgas characterization, and treatment of secondary process streams. Volatilization and entrainment of feed components were important features of the offgas characterization objective.

Based on the Request for Proposal submitted by the Westinghouse Hanford Company (WHC), seven vendors were selected for demonstration of their vitrification technologies. Table 7-1 shows a list of vendors that were selected and technologies that were evaluated. Note that the high-temperature, joule-heated melter means melters that are capable of operating at temperatures above 1,300 °C. Melters that run on Inconel® alloy 690 electrodes at 1,150 °C or less are referred to as low-temperature joule-heated melters.

WHC supplied pre-formulated, non-radioactive LLW simulant. The simulant composition and its characterization data are provided by Wilson (1996a). Each vendor was allowed to select their own feed preparation and offgas treatment systems. Vendors also had a choice of either using one of the five glass

Table 7-1. Technologies for Phase 1 testing of Hanford low-level waste (Wilson, 1996a)

Vendor	Technology
Envitco, Inc., Toledo, Ohio	Wetted, pelletized feed, high-temperature, joule-heated melter, molybdenum electrodes
Vectra Technologies, Inc., Richland, Washington	Slurry-fed, high-temperature, joule-heated melter, molybdenum electrodes
Penberthy Electromelt International, Inc., Seattle, Washington	Moist granular feed, high-temperature, joule-heated melter, molybdenum electrodes
GTS Duratek, Inc., Columbia, Maryland	Slurry-fed, low-temperature, joule-heated melter, Inconel® alloy 690 electrodes
U. S. Bureau of Mines, Albany Research Center, Oregon	Pre-reacted dry feed, carbon electrode melter, radiant heat by arcing or joule-heating
Westinghouse Science and Technology, Pittsburgh, Pennsylvania	Slurry-fed, plasma-torch-fired cupola furnace
Babcock and Wilcox, Alliance Research Center, Alliance, Ohio	Slurry-fed, gas-fired, cyclone combustion melter

compositions proposed by WHC or using their own glass composition. There were two requirements placed on the glass composition (Wilson, 1996a): (i) the waste loading should be 25 percent, and (ii) the normalized Na release rate measured by PCT shall be less than 1 $g/m^2/day$.

The following sections describe each melter technology with some discussion on feed preparation and offgas systems. Each process description is followed by testing results, technical issues, and technology strengths. The performance of all seven technologies was assessed by an Evaluation Board consisting of experts from the nuclear waste industry and the commercial glass industry. Their recommendations are presented as a summary. The information presented in the following sections has been extracted from Wilson (1996a,b) and Whyatt et al. (1996).

7.1 ENVITCO, INC.

Envitco is affiliated with the Toledo Engineering Company (TECO). TECO provides high-temperature, cold-top, commercial melting systems to the commercial glass industry. Envitco used the Clemson University Center for Vitrification Research (Marra et al., 1996a) for melter demonstration testing.

7.1.1 Vitrification Process

The Envitco EV-16 is a high-temperature, joule-heated melter that uses four molybdenum side-electrodes. A simplified melter schematic is shown in figure 7-1. This melter has a square cross section with a melt surface area of 0.21-m^2 (22.6-ft^2) and a working depth of 0.4-m (1.3-ft). The melter is heated by four horizontal electrodes that enter through the center of each sidewall. The glass production capacity is 500 to 1,000-kg/day (1,100 to 2,200-lb/day). The melter is lined with a thin layer of refractory and depends largely on a water-cooled jacket around the melter shell to form a protective layer of solid glass at the refractory-glass interface to reduce refractory corrosion. The melter also has a proprietary mechanically controlled drain assembly for glass pouring. This drain assembly penetrates through the center of the melter bottom. A batch hopper with a screw charger on the side of the top of the melter uniformly delivers dry batch materials on the surface of the glass melt pool.

Envitco selected both dry and liquid slurry feed materials for demonstration purposes and used the glass formulation specified by WHC. The simulant supplied by WHC was mixed with glass forming chemicals to attain the specified glass composition. A finely powdered activated carbon was added as a reductant additive to the slurry to break down nitrate and nitrites. Preparation of dry feeds required spray drying followed by compaction.

The offgas exiting the melter passes through a film cooler and a quench chamber, where its temperature is reduced and heavy particulates are removed and sent back to the main tank for recycling. The saturated offgas then goes to a SAS where gases and scrub solutions are aggressively mixed. The scrub solution and contaminants are then removed through a cyclone separator and flushed back to the main tank for recycling. Finally, offgas passes through a packed column where residual soluble acidic gases are removed prior to demisting and exhausting.

7.1.2 Test Results

The melter operations proceeded smoothly, with the exception of a melt reboil (foaming) at the end of the dry feed run and a cooling system interlock trip during the slurry run. The glass production rates with

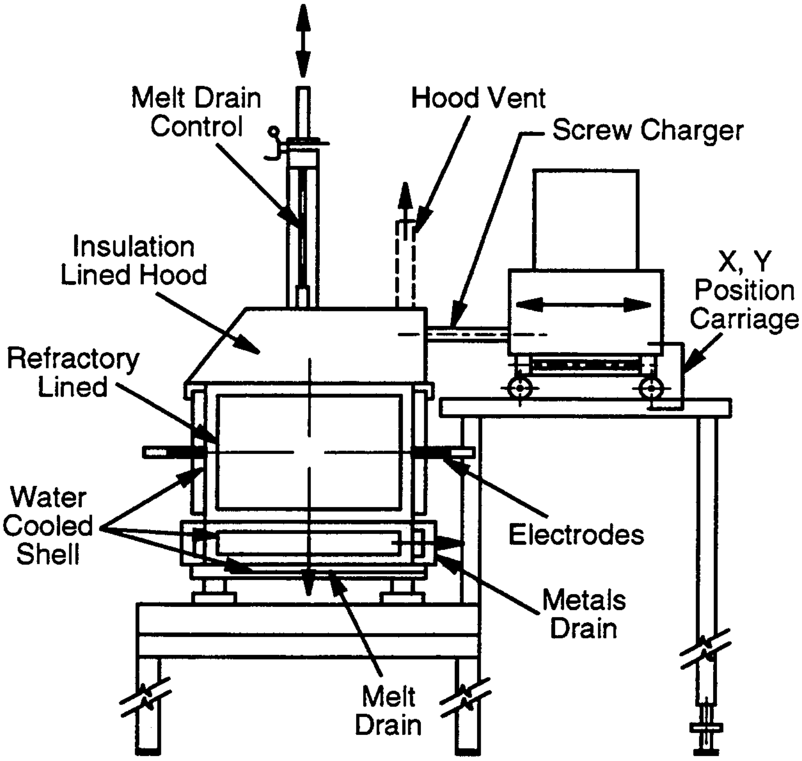

Figure 7-1. Envitco cold-cap, EV-16 melter for Hanford low-level waste (Wilson, 1996a)

slurry were essentially identical to the spray dried feed. The observed melt rates ranged from 14-kg/hr (30.8-lb/hr) at 1,350 °C to 26.4-kg/hr (58.1-lb/hr) at 1,520 °C. Offgas measurements indicated low volatility and limited feed entrainment losses.

Before the start of the demonstration testing, the melter was re-bricked and new electrodes were placed. After testing, refractory blocks and electrodes were visually examined and sectioned to determine the amount of dissolution. Examination indicated cracks on the refractory walls with little refractory loss. The electrodes showed larger diameter endcaps that were beveled on the end that faced the center of the melter. There was some minor pitting on the endcaps.

7.1.3 Technical Issues

Foaming is an issue with all melting systems that contain large pools of molten glass with transition metal oxides such as Mn, Fe, and Ni, and variable feed chemistry (e.g., reductants such as sugar and activated carbon, and oxidizers such as nitrates and nitrites). The Envitco process control strategy needs further testing and evaluation. A proper understanding of the underlying reactions, use of reductant, and its control methodology could minimize foaming in the melt.

When the melter is overfed such that the entire melt pool is covered with cold-cap, the cold-cap could bridge with melter walls and form an impermeable layer. This impermeable layer, in turn, could trap feed reaction product gases and pressurize the glass melt under the cold-cap. This could either result in sudden release of reaction gases when the pressure inside exceeds the cold-cap strength or it may automatically syphon the glass into the container if the cold-cap is not breached. In both cases, it will upset the process. Bridging could be easily avoided by proper feed rates and monitoring of the melt surface.

Molybdenum electrodes are easily corroded with LLW feeds containing corrosive salts such as halides, sulfates, phosphates, or metals such as Pb, Sn, Cu, and Ni. The demonstration testing was not long enough to determine the long-term performance of the electrodes and needs to be verified before the electrodes could be installed for LLW vitrification.

Melter drains require periodic maintenance or replacement. Due to the limited duration (2 wk) of the test, the long-term performance of the bottom drain and its ability to remove metals and conductive sludges from the floor are yet to be demonstrated. Alternate designs should be explored.

7.2 VECTRA TECHNOLOGIES, INC.

Vectra is a diversified provider of services to commercial nuclear utilities and the federal government. Their services include design and operation of nuclear waste management processes, equipment, transportation casks, and processing systems. Vectra demonstrated the performance of its Ve-Skull melter system.

7.2.1 Vitrification Process

The Vectra Ve-Skull is a joule-heated melter with nearly vertical molybdenum electrodes. The melter is a double-shelled cylindrical pressure vessel with cooling-water circulation between the inner and outer shell. The inner shell is 1-m (3-ft) in diameter and has a thin refractory lining. The melter depends largely on a water-cooled jacket between the inner and outer shell to form a protective layer of a frozen glass skull at the refractory-glass interface to reduce refractory corrosion. The effective melt surface area is 0.57-m^2 (9-ft^2). The melter has three molybdenum electrodes that enter from the top of the melter and a single port for feeding and venting offgas. For slurry feeding, the feed tube extends down through the offgas port discharging near the center of the melt pool above the glass level. For dry feeding, an auger is used to transfer powdered feed from a hopper. The melter has a single drain port located at the center of the bottom for glass pouring. The drain ring is a thick metal disc that is heated by passing electric current through it to initiate glass pour. The glass flow is stopped by inserting a water-cooled plug into the drain hole.

The Vectra process flow sheet is shown in figure 7-2. Vectra selected two types of dry feeds and one liquid slurry for the demonstration. The simulant supplied by WHC was mixed with dry glass-forming chemicals to attain the specified glass composition. Powdered sugar was added as a reductant additive to the simulant to reduce nitrate and nitrites. Smaller batches of the slurry mix were transferred using a pump to an agitated day-tank located near the top of the melter. Feed was drawn from the tank through a peristaltic pump and delivered to the melter.

The offgas exiting the stack is sent to a spray scrubber where offgas and scrub solutions (sodium hydroxide and water) are rapidly mixed to remove soluble acidic gases.

7.2.2 Test Results

The melter system functioned well during testing when it was operated with direct slurry feeding and dry feeding. The Vectra test melter ran for 32 days producing 10,000-kg (22,000-lb) of glass.

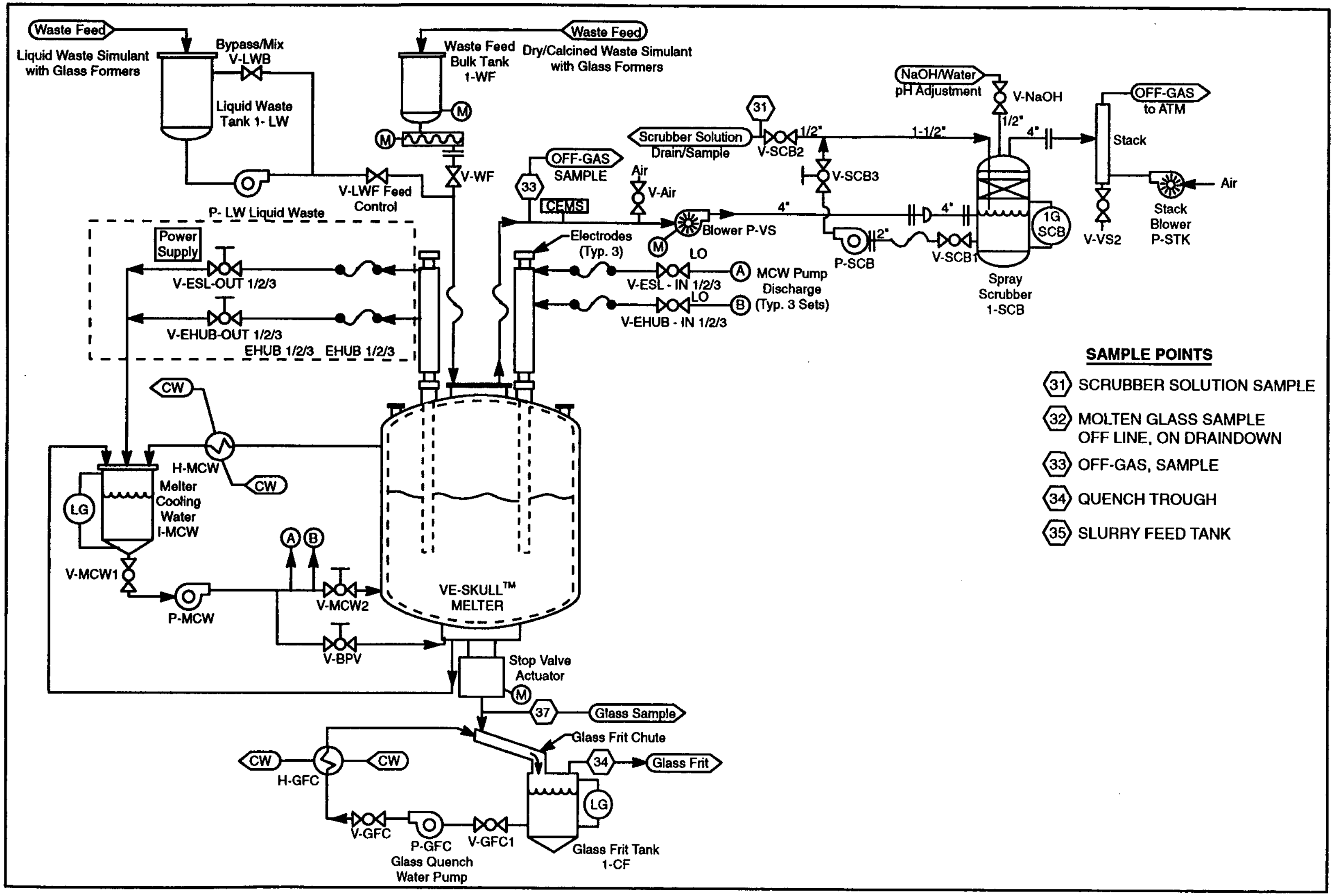

Figure 7-2. Vectra vitrification process flowsheet for Hanford low-level waste (Wilson, 1996a)

Approximately 500-kg (1,100-lb) of calcined feed was prepared and melted. Attempts to make pre-reacted dry-pressed feed were unsuccessful. The glass production rates achieved with slurry feed were greater than or equivalent to glass production rates estimated for calcined or dry feeds. The melt rate was estimated at about 34-kg/hr (74.8-lb/hr).

During the demonstration testing, severe corrosion of the electrodes was experienced. Electrode material was corroded at the melt-electrode-air interface to a point where ends of the two electrodes broke off. The ends of the electrodes that were submerged in the glass pool were not as severely corroded. The water-cooled protective jackets designed to prevent exposure of the electrodes to the atmosphere were also corroded. Excessive corrosion is attributed to the fact that, during testing, the glass level was allowed to drop below the protective sleeves, thus exposing the molybdenum electrodes to air. Molybdenum oxidizes (burns) very rapidly in air at high temperatures.

Before the start of the test program, the melter was re-bricked and new electrodes were placed. After the test program was over, refractory blocks and electrodes were visually examined and sectioned to determine the amount of dissolution. Examination indicated a significant loss of refractory mortar used between the bricks.

7.2.3 Technical Issues

Foaming and cold-cap bridging are common issues for all melters and have already been discussed in section 7.1.3. The bottom drain is an important aspect of the Vectra Ve-Skull melter. Even though it allowed draining of non-vitrified sludges and metal precipitates during normal glass pouring, the use of bottom drains is considered a high risk. Due to of the lack of experience in long-term continuous use of bottom drains and a history of problems with bottom drains in the commercial glass industry, reliable performance of the bottom drain design need to be verified before being installed for LLW vitrification.

The use of vertical electrodes with a bottom drain melter design raises special issues in regard to electrode performance. As discussed, severe corrosion of electrodes was experienced during testing. Other electrode materials or a better electrode configuration needs to be evaluated before the melter should be used for LLW vitrification.

The melter is lined with a thin layer [10-cm (4-in.) thick] of refractory and depends largely on a water-cooled jacket between the inner and outer shell to form a protective layer of a frozen glass skull at the refractory-glass interface to reduce refractory corrosion. The long-term performance of the refractory and skull layer for the Vectra Ve-Skull melter is not known.

7.3 PENBERTHY ELECTROMELT INTERNATIONAL, INC.

Penberthy Electromelt International, Inc. (PEI) is a small company with expertise in designing electrical joule-heating melters for waste vitrification. PEI used a high-temperature joule-heated melter with molybdenum electrodes for demonstration testing.

7.3.1 Vitrification Process

The PEI melter is a high-temperature, joule-heated melter that uses molybdenum sidewall rod electrodes. The melter has thick ceramic refractories [20-cm (8-in.) thick] and does not rely on the formation of protective frozen skull layer to reduce refractory corrosion. The melter has a melt area of 0.5 m^2 (5.4 ft^2) and a glass depth of 0.5 m (1.5 ft). Two molybdenum rod electrodes extend more than halfway across the melter interior. It has three electrically heated drains in the lower side wall for glass discharge.

Figure 7-3 shows the process flow schematic for the PEI vitrification process. The feed system mixes the liquid LLW with absorbent glass former additives in screw chargers. This system is called mix-in-the-charger. The reductant, sugar, is split equally between LLW and glass formers before they are mixed together. The screw chargers deliver moist granular feed directly to the melter. Even though, in this feed system, the composition of the final feed cannot be confirmed before sending it to the melter, it requires minimal radioactive material processing equipment. A cold-cap is maintained over the glass melt and provides low volatility and minor feed entrainment losses.

The offgas exiting the melter passes through an offgas filter alcove filled with ceramic fibers. When the filter becomes loaded with particulates, it is pushed into the melter where it melts away with the LLW. The offgas is quenched and scrubbed before it is demisted and exhausted.

7.3.2 Test Results

Melter drain failures caused termination of the testing before all the testing objectives were met.

7.3.3 Technical Issues

Two feed streams, LLW and dry glass former mix, are independently metered to control the glass composition. In this system, feed composition before it enters the melter cannot be confirmed. An accurate characterization of the LLW and accurate metering of the LLW and glass former mix are critical to this type of system.

Foaming and cold-cap bridging, as discussed in section 7.1.3 for the Envitco melter, is a potential concern.

As in the Envitco and Vectra melters, remote maintenance and replacement of the molybdenum electrodes is a potential concern. Extended testing is needed to ensure long-term electrode performance.

Drains, as indicated in both the Envitco and Vectra melters, are an important part of the melter. The failure of three lower sidewall drains, followed by a loss of control on the bottom drain, was the immediate cause of termination of the demonstration testing for the PEI melter. Reliable performance of the bottom drain design needs to be verified before the melter should be installed for LLW vitrification.

7.4 GTS DURATEK, INC.

Duratek provides vitrification technology to treat radioactive and hazardous waste materials. For the demonstration testing, Duratek used two low-temperature, joule-heated melter systems.

7.4.1 Vitrification Process

The Duratek melter is a low-temperature, joule-heated melter system with Inconel® alloy 690 plate electrodes. The melter has a thick-walled refractory and does not depend on melter shell cooling to form a

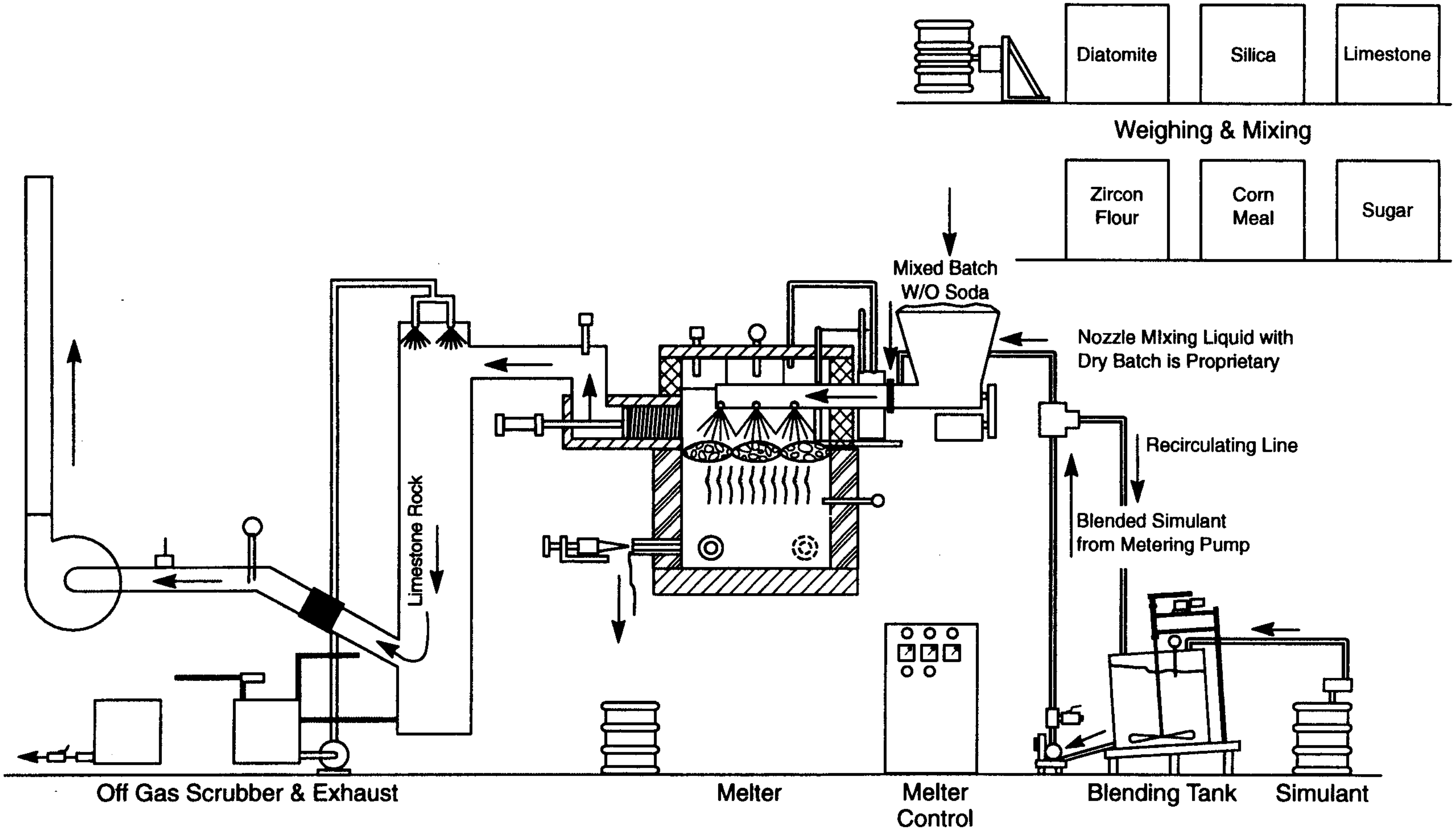

Figure 7-3. Penberthy Electromelt International, Inc. vitrification process flowsheet for Hanford low-level waste (Wilson, 1996a)

skull layer at the melt-refractory interface. The melter uses bubblers to increase mixing within the melt. In addition, the glass melt exits via an airlift assisted overflow drain. Duratek used two melters, the Duramelter® 100 and the Duramelter® 1000, for testing. The Duramelter® 100 is rated for 100-kg/day (220-lb/day) and the Duramelter® 1000 is rated for 1,000-kg/day (2,200-lb/day) of glass production.

A schematic diagram of this vitrification system is shown in figure 7-4. The feed system for the Duramelter ® 100 consisted of two 208-L (55-gal.) drums equipped with agitators. The first drum is a mixing tank with a recirculating/transfer pump and the other is a feed tank with a peristaltic pump and a single water-cooled feed nozzle in the center of the top of the melter. Feed is prepared by transferring a required amount of LLW simulant to the mixing tank and a preweighed batch of glass former additives. Additives are added via a hopper into the mixing drum. After the feed is mixed, it is transferred to the feed tank. Urea is added as a reductant to the feed to reduce NO_x production in the melter.

The glass is poured from the melter through a copper or a graphite tube extending through a water cooled melter shell just below the desired glass level.

The feed system for the Duramelter® 1000 is functionally the same as the Duramelter® 100 feed system. The Duramelter® 1000 used two 0.9-m^3 (238-gal.) tanks. In addition, the Duramelter® 1000 has two feed nozzles to feed the slurry on both sides of the bubblers.

7.4.2 Test Results

The testing for both melters, the Duramelter® 100 and the Duramelter® 1000, went smoothly and was uneventful, with both melters exceeding the rated 100-kg/day (220-lb/day) and 1000-kg/day (2,200-lb/day) production rate. The Duramelter® 100 test melted 600-kg (1,320-lb) of glass with an average processing rate of 7.7-kg/hr (17-lb/hr). The Duramelter® 1000 test melted 10,700 kg (23,100-lb) of glass with an average processing rate of 75-kg/hr (165-lb/hr). Results from the small melter indicated a significant reduction in NO_x after the addition of urea. In addition, urea improved rheological properties of the feed.

The feed entrainment losses were not greater than 0.6 percent. The volatility of components was greater than for a true cold-top melter in which 100 percent of the melt surface is blanketed but was less than that of hot-top or exposed-surface melters.

7.4.3 Technical Issues

There were no significant technical issues that need to be addressed. Foaming and cold-cap bridging, as with every melter discussed in section 7.1.3, is a potential concern.

The technology is similar to HLW technology adopted at WVDP and DWPF. The impact of bubblers on the erosion of the melter refractory lining has to be evaluated for long-term performance. In addition, bubbling gives rise to more severe feed plugging in the offgas line and should be evaluated. The testing of the M-Area melter at SRS should provide more data to support these issues (see section 5).

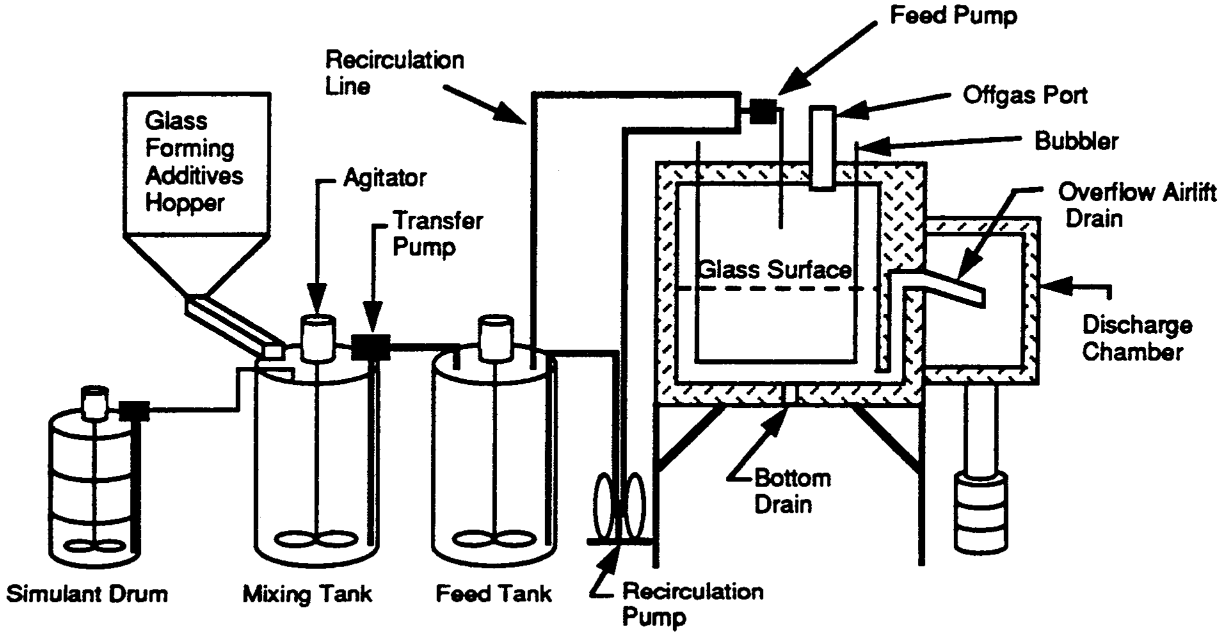

Figure 7-4. Duratek diagram of the vitrification system for Hanford low-level waste (Wilson, 1996a)

7.5 U.S. BUREAU OF MINES, ALBANY RESEARCH CENTER

The U.S. Bureau of Mines (USBM) demonstrated a carbon electrode melter at the USBM Albany Research Center in Oregon. The center is supported by several contributors including Idaho National Engineering Laboratory (INEEL).

7.5.1 Vitrification Process

USBM technology is based on a 3-phase electric arc furnace. This technology is widely used in the metals industry and is referred to by several names such as electric arc furnace, electric arc melter, carbon arc furnace, and carbon electrode melter. A schematic diagram of the feed preparation and melter is shown in figure 7-5.

The melter uses top-entering vertical carbon electrodes of 10.16-cm (4-in.) diameter. The electrodes are arranged in an equilateral triangle with about a 28.5-cm (17.2-in.) separation between the electrode centers. The depth of the electrodes can be adjusted during melter operations. The heat could either be supplied as radiant heat by arcing above the melt surface or as joule-heat with the electrode submerged in glass melt. The melter consists of a steel shell lined with a thin layer of alumina refractory. Water cascades

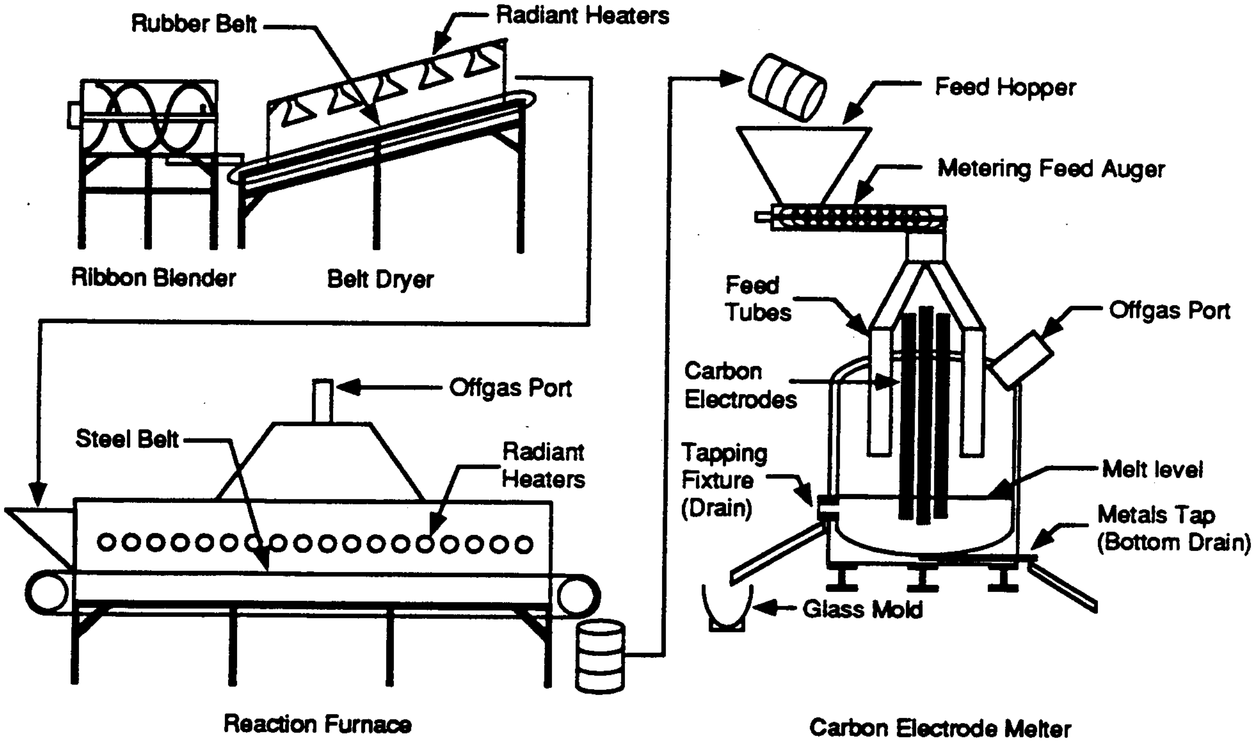

Figure 7-5. Feed preparation and melter schematic for carbon electrode melter system (Wilson, 1996a)

down over the outer shell of the melter, cooling the refractory and forming a protective frozen skull layer at the refractory-glass interface to reduce refractory corrosion. The bottom of the melter is lined with a thicker refractory layer and is cooled only by ambient air. The melter operates using dry materials to avoid reaction between water and the carbon electrodes. The melt surface has a circular cross-section with about 1.12 m^2 (12 ft^2) surface area.

The USBM developed two dry feed preparation processes in which nitrite and nitrate were mostly reduced by reaction with sugar and activated powdered carbon during feed drying. Type A feed is prepared by pelletizing high-surface-area glass-forming chemicals and combining with liquid waste which is absorbed in the pellets. The Type B feed is prepared by mixing the glass-forming chemicals with the LLW before pelletizing. In both cases, the feed is dried and reductant additives reacted with NO^-_3/NO^-_2 before being fed to the melter. The feed tubes enter from the top of the melter and are within 46-cm of the melt surface. The glass melt is poured from the melter through a water-cooled copper tapping fixture.

7.5.2 Test Results

During the demonstration, the USBM melter produced 4,700-kg (10,340-lb) glass in a 24-hr period. However, excessive melting temperatures resulted in high-volatile component losses. In the other two demonstrations runs, USBM reduced the volatile losses by using large-diameter electrodes and lower voltage. The volatile losses were lower but were still greater than cold-top, joule-heated melters. Volatility was high for boron, alkali metals, and halides.

A total of 1,784-kg (3,925-lb) of Type A or 11,889-kg (26,156-lb) of Type B feed were produced. The sugar plus activated carbon feed effectively destroyed an average of 78 percent of the NO^-_2 and NO^-_3 in the Type B feed while with only activated carbon present in Type B feeds, the destruction varied from 15 to >90 percent. The degree of reaction for Type A feed was not determined.

During the initial test run, the electrode consumption per ton of glass was 12.6-kg (27.7-lb). After replacement with large-diameter electrodes, the electrode consumption (per ton of glass) was 10.5-kg (23.1-lb), indicating lower electrode consumption with increasing electrode diameter. Most of the glass product was homogeneous except for some cases where inclusions were observed, but the glass was mostly in the reduced state. The measured Fe^{2+}/Fe (total) was 1.0. The visual examination indicated refractory corrosion, which was also reflected as an increase in Cr content in the glass composition.

7.5.3 Technical Issues

There were several technical issues that need to be addressed before this technology could be adopted for LLW vitrification. Preparation of dry feed requires extensive equipment and mechanical complexity that may not be suitable for radioactive operations. The wear and consumption of electrodes are matters of concern. It is necessary to change and feed the electrode into the melter as it is consumed. The presence of additional carbon arising from the electrodes causes significant reduction in glass.

Volatility and entrainment of feed were significant; even though the use of a larger electrode reduced the volatility, design changes need to be made to operate this melter like a cold-top melter. The glass pour system is not suitable for continuous pouring of viscous glass, and excessively high temperatures are required to be maintained for continuous glass flow. The situation becomes worse when the alkali metals and boron volatilize, resulting in a high-viscosity glass. A glass tapping temperature of 1,600 °C was required for pouring, which will cause volatilization of Cs and Tc during pouring.

Carbon electrode arc melters have been widely used in melting specialty metals, steel, and ceramic refractories. The melt rates are higher than all the joule-heated melters, and the melter can melt wastes with a variety of characteristics.

7.6 WESTINGHOUSE SCIENCE AND TECHNOLOGY CENTER

The Westinghouse Science and Technology Center (WSTC) is a division of Westinghouse, Inc. and the demonstration test was performed at the Westinghouse Plasma Center at the Waltz Mill Site, Madison, Pennsylvania.

7.6.1 Vitrification Process

The vitrification technology is based on a plasma torch fired furnace. A cupola furnace is equipped with a single Marc® 11 plasma torch with a output power of 700 to 1,400 kW. A schematic diagram of the overall vitrification system is shown in figure 7-6. The plasma melter is 6.7-m high (2.2-ft) with an outer shell diameter of 1.2-m (3.9-ft) and an inner shell diameter of 0.76-m (2.5-ft). The melter is fired by a single

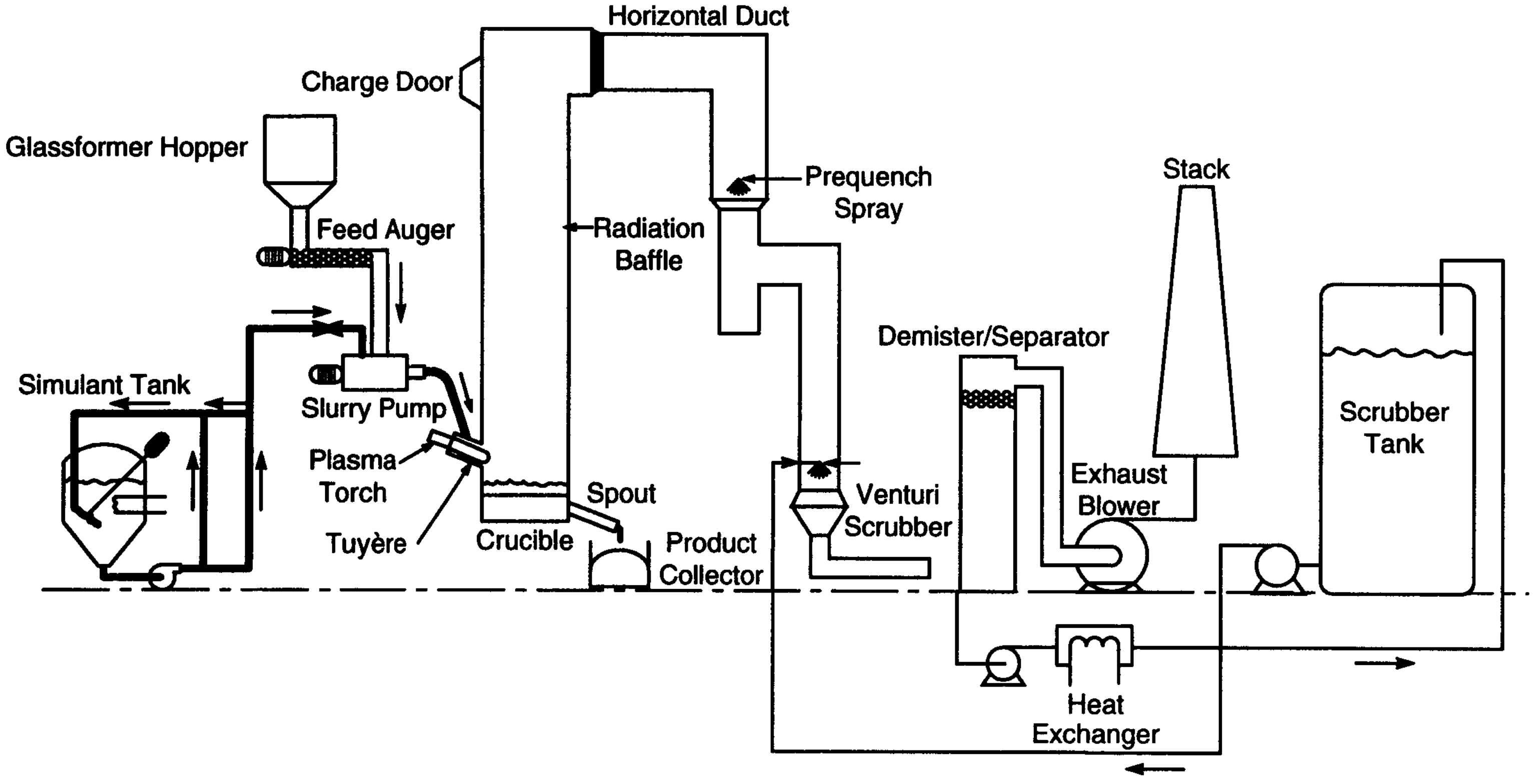

Figure 7-6. Westinghouse Science and Technology Center vitrification process flowsheet for Hanford low-level waste (Wilson, 1996a)

Marc® 11 plasma torch mounted on a tuyère that directs the plasma plume to the melt crucible. A tap hole on the bottom side of the crucible connects to an overflow side pour spout for glass pouring. The cupola shaft is lined with Al_2O_3/SiO_2 refractory, the crucible is lined with high-chrome refractory, and the tuyère is lined with Al_2O_3/CaO insert sleeves. Figure 7-7 shows a cross section of the cupola. The tuyère and crucible are water-cooled by copper tube cooling coils.

WSTC uses glass frit as a raw material to be mixed with LLW simulant. The frit is volumetrically metered through an auger while LLW simulant is metered through a mass flowmeter. Both simulant and the glass frit are fed as separate streams to a slurry pump where they are mixed and fed as a slurry to the furnace tuyère. In the tuyère, feed is rapidly heated and carried along with the hot plume from the plasma torch to the melt crucible. The glass product is continuously tapped from an overflow pour spout and poured into carbon steel boxes. The gas/solid streams exit the tuyère and entrained solids impinge on the glass plume and

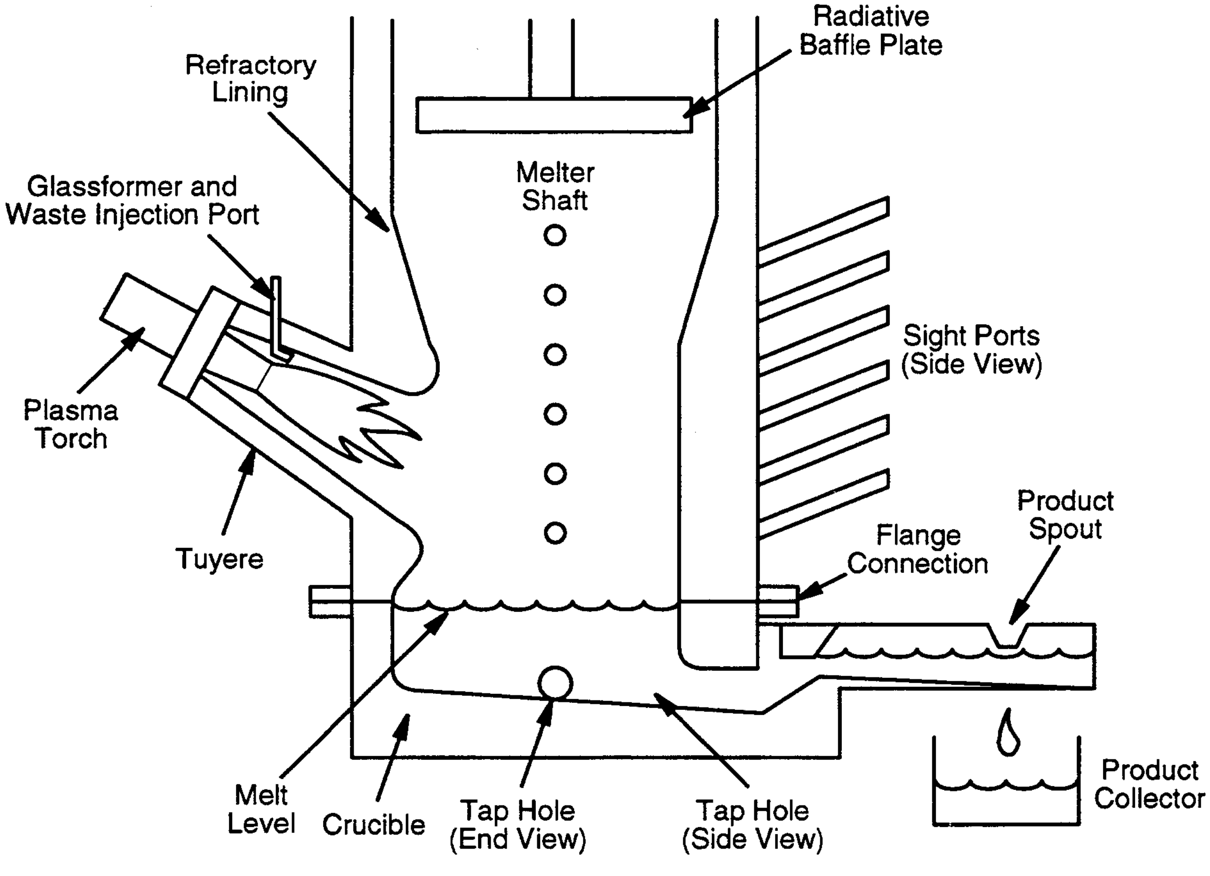

Figure 7-7. Westinghouse Science and Technology Center Marc® 11 plasma torch and melter system (Wilson, 1996a)

dissolve in the melt. Offgases proceed up the melter shaft. The offgases travel up the shaft, are partially air quenched, and flow out the top of the melter shaft via a horizontal duct to a vertical duct where they are water quenched, and scrubbed in a venturi scrubber. The scrubbed offgas passes through a demister and is sent out to the stack through an exhaust fan.

7.6.2 Test Results

WSTC produced approximately 7,000 kg of glass during a 24-hr run. The glass composition was close to target composition. The glass was well reacted and transparent but had numerous chords resulting from limited convection and mixing due to low melt level in the crucible. The glass production rate was about 300-kg/hr (660-lb/hr) at 1,550 kW.

High volatility and entrainment losses were observed. Entrainment losses were estimated to be 2.7 percent, while volatilization of B_2O_3 and Na_2O was 22 and 15 percent, respectively. Significant offgas deposits were observed in the upper horizontal duct. A 7- to 100-cm (2.7- to 39.4-in.) width in a 30-cm (12-in.) diameter duct was completely filled with deposits. The analysis indicated sodium and borate salts as major constituents. The offgas deposits blocked the offgas scrubber solution flow resulting in a temporary shutdown of the system.

Refractory wear was highest in the alumina-calcia lining of the tuyère while the melt crucible, pour spout, and shaft plate surface refractories performed well. The vertical shaft showed some attack by the glass in the lower levels of the shaft. Some spallation of refractory was also observed in the upper section of the shaft.

7.6.3 Technical Issues

The high feed entrainment and volatility losses were a major issue with this technology. Since this melter cannot be operated in a cold-top mode, minimization of losses may be difficult. Erosion was significant in the refractory used for tuyère lining. A redesigning of the tuyère should reduce wear of its lining.

This technology can melt feeds with a variety of compositions and characteristics. Its advantage consists of significantly higher production rates than joule-heated melters.

7.7 BABCOCK & WILCOX, ALLIANCE RESEARCH CENTER

The Babcock & Wilcox (B&W) cyclone vitrification technology is based on 50 yr of experience with slagging combustion units for the electric utility industry. Slag is a vitreous byproduct of impurities in coal from coal combustion. The B&W cyclone vitrification technology has been demonstrated for soil vitrification for the EPA Superfund Innovative Technologies Evaluation Program. B&W demonstrated a slurry-fed cyclone melter system for the Hanford LLW at the Alliance Research Center in Alliance, Ohio.

7.7.1 Vitrification Process

The cyclone furnace is a water-cooled horizontal cylinder attached to the wall of the main furnace cavity. The cyclone wall consists of a network of water-cooled metal tubes fitted with metal studs pointing into the center of the cylinder. A 19- to 51-mm (0.75-to 2-in.) layer of refractory cement is imbedded between and over the studs to protect the metal structure. During operation, formation of a skull layer on the walls of the cyclone melter minimizes corrosion. Figure 7-8 shows the schematic of the B&W LLW vitrification system. The cyclone furnace is fired by natural gas with a small amount of excess air.

LLW and dry glass formers are mixed outside the melter and injected into the melter through an atomizing nozzle. Slurry is injected onto the cyclone wall where it melts and flows down the cylindrical wall and is collected in the bottom of the cyclone. Glass drains from the cyclone section through a notch in the back baffle of the cyclone to a sump in the main furnace cavity. The sump is drained to a quench tank.

7.7.2 Test Results

The glass production rate was approximately 600-kg/day (13,200-lb/day). The volatile and feed entrainment losses were the highest among all the melter systems. Estimates indicate that 23.4 percent of the glass forming components were lost due to volatilization. In addition, dry feed accumulated as stalagmites hanging off the injector tube and the glass buildup on the combustion air inlet resulted in globs of molten glass falling and interfering with the feed atomizer.

The post-test inspection of the melter indicated significant erosion of the cyclone chamber refractory during the demonstration. The glass product indicated the presence of unmelted refractory grains and significant glass inhomogeneity suggesting a need for longer refining times.

7.7.3 Technical Issues

Entrainment losses during testing were 7–10 percent of the feed and were the highest observed among the various technologies. A modification to the feed delivery system that will allow feed to be delivered to the cyclone system before entrainment is needed. The high volatilization losses of alkali metals, halides, and B are attributed to temperatures as high as 1,600 °C at the combustion section. The volatilization losses have to be minimized before this technology can be used for LLW vitrification.

The glass composition was significantly depleted of B and Na due to entrainment and volatilization losses and the glass was visually inhomogeneous. Some of the contamination was from refractory erosion. A longer residence time is needed for glass to completely homogenize and produce an acceptable product. Extensive erosion of refractory indicates that the cyclone chamber needs to be redesigned and cooled enough to form a thick skull layer.

Cyclone vitrification technology could provide a modular melter design that is smaller than conventional joule-heated melters. This technology is capable of producing glass throughputs in the range of 100 to 200 ton/day. This technology produced a self-draining glass and, therefore, potential for drain valve failure does not exist. The electrically conductive glass is not a limitation.

7.8 RECOMMENDATIONS OF THE EVALUATION BOARD

An evaluation board consisting of experts was chartered by the Westinghouse Hanford Company to review the performance of melter technologies. This evaluation rated cold-top, joule-heated melters as the best available technology. These technologies were considered mature and exhibited superior mass balance. However, the evaluation board was concerned about the use of a bottom drain on a large-capacity production melter and the control of the glass level so as not to expose the top-entering molybdenum electrodes to

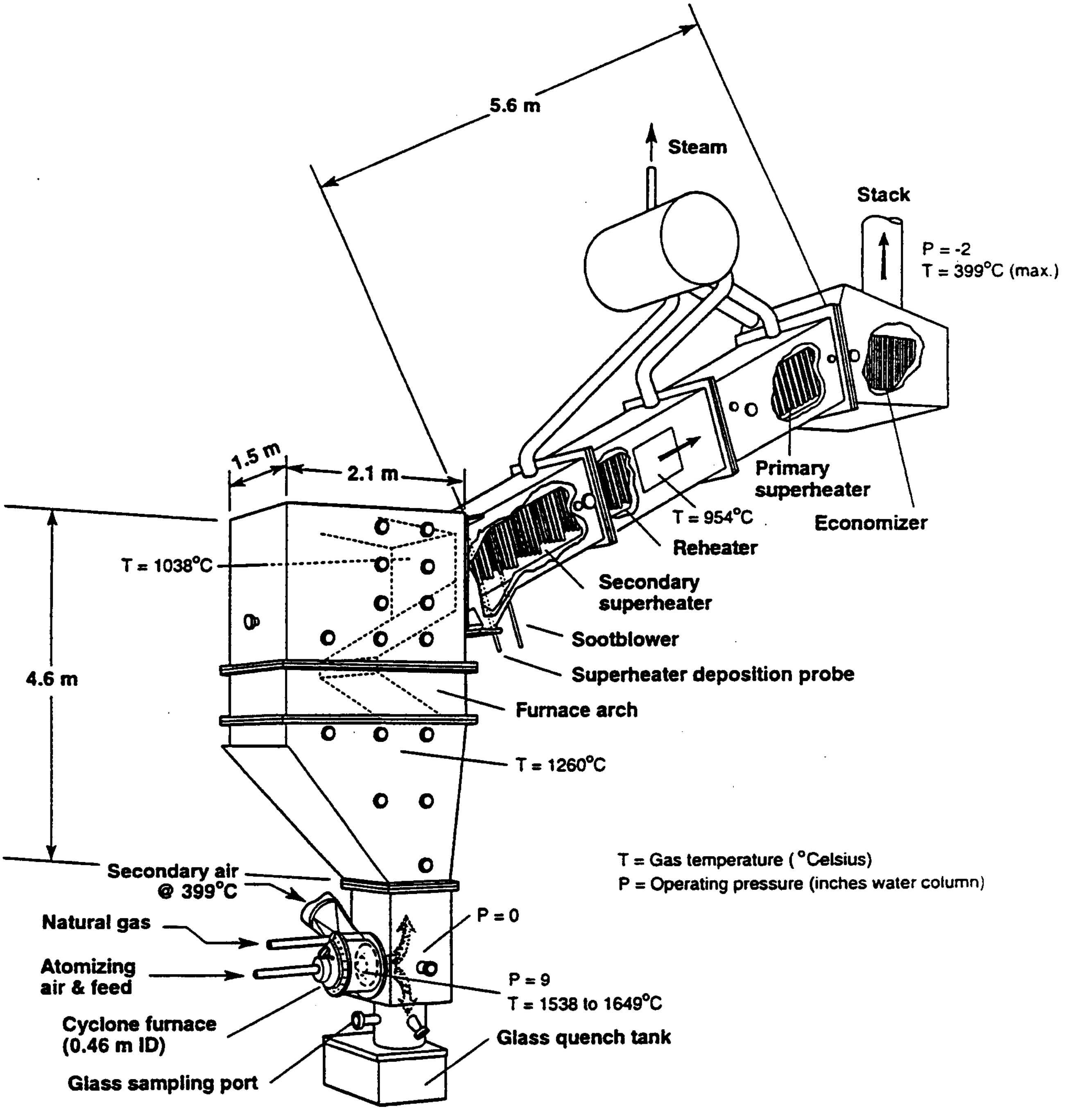

Figure 7-8. Babcock & Wilcox vitrification system for Hanford low-level waste (Wilson, 1996a)

oxidation. The board preferred the Envitco overflow side drain and Duratek airlift drain design over the Vectra bottom drain.

The board rated slurry feeding and mix-in-the-charger damp feeding as used by PEI superior to dry feeding. The size and complexity of equipment required for preparing dry feed was a concern. In addition, complexity of the equipment would result in difficult remote maintenance and operations. The slurry feed was further supported by the fact that there is no significant difference in production rate between liquid and dry feeds.

The board recommended that further testing of cyclone combustion and plasma technology should not be continued. In their opinion, these technologies require significant additional modifications and data at this stage. The carbon electrode technology is worthy of additional consideration. The board believed that the incorporation of an improved drain design will allow the melter to operate continuously in a cold-top mode, reducing entrainment and volatilization.

8 MIXED WASTE SOLIDIFICATION TECHNOLOGY EXPERIENCE

In 1992, Congress passed the Federal Facilities Compliance Act mandating the treatment and disposal of the DOE mixed waste inventory (Office of Science and Technology, 1996). The DOE complex has approximately 167,000 m^3 (44.1 million gal.) of mixed waste in storage including 51,600 m^3 (13.6 million gal.) of mixed transuranic (MTRU) and 115,400 m^3 (30.5 million gal.) of mixed low-level waste. It is anticipated that this inventory will increase due to ongoing processes, environmental restoration, facility decontamination, and facility transition activities within the DOE complex. The Mixed Waste Focus Area (MWFA) was established by the Office of Science and Technology of the DOE to develop and facilitate implementation of technologies required to meet DOE commitments for characterization, treatment, and disposal of mixed wastes. Under MWFA sponsorship, a number of thermal treatment technologies to stabilize mixed wastes have evolved. In this survey, technologies that are relevant to the scope of this report will be discussed. Several technologies that were evaluated under this program are not solidification technologies but were thermal treatment technologies such as steam reforming or system integration concepts like minimum additive waste stabilization (MAWS) and reactive additive stabilization process (RASP). The MAWS (Pegg, 1994) is not a solidification technology but a systems approach to integrate multiple technologies into one and is not discussed in this review. Similarly, RASP (Jantzen et al., 1994) is not a technology but a systems approach to optimize glass composition by using various waste streams and reactive chemicals as glass formers. The information reported in this section has been extracted from a series of reports prepared by the Office of Technology Development (1995a,b,c).

8.1 PLASMA HEARTH PROCESS

Plasma arc technology is widely used in various industry applications (Gillins and Poling, 1994). Some of the applications are

- Metal and ceramic powder production
- Composites (metal on metal, metal on ceramic, etc.) production
- Titanium dioxide pigment production
- Chemical production (acetylene, ethylene, etc.)
- Metal ore smelting
- Metal and refractory recycling
- Metal refining
- Metal cutting and welding

Plasma hearth process (PHP) technology for stabilizing mixed wastes is being developed by the Science Applications International Corporation (SAIC) for the MWFA (Science Applications International Corporation, 1996). This technology is targeted for mixed wastes such as sludges and heterogeneous debris that cannot be treated by conventional technologies. Nonradioactive testing was done on a bench-scale plasma system at the SAIC Science and Technology Applications Research (STAR) Center. The PHP is a high-temperature thermal treatment process using a plasma direct current (DC) arc torch in a stationary, refractory lined melter. The plasma arc destroys organics and stabilizes residuals in a vitrified slag. The major advantage of the process is that whole drums could be fed into the process chamber, thus reducing waste handling and potential exposure to toxic and radioactive contaminants.

Major components of the STAR Center plasma system are the plasma chamber, secondary chamber, quench air, dry absorbent air, bag house, HEPA filter, stack, and instrumentation and controls. A PHP system process schematic is shown in figure 8-1. The plasma chamber is a 79-cm (31-in.) diameter by 76-cm (30-in.) long horizontal cylinder with interior walls lined with the combination of MgO, Al_2O_3 and Cr_2O_3 refractories. A water-cooled plasma torch is mounted from the top of the plasma chamber. The torch uses nitrogen as its primary gas to stabilize electric discharge between two electrodes. The second electrode is the material that is being processed. The plasma chamber also contains additional ports for viewing, material feeding, and offgas exit. The feed port is used to feed either 0.95 L (1 quart) or 3.7 L (1 gal.) steel containers to simulate 208-L (55-gal.) drums. The materials are drip melted into the plasma chamber.

The reaction gases from the plasma chamber go to the secondary chamber. The secondary chamber ensures full destruction of the residual organics left in the offgas. The secondary chamber is a vertical cylinder and operates at a temperature of 980 °C by a natural gas burner at the side of the chamber. The offgas enters the chamber from the bottom and flows in the chamber in a cyclonic fashion. The mean residence time in the chamber is about 2 sec. The offgas leaving the chamber is quenched by injecting water/air at a temperature of 540 °C and is sent for acid removal by a dry sorbent injection with sodium bicarbonate. The sodium bicarbonate is injected into the offgas. At 540 °C, sodium bicarbonate is converted to sodium carbonate, and sodium carbonate reacts with acidic gases to form sodium salts. The offgas and alkali reagents are then passed through a dry reactor, which provides enough residence time for reaction of acidic gases. The offgas then passes through a baghouse that collects unused sodium bicarbonate, sodium salts, and fly ash. Collected solids are recycled back into the offgas. As needed, fresh sodium bicarbonate is added to the system. Results indicate 95-percent removal of HCl and 98-percent or more for metal removal except for Hg which is 50 percent. The HEPA filter then removes fine particulates from the offgas with a removal efficiency of 99.97 percent. The offgas is then exhausted to the stack.

This technology has the ability to process large amounts of metal-bearing wastes. The technology is robust enough to accept and process papers, plastics, metals, soils, liquids, and sludges. The resulting waste forms do not require additional stabilization. Because the wastes can be processed at high temperatures (1,500 °C), a wide range of feed compositions can be accommodated.

A major disadvantage is the increased volatilization of metals such as Pb, Hg, and Cs compared to the joule-heated systems. Other disadvantages are the short life of plasma torches, remote material handling, and plugging of slag drains. These characteristics make radioactive operations risky and difficult, requiring frequent maintenance.

8.2 PLASMA ARC CENTRIFUGAL TREATMENT SYSTEM

The plasma arc centrifugal treatment (PACT) system was installed at the DOE Western Environmental Technology Office and was operated by MSE, Inc., Butte, Montana. MSE, Inc. has been involved in the development of this system since 1989. Some of the waste streams that have been tested and evaluated include copper mill tailings from a Superfund site in Montana, small caliber and handheld

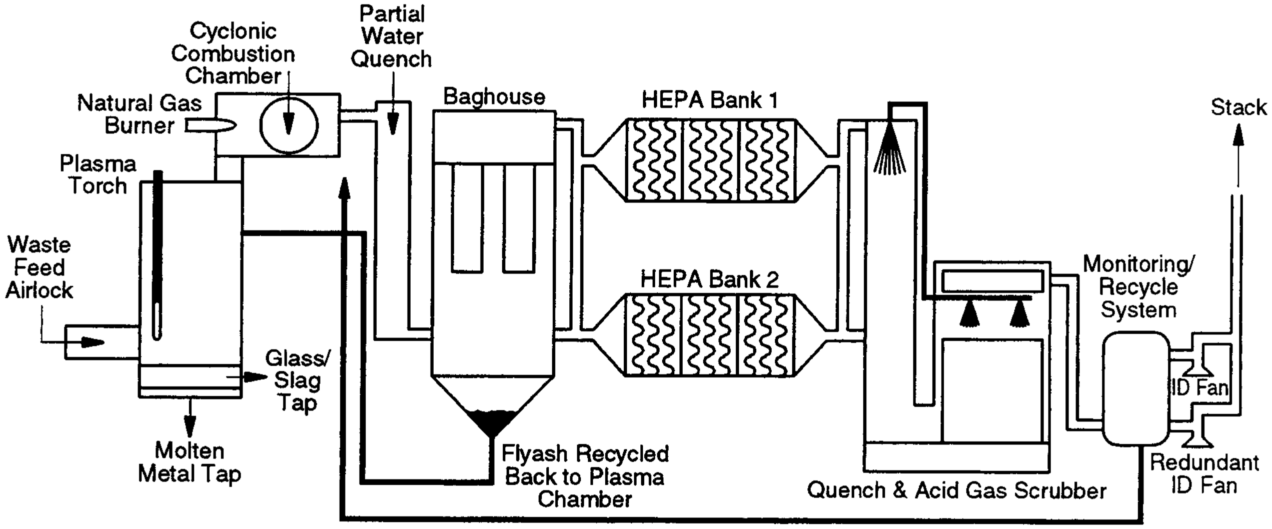

Figure 8-1. Plasma hearth process system flowsheet (Science Applications International Corporation, 1996)

pyrotechnic devices, smoke and spotting dyes from the Department of Defense Ordnance demilitarization stockpile, and several simulated DOE mixed waste streams.

The system uses a transferred electric arc, similar to PHP, as a heat source. Figure 8-2 shows a general process schematic of the PACT system. A screw feeder is used to feed waste uniformly and continuously into a primary chamber through a chute connecting the feeder and the primary chamber. The primary chamber consists of a rotating tub with a central orifice or throat lined with copper.

The system uses a transferred electric arc as a heat source. The copper lined throat is used to strike the arc of the plasma torch. As waste is fed to the primary chamber, the torch is moved away from the throat. The molten slag remains in the primary chamber by the centrifugal force generated by the rotating tub. The torch is slowly moved around to provide uniform distribution of heat. After about 450 kg (1,000 lb)of material is fed to the chamber and has attained molten state, the rotation speed of the primary chamber is reduced, and the glass/slag is allowed to pour into a 208-L (55-gal.) drum under the primary chamber. The temperature of the melt is approximately 1,600 °C. After pouring, the process is started again.

The offgas from oxidation of the organic materials consists of combustion gases, mostly CO_2 and H_2O, and NO_x in case of nitrated waste. The temperature of the offgas exiting the primary chamber is around

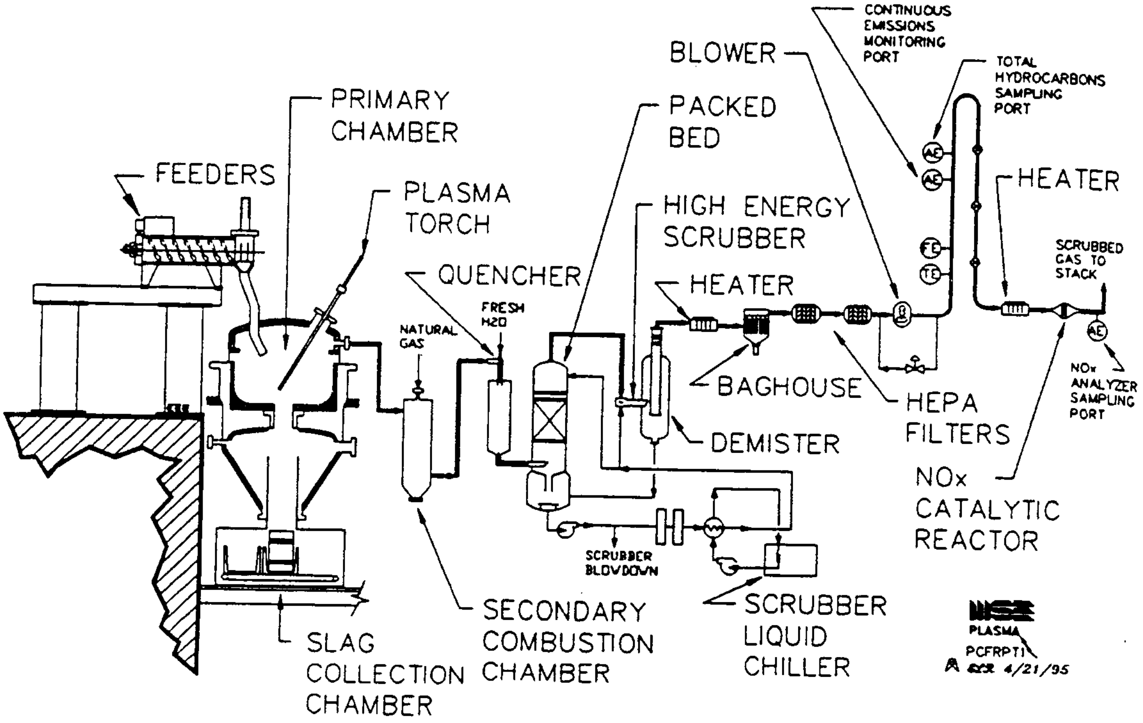

Figure 8-2. Plasma arc centrifugal treatment system flowsheet (Whitworth and Filius, 1995)

1,100 to 1,300 °C and it is sent to a secondary combustion chamber to ensure complete destruction of any residual organic species. The secondary chamber is a natural gas fired system. The exhaust gases are then passed through a quencher/absorber, particulate scrubber, high-energy scrubber, super heater, baghouse, HEPA, carbon absorption bed, induced draft blower, gas preheater, NO_x removal system, and released to the stack.

Advantages and disadvantages of this technology are similar to the PHP technology and are discussed in section 8-1. The entire system is sealed from the atmosphere and is operated under a slightly negative atmosphere. Even though the PACT system is operated under slightly negative pressure, the failure of the rotating tub could result in premature pouring of the waste into the canister and possible release of offgas from the primary chamber into the facility.

Currently there are several PACT systems that are either in their construction phase or have been installed to vitrify heterogeneous mixed wastes (Haun et al., 1996). Three PACT-8 units, with a 2.4-m (8-ft) diameter centrifuge, are being constructed, and one unit is being built for remediating Pit 9 waste at the INEEL. One unit is at the Retech Plant in Ukiah, California, for further development, and another unit will be located at Munster, Germany. In addition, two PACT-2 units, with a 0.6-m (2-ft) diameter centrifuge, have been installed at the Retech plant.

8.3 HIGH-TEMPERATURE, JOULE-HEATED MELTER

High-temperature, joule-heated melters have been discussed in detail in chapter 6.

8.4 DIRECT CURRENT GRAPHITE ARC MELTER

DC arc furnaces with graphite electrodes have been used in the steel industry since the beginning of this century. Drawn from the steel industry experience, the DC graphite arc melter system for mixed wastes was developed and tested by a collaborative National Laboratory-University-Industry program between PNNL, Massachusetts Institute of Technology (MIT), and T&R Associates. The program was initiated in 1992. Currently there are three graphite electrode DC arc furnaces available for testing. A pilot scale furnace, Mark II, with processing rates of 450 kg/hr (1,000 lb/hr) is installed at the Plasma Fusion Center Laboratory at MIT. An engineering-scale system, capable of processing 45 kg/hr, and a bench-scale system are being installed at PNNL to perform radioactive, mixed, and hazardous waste processing. In this section, discussion will be focused on the Mark II Pilot Scale Furnace system installed at MIT.

The Mark II melter is a carbon steel vessel lined with refractory and is approximately 6.9 m (23 ft) high and 2.1 m (7 ft) in diameter. The feed system and the glass discharge system are attached diametrically opposite to each other. The electrode is a unique coaxial arrangement with a 40.6-cm (16-in.) outside diameter and 25.4-cm (10-in.) inside diameter outer electrode, and a 15.2 cm (6 in.) diameter solid inner electrode. This electrode system provides the capability of operating either in the transfer mode (arcing from the electrode to the material) or non-transferred mode (arcing between the inner and outer electrode).

A significant effort is being made to develop a furnace diagnostic system. The efforts include development of analytical equipment for spatially resolved measurements of furnace and glass temperatures as well as continuous *in situ* monitoring of offgas emissions.

Like all other plasma systems, this technology is suitable for heterogeneous wastes difficult to vitrify when volatilization is not a major issue in stabilization. This technology is still in its development stage.

8.5 ALTERNATING CURRENT ARC MELTER

A pilot-scale alternating current arc plasma melting technology for mixed wastes and contaminated soils is being developed at the Albany Research Center of the USBM, Albany, Oregon. The technology is similar to the three-phase carbon arc technology discussed in section 7.5.

8.6 HYBRID PLASMA-INDUCTION, COLD-CRUCIBLE MELTER

The hybrid plasma-induction cold-crucible Melter (PICCM) technology is discussed in chapter 11 on Emerging Solidification Technologies.

8.7 MICROWAVE MELTER

Microwave technology is not new to United States industry or to the public. For the last two decades, microwave technology has been used daily by millions of people for cooking. Other extensive users include the chemical and food industries. Since 1985, the Rocky Flats Plant (RFP) in Colorado has been developing this technology for solidification of radioactive wastes. Several studies have been conducted in bench-, pilot-, and full-scale demonstration systems. The bench-scale studies have included both radioactive as well as nonradioactive processing using microwave systems. The full-scale demonstration plant has shown that the technology is scalable from bench to production level but, due to the lack of funding, integrated testing of ancillary units like the offgas treatment systems has stopped.

The microwave melting system developed by INEEL is called the In-Drum Melting System. In this process, a 113-L (30-gal.) drum is placed in an insulation cage and connected to a microwave source. The microwave energy is transmitted via a 60-kW, 915-MHZ generator. A small amount of waste material is first transferred from a hopper to the drum through a screw conveyor. The microwave energy raises the temperature of the waste materials to 1,000 °C. After an initial charge is melted, a continuous charge of waste materials is fed to the drum. After a required amount of waste material is fed, the microwave system is stopped, and the drum is removed from the insulation cage and allowed to cool. Offgas is removed from the processing chamber by a down-stream blower system. The offgas is passed through a bed of granulated, activated carbon filter to remove oxides of sulfur and nitrogen and through HEPA filters to remove particulates before being released to the stack.

Microwave technology for waste treatment and solidification is not fully developed and its performance as an integrated system has not been established. The technology is itself robust and can be applied to a large number of waste streams. In addition, a single container can act as a melting crucible and waste form canister, thus reducing costs and maintenance. However, due to low throughput and inability of the microwaves to penetrate large-diameter drums, the technology is only useful for processing small quantities of waste.

8.8 QUANTUM-CATALYTIC EXTRACTION PROCESS

The Quantum-Catalytic Extraction Process (Q-CEP) technology is discussed as part of Nonvitrification Solidification Processes Experience in chapter 12.

8.9 VORTEC COMBUSTION AND MELTING SYSTEM

The Vortec patented Combustion and Melting System (CMS) is a high-temperature thermal/chemical solid waste treatment and recycling process for remediating soils, sediments, sludges, and mill tailings that have organic, inorganic, and heavy metals contaminations (Hnat et al., 1994). The process oxidizes organic contaminants and immobilizes inorganic contaminants in a vitrified matrix.

Figure 8-3 shows the Vortec process schematic. The basic elements of the system are CMS; material handling, storage, and feeding system; vitrified product separation and reservoir assembly; waste heat recovery unit; flue gas (offgas) cleanup system; and vitrified product handling system. The CMS consists of two major assemblies: a counter-rotating vortex (CRV) in-flight suspension pre-heater and a cyclone melter. First, feed (wet or dry) is introduced into the CRV combustor. The CRV combustion burner preheats the suspended waste and oxidizes organics. The average temperature of the materials leaving the CRV is between 1,200 and 1,540 °C. The preheated solids exit the CRV and enter the cyclone melter, where they are dispersed onto the chamber walls to form a molten glass product. The vitrified molten glass product exits the cyclone melter through a tangential exit channel into a glass/gas separation chamber. The exhaust

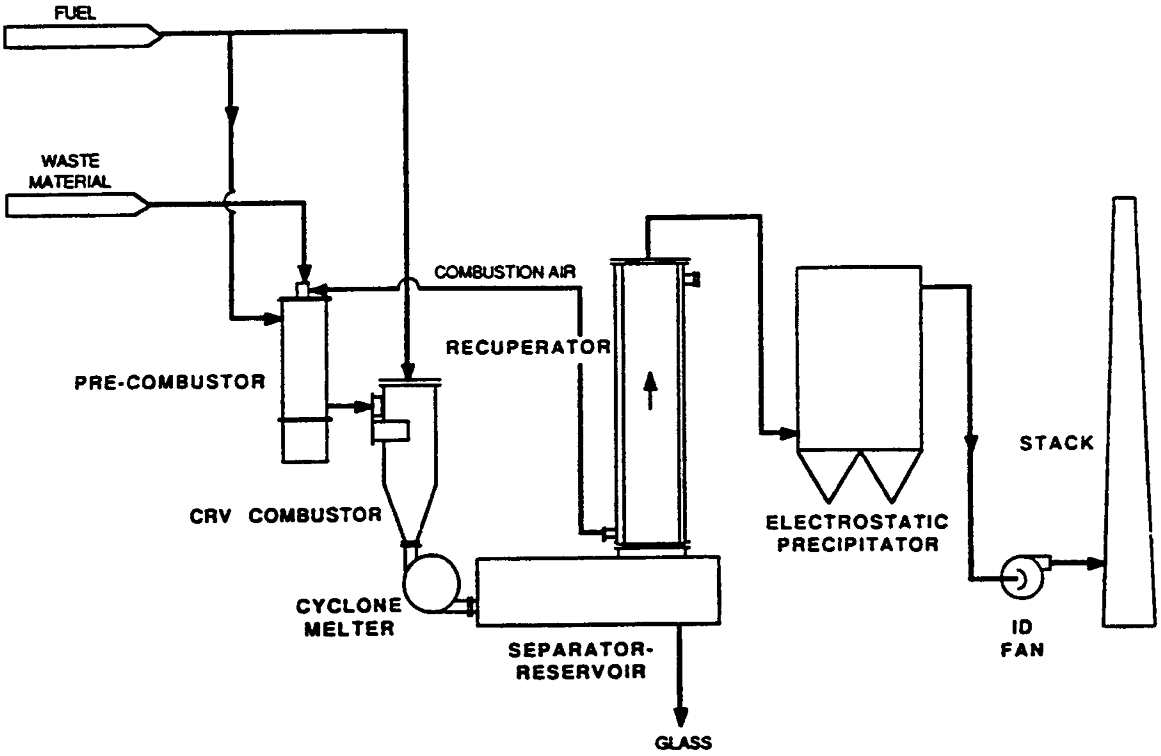

Figure 8-3. Vortec combustion and melting system flowsheet (Hnat et al., 1994)

gases then enter a pre-heater for waste heat recovery and are sent to the offgas treatment system. The glass exits through a tap to a water quench assembly for subsequent disposal.

Since 1988, Vortec has been processing nonhazardous industrial waste materials at its 20-ton per day operational pilot-scale facility. Even though CMS technology offers high production rates, the issues relating to the safety of fuel/air mixtures in the presence of organics and other contaminants is unknown. In addition, the lack of a cold-cap and temperatures in the range of 1,600 °C could result in extremely high volatilization losses.

8.10 *IN SITU* VITRIFICATION

The *In Situ* Vitrification (ISV) process (Luey, 1995) was invented in 1980 and patented in 1983 by the PNNL. The technology is commercially available through Geosafe Corporation. In recent years, the

ISV has been extended to *In Situ* Plasma Vitrification (Kielpinski et al., 1995) and *In Situ* Waste Destruction and Vitrification (IWDV) (Ferrar, 1995).

ISV has been evaluated and implemented for a number of waste streams/sites within the DOE, Department of Defense, and Superfund sites in the United States, and internationally in Australia and Japan. Waste types that have been vitrified include contaminated soil, contaminated soil with debris, liquid seepage cribs, buried waste, and underground storage tanks. The waste streams include organics, heavy metals, radionuclides, and construction debris.

The ISV process involves forming a molten pool of soil in the treatment zone. The treatment zone is determined by the placement of electrodes in the soil. As the electrical energy is applied between the electrodes, the joule heating starts melting the soil. Typical melting temperatures are 1,600 to 2,000 °C. The process continues until the desired depth and width is reached. The power is shutdown, electrodes are pulled out (if required) and the molten mass is allowed to cool. A typical single full-scale ISV setting is 10 m (30 ft) in diameter and 5 m (15 ft) deep and takes about 10 to 15 days per setting to vitrify.

The vitrified product is analogous to natural obsidian and is estimated to retain its integrity for geologic periods. The vitrified product has outstanding physical, weathering, and chemical properties and is typically 5 to 10 times stronger than reinforced concrete. In a typical ISV product, unlike vitrification, which produces a single homogeneous product, there are generally five distinct regions: (i) the vitreous frothy surface layer, (ii) the partially reacted ring layer, which marks the vitrification surface of the monolith, (iii) the vitrified material, (iv) the devitrified material near the center of the monolith, and (v) the potential pools of metals at the electrodes or at the bottom of the monolith. To characterize such a monolith, a detailed characterization of megascopic regions is necessary. If major regions can be identified, a stratified random sampling can provide sufficient data to determine chemical, morphological, and durability properties of each region.

ISV can be used to treat the waste at its origin and organics, inorganics, and radioactive contaminants can be processed simultaneously. In addition, the process has high tolerance for debris. Some of the limitation of this technology are that the media must be acceptable for joule heating. The total organic loading must be less than 10 wt.% and the treatment depth less than 6.6 m (20 ft). The presence of high groundwater recharge rates or very large voids makes the process difficult. The presence of sealed containers also poses a processing risk.

In the *In Situ* Plasma Vitrification (ISPV), a plasma torch, in a non-transferred mode, is inserted to a target depth and, as the soil is melted, the torch is slowly withdrawn upwards. The technology does not require that the soils be conducive to joule-heating and avoids safety concerns of explosion due to vapor pressure buildups in the top-down vitrification. In addition, ISPV uses the existing systems technology for ISV such as site preparation/characterization, in-field power systems, and offgas capture and treatment. *Ex situ* test trials were conducted on SRS soils at Georgia Institute of Technology and Mississippi State University, and it was found that fluxing agents were necessary to achieve a good vitrified product. Actual field testing of this technology has not been performed.

The IWDV is another extension of ISV technology. In this process, a steel-lined borehole is installed through a waste pit. Then, a high-temperature graphite arc-melter system is lowered through the bore hole to the bottom of the buried waste and arc melting is initiated. The melter consumes the steel liner, volatilizes organics, and melts the inorganic wastes and soils at the bottom. As the waste and contaminated soils are vitrified, the torch is withdrawn slowly until a required depth and width is reached. This technology has only gone past the proof-of-concept stage and needs major resources for pilot-scale demonstration of waste remediation.

One of the major concerns related to the ISV technology is the unknown and probably non-uniform melting characteristics of the underground materials including offgas (steam from soil moisture and reaction products) characteristics. This issue is evident from the recent melt expulsion in the ISV plant at the ORNL in Oak Ridge, Tennessee. A 20,000-kg (44,000-lb) melt expulsion of radioactively contaminated soil occurred at the plant on April 21, 1996 (Oak Ridge National Laboratory, 1996). The expulsion was caused by pressurized steam venting rapidly through the molten glass body. The ISV was going on for the previous 17 days. The vitrification pit was covered by a stainless steel hood and maintained under negative pressure to collect, filter, scrub, and monitor offgas. During expulsion, the offgas was rapidly heated from 250 to 1,000 °C and the pressure surge was sufficient to lift the 6,750 kg (15,000-lb) hood approximately 30-cm (12-in.) off the ground. A pool of glass was able to flow up to 3 ft outside the hood while the hood was still raised. The escaping offgas and molten glass ignited several small fires in the combustible components near the hood.

The air sample analysis indicated that there was no airborne contamination. However, gas samples directly from the ISV hood coupled with an estimated volume of offgas release indicated a maximum release of 0.13 μCi of Cs-137. The analyses of offgas processing filters indicated that 99.7 percent of all offgas radioactivity was retained in the filters. The residual molten glass was found to contain 99.99 percent Cs-137. Small fragments of the glass pieces were found as far as 100-m (300-ft) away from the site. The overall environmental impact of the incident relative to the spread of contamination was considered to be insignificant. The root cause of the melt expulsion incident was inadequate vent design. Although similar expulsion events have been reported in 3 out of 70 large-scale ISV melts, previous incident investigations implicated man-made subterranean structures like tanks, concrete vaults, and drums, which were thought to constrict the normal flow and dissipation of offgas around the growing molten mass. The offgas hood was modified to handle future expulsion events in a controlled manner.

Due to operating temperatures of greater than 1,600 °C, and the absence of cold-cap to prevent volatilization of radionuclides such as Tc and Cs, ISV technology in its present form cannot be applied to vitrification of HLW in the tanks. In contrast, the risk of having melt expulsion in the joule-heated slurry-fed melter systems is extremely low, even though the slurry may contain 40–50 percent waste, which will flush as steam in the melter. This is mainly due to the fact that the slurry is fed on top of the hot melt and does not percolate through the melt, as is the case with the Q-CEP process, for example. This risk of expulsion is consequently much higher in the Q-CEP process.

8.11 RUSSIAN HIGH-FREQUENCY INDUCTION MELTER

The Russian high-frequency induction melter is combined with the cold-crucible melter and is discussed in section 11.1.

8.12 TRANSPORTABLE VITRIFICATION SYSTEM

The TVS has been discussed in section 6.2.

8.13 VITREOUS CERAMICS

The vitreous ceramics concept is still at the laboratory-testing phase. Laboratory testing has shown that a vitreous ceramic waste form offers high waste loadings and much higher volume reduction. Since this concept is still experimental, and an adequate technology has not been developed, further discussion on the topic at this time is beyond the scope of this report.

9 RESEARCH AND TEST MELTER EXPERIENCE

The PNNL, the Vitreous State Laboratory (VSL) at the Catholic University of America (CUA), and the Clemson University Vitrification Research Laboratory have established a set of pilot-scale melter systems to provide industries preliminary process evaluation for their waste types. In fact, the PNNL ran the first radioactive melter that provided information for the WVDP melter at West Valley and DWPF melter at the SRS. In addition, WVDP and DWPF both used pilot-scale melters to develop process flow sheets. In this section, an overall description of the technologies is presented and discussed.

9.1 CLEMSON UNIVERSITY VITRIFICATION RESEARCH LABORATORY

In 1992, the DOE/Industrial Laboratory for Vitrification Research was established in cooperation with the Westinghouse Savannah River Company, Envitco, Inc., and Stir Melter, Inc. The Vitrification Research Laboratory (VRL) currently houses three melters. Of these, two are joule-heated melters supplied by Envitco, Inc., and Stir Melter, Inc., and the DC arc graphite electrode melter supplied by Electro-Pyrolysis, Inc. Each melter system has its own offgas system. Since the inception of the program, VRL has evaluated several waste streams, using surrogate waste compositions. Table 9-1 lists the type of waste stream processed, the number of campaigns associated with each waste stream, and the melting system used.

The discussion of results for each waste stream shown in table 9-1 is beyond the scope of this review but in the sections that follow, a brief description and discussion of each melter technology is provided, along with the operating experiences. The information presented here has been extracted from Erich and Overcamp (1996), Overcamp (1995), Overcamp et al. (1996), and Marra et al. (1996a).

9.1.1 Envitco EV-16 Melter

The Envitco EV-16 is a high-temperature, joule-heated melter that uses four molybdenum side-electrodes. This is the same melter and offgas system that was used by Envitco in the Hanford LLW vitrification test program discussed in section 7.1. In addition to the Hanford program, vitrification tests were conducted for other waste management programs as shown in table 9-1.

A significant amount of devitrification was observed in the Oak Ridge West End Treatment Facility and the RFP precipitate sludge campaigns. This was attributed to relatively high concentrations of calcia which resulted in the formation of wollastonite ($CaSiO_3$) phase having a melting temperature of 1,800 °C. The devitrification caused extreme difficulties in discharging glass from the melter. It is recommended that, for calcium aluminosilicate glasses, the calcia concentration should not exceed 18 percent. A complete characterization of the glass is warranted before processing waste through the melter.

Severe corrosion of the molybdenum electrodes was observed after the SRS M-Area and RFP campaigns. The electrodes lost about 10 cm (4 in.) of their length during testing. Both high temperatures and reducing conditions resulted in alloying of electrodes with reduced metals. Nickel alloying was clearly evident. This warrants careful control of redox conditions in the melter and nickel contents in glass.

Table 9-1. Surrogate studies performed at Clemson University (Overcamp, 1995)

Surrogate Waste	Envitco EV-16	Stir-Melter WV-0.25	EPI Mark I
Ion exchange resins & high-level waste slurry	—	1	—
Savannah River Site M-Area sludge (dry feed)	4	1	—
Savannah River Site M-Area sludge (slurry)	1	1	—
Oak Ridge Reservation Y-12 West End Treatment Facility sludge	4	2	—
Rocky Flats Plant precipitate sludge	1	—	—
Los Alamos National Laboratory TA-50 precipitate sludge	1	—	—
Hanford high-sodium waste	1	—	—
Oak Ridge K-25 Plant B & C Pond sludge	1	—	—
Soil and debris	—	—	4

During one of the campaigns, four different refractory materials were used for the melter walls. These included an AZS sintered refractory, an AZS fused cast refractory, a high-chrome pressed refractory, and a chromium-aluminum-zirconium-silicate fused cast refractory. After the campaign, the AZS sintered refractory was heavily damaged near the electrode opening losing about 5-cm (2-in.) of 7.56-m (3-in.) thickness. The AZS fused cast, high-chrome sintered, and Cr/Al/Zr silicate showed about 2.2-cm (0.875-in.), 1.25-cm (0.5-in.), and negligible degradation, respectively.

Based on the above results, the authors recommend that either AZS fused cast or high-chrome refractories should be used in actual radioactive melter operations.

The melt rates were severely affected by (i) reactive offgassing and foaming, and (ii) sulfate salt formation in the high sulfate feeds. Dry feeding in the M-Area tests caused significant offgas line plugging. The plugging of offgas lines was attributed to the entrainment of relatively fine particles of the feed materials in the offgas line.

9.1.2 Stir-Melter WV-0.25

The stir-melter WV-0.25 is a joule-heated melter that uses an Inconel® alloy 690 chamber. A simplified melter schematic is shown in figure 9-1. This chamber has a square cross section with a melt surface area of 0.025 m^2 (0.27 ft^2) and a working depth of 0.3 m (1 ft). The melter has an Inconel® alloy 690 stirrer. The stirrer is driven by a 325-W variable speed motor at speeds up to 1,000 rpm. The impeller can be raised or lowered to optimize mixing. The stirrer and the chamber act as electrodes. A 10-kW power source is available for joule heating through the stirrer/chamber circuit. In addition, there are external

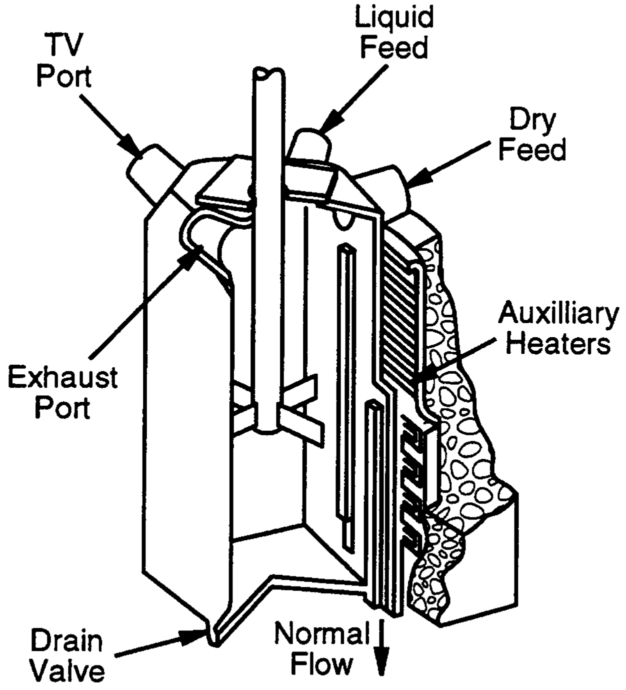

Figure 9-1. Stir-Melter WV-0.25 at Clemson University (Marra et al., 1996a)

resistance heaters with 7 kW power for startup and maintaining temperature during melting. The maximum operating temperature of the melter is 1,070 °C because of the melter construction material. The melt chamber has an internal "teapot" spout with an external drain tube. The melter has separate ports for dry feeding, slurry feeding, and other additives. The offgas system consists of a spray/ejector venturi, jet sparging scrubber, and a counter-flow packed tower for acid gas removal and neutralization. The vitrification campaigns are shown in table 9-1.

The operation of the stir-melter was limited due to the lower operating temperatures of the melter. Inconel® alloy 690 has a melting point of about 1,350 °C, but the creep rate increases with a decline in the elastic modulus above 1,100 °C. Therefore, a maximum use temperature of 1,070 °C was placed in the melter to avoid damage to its impeller and the melt vessel. Despite operation at 1,070 °C, the impeller was severely damaged. The bottom ring of the impeller was missing, and severe corrosion of the blades was evident. Large metallic drops were found on the bottom of the melter. Analysis of the melter after the failure indicated that, in addition to the reducing conditions, localized extreme temperatures (resulting from excessive power dissipation caused by a faulty controller) in the impeller caused severe degradation.

During the RFP campaign, waste containing high sulfur and activated carbon were processed. Inconel® alloy 690 under reducing conditions is susceptible to severe corrosion and failure from aggressive chemical attack, especially sulfidation; the operation of the melter in the presence of activated carbon increases the potential for extremely reducing conditions. Due to catastrophic impeller failure with the RFP feed, the campaign never extended beyond operational parameter studies.

Foaming and sulfate salt formation were much more severe than in the Envitco melter. At times, the glass drained from the melter, was foamy indicating the inability of the melter to remove foam from the melt. At times, the molten salt layer volatilized or became entrained with particulates in the offgas line. Significant offgas plugging problems similar to those of the Envitco system were observed in this system. This plugging severely impaired the melter performance.

As in the case of the Envitco melter, the high calcia feeds caused plugging of melter drains, foaming in the melter, and devitrification of glass.

9.1.3 Electro-Pyrolysis, Inc., DC Arc Melter

The Electro-Pyrolysis, Inc. (EPI) DC arc melter consists of a graphite crucible contained inside a sealed, water-cooled, atmosphere-controlled vessel. This melter has a circular cross section with a melt surface area of 0.085-m^2 (0.91-ft^2) and a working depth of 0.53-m (1.6-ft). The melter is capable of processing about 50-kg (110-lb) of feed per charge. The melter can be operated either in a cold-top or hot-top mode. Power at 100 kW is supplied through consumable electrodes. The melter has three ports, located 120 degrees apart, for installation of extra cameras, feed systems, or thermocouples.

Several test runs were made (Overcamp et al., 1996) on INEEL soils and South Carolina high-silica soil with fluxing agents but operational data or process upsets and issues were not discussed.

9.2 VITREOUS STATE LABORATORY AT THE CATHOLIC UNIVERSITY OF AMERICA

The VSL of the CUA has been operating a variety of joule-heated melters since 1985 and a radioactive system since 1987. The joule-heated melter systems installed range from production rates of 1-kg/hr to more than 1,000-kg/hr (2,200-lb/hr) and are innovative derivatives of the joule-heated systems for the HLW vitrification. CUA-VSL is extending the HLW vitrification systems that operate at 1,150 °C to high-temperature, joule-heated systems that operate up to 1,500 °C, by the use of new materials. Several melters installed and operated by CUA-VSL have been designed by GTS Duratek.

Some major accomplishments (Pegg, 1995) include: (i) the glass development as well as the melter and offgas test runs to support GTS Duratek M-Area mixed waste facility at SRS; (ii) glass development and melter and offgas test runs to support the MAWS demonstration conducted at the Fernald site; (iii) process development, and melter and offgas runs for DuraChem commercial nuclear power spent organic ion exchange resins; and (iv) development, characterization, and melter testing of glasses for the WVDP at West Valley.

9.2.1 High-Temperature, Joule-Heated Minimelter System

This high-temperature, joule-heated system is a scaled version of the melter installed at Fernald (section 6.1). Before the full-scale melter was installed at Fernald, this scaled version provided data on the performance of innovative designs incorporated in the melter chamber. Even though this minimelter has been successfully operated at the CUA-VSL for the last 18 mo for a variety of waste streams, the full-scale version at Fernald suffered a catastrophic failure and was shut down within 6 mo of operations as noted in section 6.1.

Similar to the Fernald melter, this melter consists of a center chamber separated by conductive ceramic bricks. The center chamber is used for melting waste glasses. The side chambers contain molybdenum rod electrodes immersed in benign glass to avoid oxidation. The surface area of the melting chamber is 194-cm^2 (30-in^2) with a volume of 2.95-L (0.78-gal.) for waste glass. The side chambers have a volume of 2-L (0.64-gal.). The melter can be operated between 1,150 to 1,350 °C. The offgas leaving the melter is successively introduced into a film-cooler, a water-spray quencher, a NaOH scrubber, and a mist eliminator. After the mist eliminator, gases are heated to reduce the relative humidity before entering the baghouse, where residual particulates are removed on bags precoated with diatomaceous earth. Finally, gases pass through a HEPA filter before being exhausted to stack.

The melter was operated to show the feasibility of melting feeds high in lead, barium, phosphorous and sulfur (Fu et al., 1996). The results indicated that the feeds containing up to 9 wt.% PbO, 5 wt.% BaO, 8 wt.% P_2O_5, and 12 wt.% SO_3 can be processed in the temperature range of 1,150 and 1,350 °C. The results also indicated that feeds with more than 5 wt.% SO_3 can produce excessive foaming events but with the addition of urea (a reducing agent) the number of foaming incidents was reduced. Urea was found to reduce sulfates to SO_2, decrease the concentration of NO_x, and produce a homogeneous product.

It should be noted that the use of urea in excessive amounts can promote significant reducing of the melt and result in the formation of conductive sludges that could cause premature failure of the melter. In addition, urea, when not present in stoichiometric amounts, can result in formation of ammonia in the offgas. The presence of ammonia and NO_x can be a major safety issue. Even though the minimelter runs did not indicate severe molybdenum, molydisilicide, or refractory corrosion, the full-scale melter failed due to excessive corrosion and erosion.

9.2.2 Duramelter® 100 Melter

The Duramelter® 100 is a joule-heated melter that uses Inconel® alloy 690 side electrodes (Bowan et al., 1994a). This same melter and offgas system was used by GTS Duratek in the Hanford LLW vitrification test program discussed in section 7.4. A simplified melter schematic is shown in figure 9-2. This melter has a square cross section with a melt surface area of 0.13-m^2 (1.38-ft^2) and melt volume of 49-L (13-gal.). The melter is lined with high-chrome refractory in the glass contact area. The contact refractory is backed up by AZS refractory and 95 percent alumina castable. The entire glass containment is housed in an interior Inconel® alloy 690 liner. A thick ceramic fiberboard is placed between the Inconel® alloy 690 liner and external melter shell. The melter has three drains; a bottom drain, a surface sulfate layer drain, and a side discharge riser with a pour spout for glass pouring. The glass pouring is initiated by an airlift mechanism. Multiple air bubblers are installed near the floor to enhance convection in the melt pool and increase production rate. The melter operates between 1,100 and 1,200 °C. The glass production capacity is 100-kg/day (220-lb/day).

Duramelter® 100 has been used for testing a variety of waste streams. A discussion on processing of the simulated Hanford high-sodium waste was provided is section 7-4. This melter was also used for processing radioactive Fernald Pit 5 sludge (containing as much as 25 percent fluorine as fluorides) as a part of the MAWS program. The offgas system for this testing for specifically designed to handle high fluoride content. A process schematic is shown in figure 9-3. The major offgas components are the quencher, which operates as a spray-drying wet scrubber, and a conventional wet scrubber. The hot offgases flow from the melter into the quencher. In the quencher, 2–3 M sodium hydroxide solution is sprayed and evaporated to aid in decreasing offgas temperature. Fluoride in the offgas reacts with sodium hydroxide to form sodium fluoride solid. The solids are collected at the bottom of the quencher and recycled back into the melter

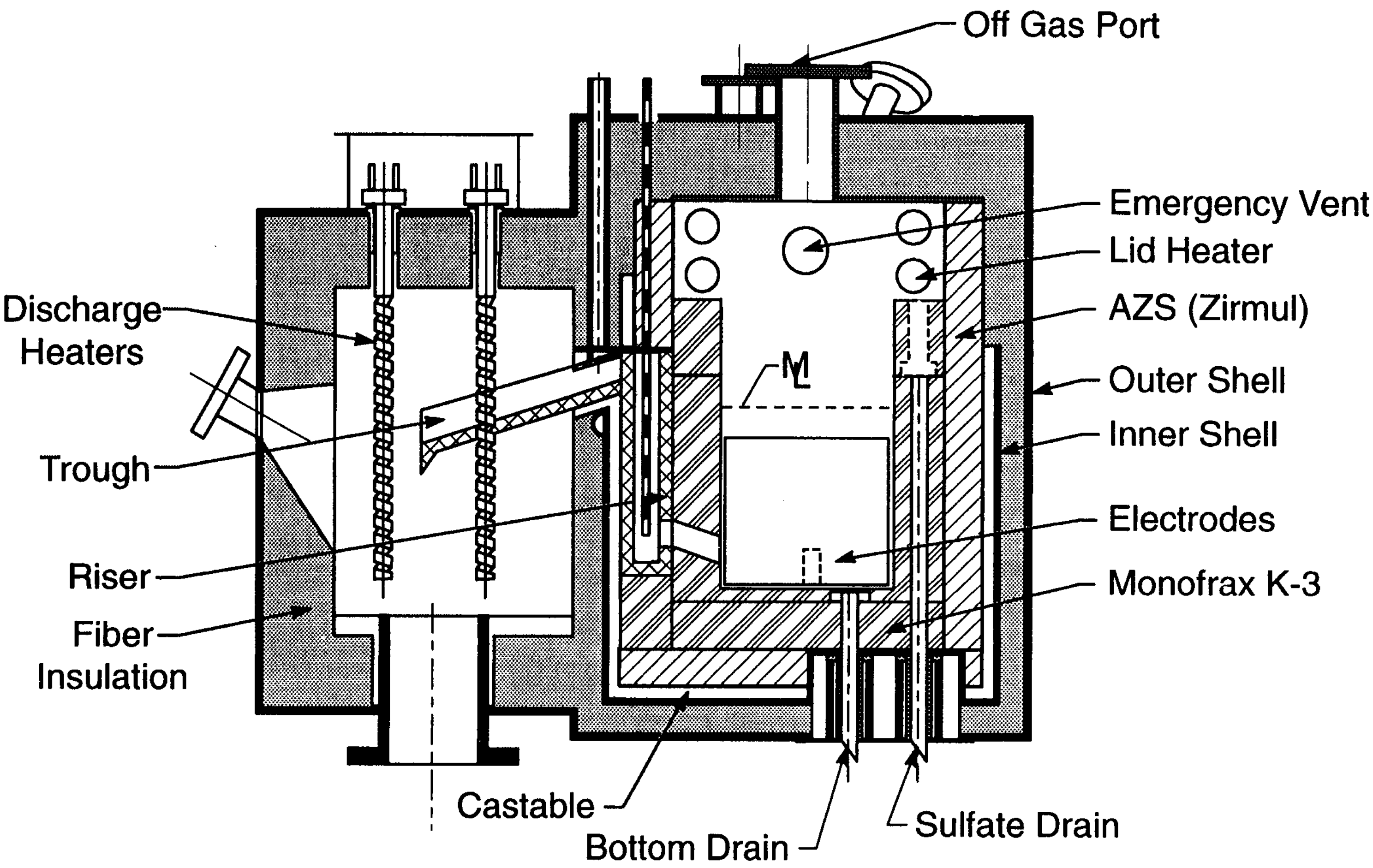

Figure 9-2. Duramelter® 100 melter schematic (Bowan et al., 1994a)

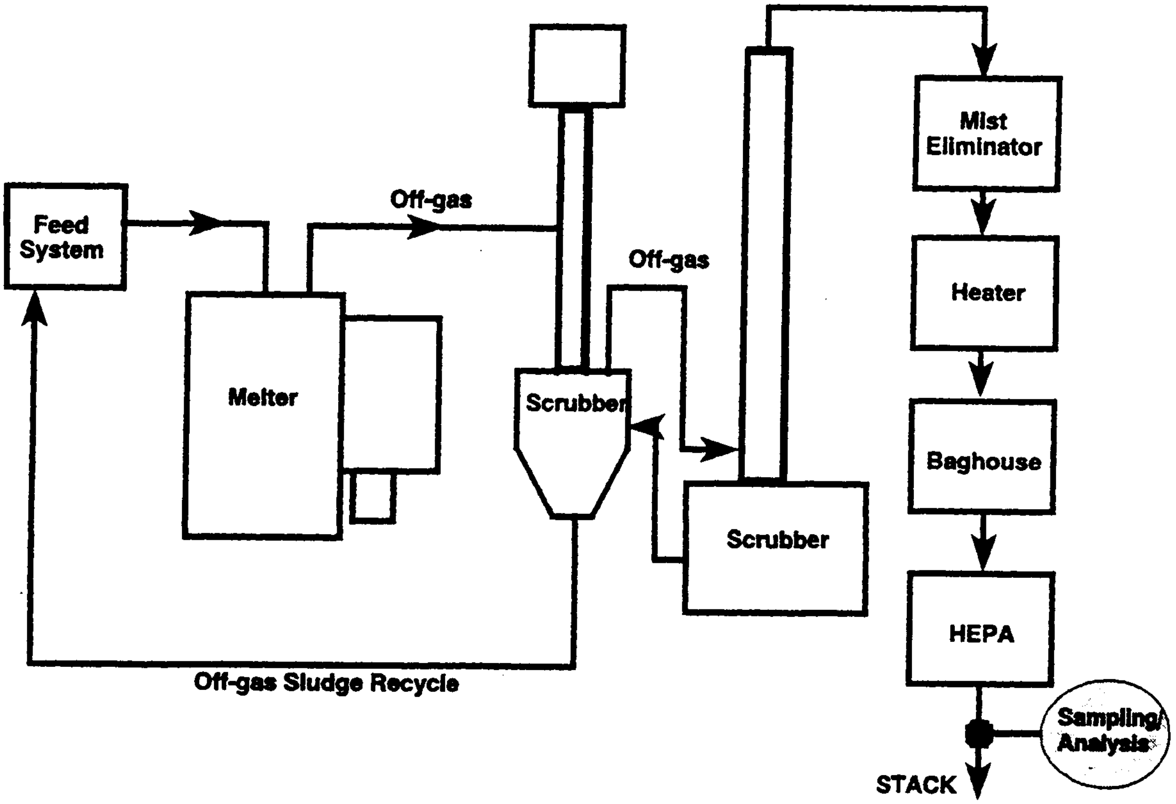

Figure 9-3. Duramelter® 100 process flowsheet (Bowan et al., 1994a)

through the feed system. The wet scrubber is a secondary cleaner that uses 0.1 M sodium hydroxide. From the scrubber, offgases pass through the mist eliminator, heater, baghouse, pre-filter, and a HEPA before they are released to the stack.

The performance data presented by Matlack et al. (1996) do not indicate any problems or issues related to the processing of the high-fluoride radioactive wastes. A Duramelter® 300, of similar design, was installed at the Fernald site under the MAWS program to vitrify Pit 5 radioactive sludges. No information is available on the performance of this melter.

9.2.3 Duramelter® 1000 (Asbestos Melter)

Another major pilot-scale melter system installed at CUA-VSL is a demonstration plant for the vitrification of the asbestos-containing wastes. This was the second of the two melter and offgas systems used by GTS Duratek in the Hanford LLW vitrification test program discussed in section 7.4.

The pilot-scale asbestos melter is a joule-heated melter that uses Inconel® alloy 690 side electrodes (Bowan et al., 1994b). A simplified melter schematic is shown in figure 9-4. The melter is lined with a 12.7-cm-thick (5-in.) layer of high-chrome refractory in the glass contact area. The contact refractory is backed up by a 15.2-cm-thick (6-in.) layer of AZS refractory and a 6.4-cm-thick (2.5-in.) layer of 95 percent alumina castable refractory. The entire glass containment is housed in a 0.64-cm-thick (0.25-in.) interior liner constructed from Inconel® alloy 690. A 10.2-cm-thick (4-in.) ceramic fiberboard is placed between the Inconel® alloy 690 liner and external melter shell. The melter electrodes are two pairs of 2.5-cm-thick (1-in.) Inconel® alloy 690 plates on the opposing walls of the melter. The melter has a bottom drain and a side discharge riser with a pour spout for glass pouring. Glass pouring is initiated by an airlift mechanism.

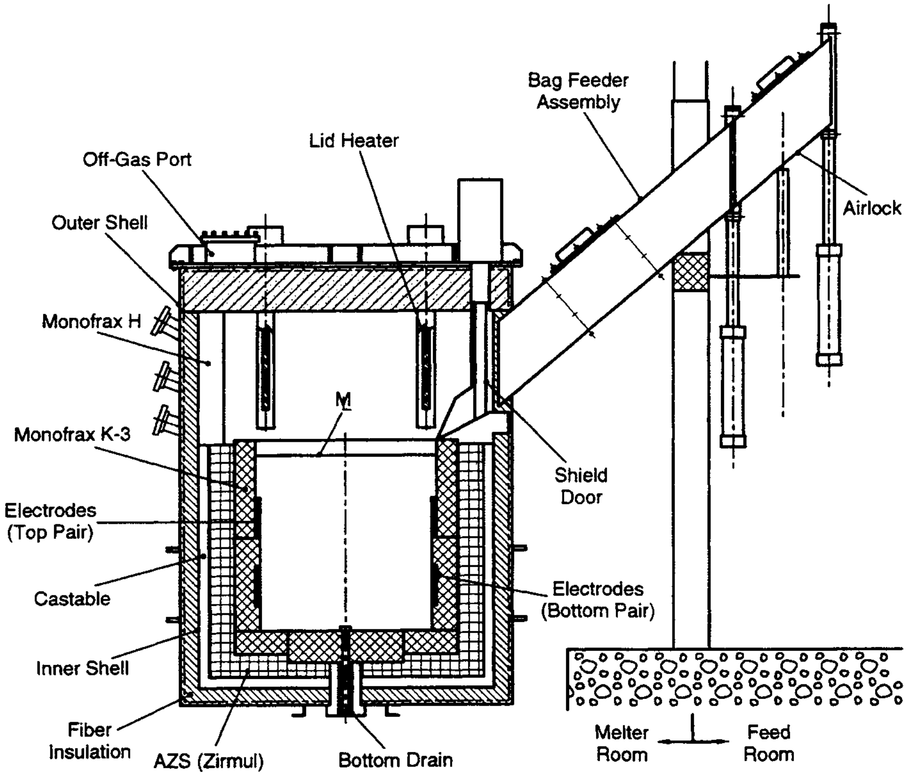

Figure 9-4. Duramelter® 1000 melter (Bowan et al., 1994b)

Multiple air bubblers, installed near the floor to enhance convection in the melt pool, increase the production rate. The melter operates between 1,100 and 1,200 °C. The glass production capacity is 900-kg/day (1,980-lb/day).

Asbestos wastes are typically contained in approved, multiple polyethylene bags in amounts not exceeding 22.5 kg. (50 lb). The wastes can contain wire, gypsum, cements, sections of steel pipes, water, and other debris collected during remediation. Large steel pipes are usually not fed to the melter. Figure 9-5 shows a process flow diagram for the asbestos waste vitrification. The melter receives these bags and feeds them directly along with some glass-forming chemicals. Organic components of the waste are oxidized and inorganic components are vitrified in the melter. Offgas, steam, and particulates from the oxidation and reaction processes are sent to an offgas treatment system. The offgas system consists of a water spray quencher in series with a packed bed scrubber. Following the packed bed scrubber is a mist eliminator and a multistage dry filtration system including HEPA. The residuals accumulated by the scrubber are recycled with the feed. Glass is discharged from the melter through either a bottom drain or a side exit to a riser-pour discharge system.

The information presented in Bowan et al. (1994b) does not indicate any problems or safety issues related to the processing of asbestos wastes. It is interesting to note that the Duramelter® 1000 was also used to convert about 2,000 kg of hazardous asbestos waste from the White House into glass.

9.3 PACIFIC NORTHWEST NATIONAL LABORATORIES

PNNL has been developing joule-heated ceramic lined glass melters since 1973. The first experimental, full-scale electric melter began operation in February 1977. The vitrification systems that have been operated at the PNNL include (i) Liquid-Fed Ceramic Melter (LFCM), (ii) Pilot-Scale Ceramic Melter

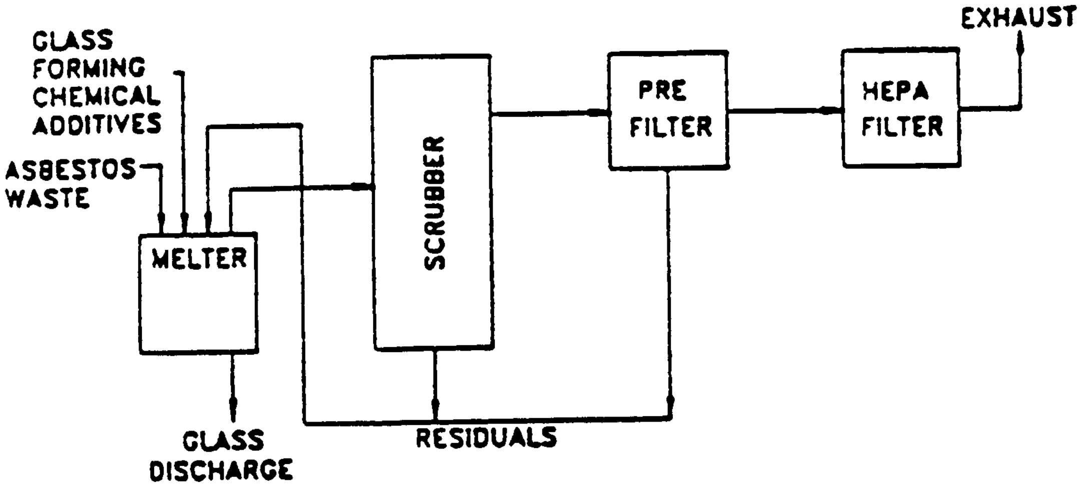

Figure 9-5. Duramelter® 1000 process flowsheet for asbestos processing (Bowan et al., 1994b)

(PSCM), (iii) Radioactive Liquid-Fed Ceramic Melter (RLFCM), (iv) Engineering-Scale Melter, (v) Research-Scale Melter, (vi) Small-Scale High-Temperature Melter, (vii) Pilot-Scale High-Temperature Melter, and (viii) DC Arc Melter.

A major thrust of research at PNNL has been on joule-heated melter systems. A summary of all the tests and melter research conducted at PNNL is beyond the scope of this report. However, the information relevant to this report, presented in the following sections, has been extracted from publications by Barnes and Larson (1981), Larson (1996), Holton et al. (1988), and Koegler (1987). Most of the discussion is focused on the RLFCM.

9.3.1 Radioactive Liquid-Fed Ceramic Melter

The fundamental design of the RLFCM is based on the successful designs of the PSCM and the LFCM. The pilot-scale RLFCM was designed, fabricated, and remotely operated in shielded cells from 1983 to 1987. Radioactive operations were initiated in October 1984. The operations were concentrated on testing vitrification flowsheets simulating wastes stored at the West Valley site and preparation of special isotopic heat and radiation dose canisters for the FRG. Radioactive operations were terminated in March 1987. The RLFCM consists of a melter system and supporting equipment for slurry preparation and an offgas treatment system. Figure 9-6 shows a schematic diagram of the vitrification process.

The feed preparation system consists of two tanks, each equipped with its own agitator system. Both the feed make-up tank and the melter feed tank have a volume capacity of 1,250-m^3 (330,000-gal.).

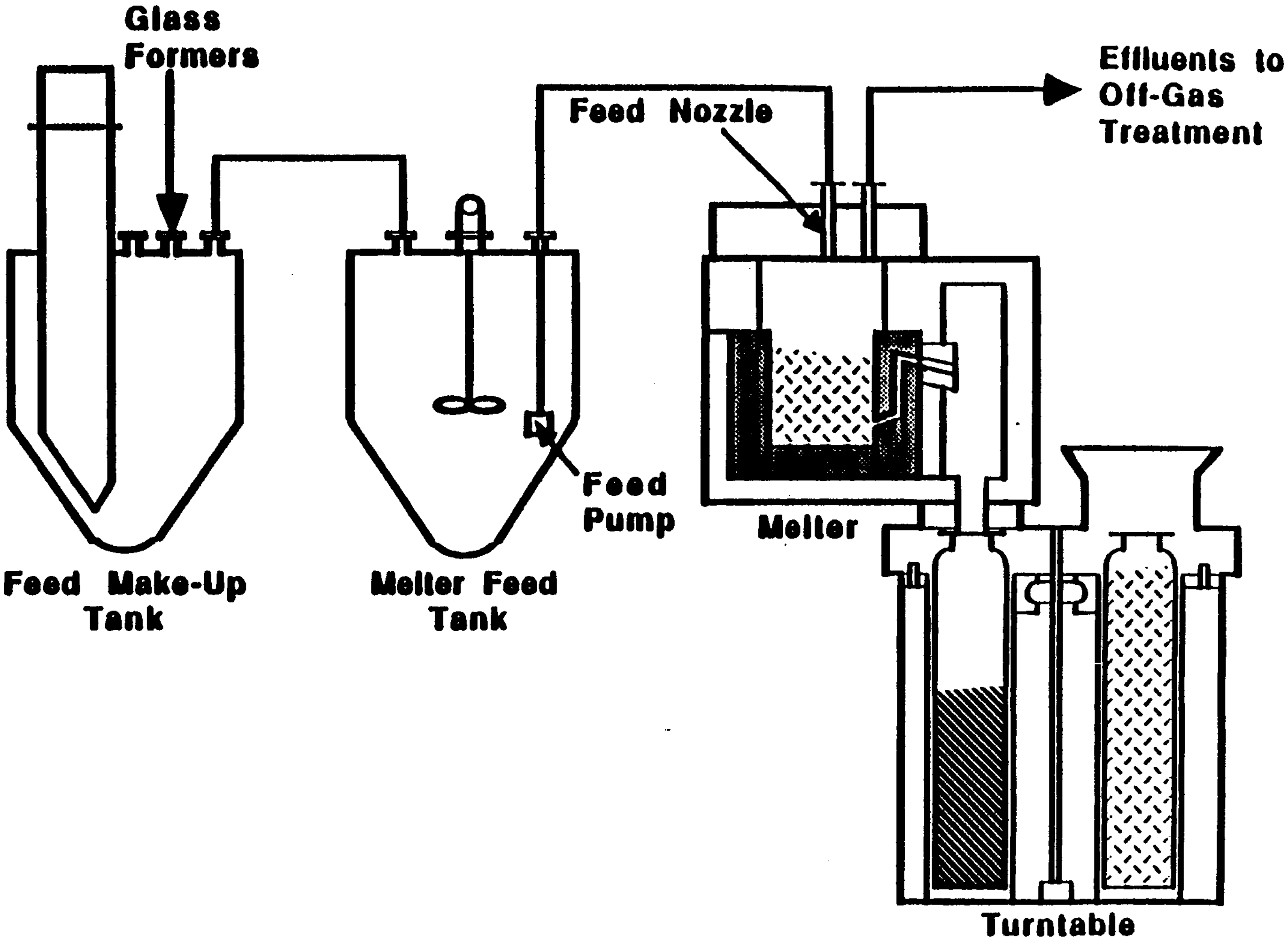

Figure 9-6. Process flowsheet for the radioactive liquid-fed ceramic melter at Pacific Northwest National Laboratories (Dierks et al., 1987)

Radioactive slurries are prepared in the feed make-up tank where radioactive waste is blended with glass-forming chemicals. The contents are allowed to fully mix before transferring to the feed tank. An air displacement pump is used to move the slurry through the feed line to a water-cooled feed nozzle located on the top of the melter.

The RLFCM is a joule-heated, ceramic-lined melter. A schematic of the RLFCM is shown in figure 9-7. The molten glass is contained in a high-chrome refractory. The melt cavity measures 0.61-m (2-ft) by 0.99-m (3-ft) with a nominal glass depth of 0.36-m (1.2-ft) and the nominal melt surface area is 0.6-m^2 (6.45-ft^2). The melter is designed to operate at a feed rate of 40-L/hr (10.6 gal.) and glass production rate of 20-kg/hr (44-lb/hr). The melt cavity contains two air-cooled Inconel® alloy 690 plate electrodes. The nozzles penetrating the melter lid provide access to the interior of the melter tank. Five 5.1-cm. (2-in.) nozzles are used for glass tank thermocouples, electrode surface thermocouples, refractory wall thermocouples, an airlift lance, and cold-cap thermocouples. Two 7.6-cm (3-in.) nozzles provide access for the water-cooled slurry feed nozzle and the melt level detection sensor. Two 10.2-cm (4-in.) nozzles provide an offgas port and plenum sampling package. One 12.7-cm (5-in.) nozzle is provided for a television viewing system. The melter is also equipped with various sensors for process control and interpretation of off-normal events. These include sensors for the glass weight factor and specific gravity, the melter plenum pressure, and seven sensors for monitoring the temperature of the molten glass at different levels. The temperature sensors were used to control the power to the melter, determine feeding conditions, and identify off-normal conditions. The melter plenum pressure sensor was used to indicate stability of the feed pump. The dip tubes were used for measuring melt level and specific gravity of the melt in the melter. The dip tubes needed replacement every 6 mo due to corrosion.

The canisters are stationed on a turntable. The turntable consists of a three-position motor-driven carousel located inside a containment vessel. Three canisters can be loaded on the turntable at a time. The glass level in the canister being filled is monitored by a gamma detection system. Once the canister is full, it is rotated from the filling position while an empty canister is rotated into the filling position. The glass level detection system was an indispensable tool for monitoring the glass level in the canisters. The system encountered several design problems that compromised its performance during initial operation, that were eventually corrected by out-of-cell modifications to the system electronics. The filled canister is allowed to cool, is removed from the turntable, covered, and transferred to another part of the process cell for decontamination by electropolishing and nondestructive characterization.

The offgas from the melter consists mostly of in-leakage air, water vapors, chemical decomposition products, and entrained particulates. The offgas is treated through an ejector venturi scrubber, a packed-bed scrubber/condenser, an evaporator/fractionator system, offgas heaters, HEPA filters, and process offgas blowers. The decontaminated offgas is then discharged to the stack.

During initial radioactive operations, the reliability of the delivery system to feed the melter adequately was one of the major concerns. Too-high or too-low feed rates could result in major off-normal conditions in the melter. A series of modifications were made to the feed make-up tank, the feed tank, the feed transfer pump, the feed transfer line, the feed flow rate indicator, and the melter feed nozzle to improve the reliability of the system. In addition, both the feed make-up tank and the feed tank exhibited erroneous weight and specific gravity readings from the conventional dip tube assembly. The agitating system compromised both the weight and the specific gravity indications. In addition, the dip tubes plugged frequently as slurry evaporated at the tips. Clearing the dip tubes required prolonged soaking, followed by water flushing through the purge air inlet. The design and installation of replaceable flange units resolved

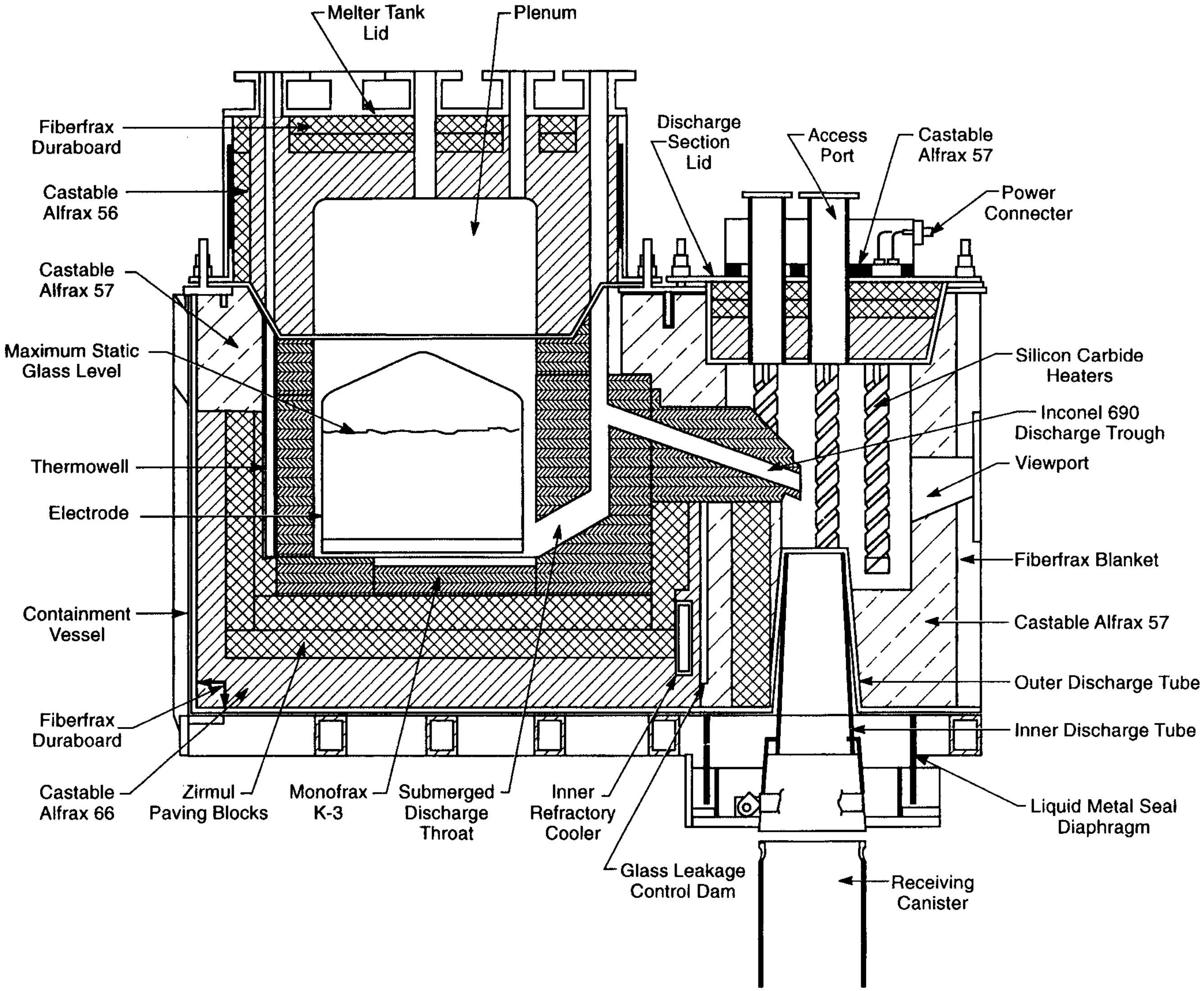

Figure 9-7. Sectional view of the radioactive liquid-fed ceramic melter system (Dierks et al., 1987)

the problem. Also, the sensitivity of the slurry flow sensor in the cell was compromised due to high-radiation fields. Special radiation-hardened components were required to operate the sensors accurately.

During radioactive operations, typical off-normal conditions included bridging of the cold-cap and foaming in the melter. The foaming incidents were detected mainly by the melter specific gravity sensor and glass temperatures near the melt surface. The cold-cap bridging was detected by the glass weight factor sensor. The weight factor, which is measured as a pressure, increases rapidly and becomes very unstable with the formation of a cold-cap bridge. The weight-factor increase is a direct result of reaction gases pressurizing the melt. The molten glass exits the melting cavity through a hole (throat) in one of the side walls near the floor of the melter. The glass pouring is activated by bubbling air via the air-lift lance into the riser tube. The riser tube connects the throat to the discharge trough. As the bubbles are introduced, a decrease in the pressure head in the riser tube allows the glass from the melt cavity to push up the riser tube. After the glass leaves the riser, it flows down the Inconel® alloy 690 discharge trough into the receiving canister. Glass flow to the canister is controlled by the airflow rate in the riser.

During one of the runs, bridging of the cold-cap caused pressurization under the cold-cap, resulting in an uncontrolled glass discharge that not only completely filled the canister in one pour but caused some glass overflow onto the discharge floor. This eventually acted as an anchor for forming a glass plug in the discharge cavity on subsequent pours. After the glass had cooled in the discharge cavity, a rotary masonry drill with extended shaft was used to penetrate the glass plug 45.7 cm (18 in.) deep with successively larger drill bits. This was followed by heating the discharge cavity by a silicon carbide heater in a mild steel shroud. The heater was lowered into the hole to completely melt the glass plug in the discharge tube. The discharge section is heated with six silicon carbide electrical-resistance heaters, arranged in a circular pattern around the discharge trough, to maintain glass in a molten state while it is discharged into a stainless steel canister. The discharge heaters failed on a regular basis. The failure was attributed to electric arcing caused by condensation of conductive volatile salts on the non-heated zone of the discharge heaters. The failures were minimized by increasing the nominal spacing between heaters.

Offgas plugging was frequent during the initial operations. The plugs occurred in the offgas line between the melter and the inlet to the venturi scrubber. Monitoring the plug was difficult because a pressure drop in the offgas line does not occur until the line is more than 80 percent plugged. Also, the pressure spikes caused by the cold-cap bridging and foaming interfered with the monitoring of offgas plugging. Plugging was virtually eliminated by designing an offgas reamer, a cleaning device that rotates a shaft connected with four stainless steel chains. The centrifugal force generated from the chains is enough to clear salt deposits in the offgas line. The lessons learned from the RLFCM operations proved to be very useful for other HLW sites in optimizing their designs, as well as process flow sheet.

9.3.2 Liquid-Fed Ceramic Melter

The LFCM was designed to vitrify simulated high-level waste (Barnes and Larson, 1981). The melter operated from February 1977 to February 1980, and processed both slurry and dry feeds. The LFCM produced 80,000-kg (176,000-lbs) of glass from 54,000-kg (118,800-lb) of calcine plus glass formers and 19.0-m^3 (671-ft^3) of slurry feed.

During the 3-yr service period, the LFCM was used to develop ceramic lined melter technology, establish melter operating parameters, and study processing characteristics of glass formulations.

In February 1980, the melter was shut down and a comprehensive investigation was conducted to determine the performance of melter materials. The investigation indicated that the service life of the melter can be increased beyond 3 yr. The most important factor for extended life is adequate accommodation of thermal expansion properties of the construction materials.

9.3.3 Pilot-Scale Ceramic Melter

The PSCM operated for 5-1/2 yr between 1978 and 1985, producing 57,000-kg (125,400-lb) of glass.

The melter was shut down due to the corrosion of tank refractories and Inconel® alloy 690 electrodes (Koegler, 1987) in 1985 and was rebuilt with an improved lid, electrode, and overflow drain designs. A portion of the lid had fallen into the tank due to inadequate vertical support at the walls and failure of anchors welded to the lid. The anchors were replaced by more corrosion-resistant ceramic anchors and Inconel® alloy 690 clips. The electrodes failed at the upper bus connection and showed severe corrosion at the glass melt interface. Corrosion may have been due to a combination of oxidizing material buildup and mechanical stress at the welds. The overflow trough was modified because of corrosion at the pour tip. The ceramic components were replaced with an Inconel® alloy 690 trough and dam to increase corrosion resistance and prevent glass seepage.

10 PILOT-SCALE VITRIFICATION SYSTEMS FOR HIGH-LEVEL WASTE PLANTS

10.1 SCALE VITRIFICATION SYSTEM AT THE WEST VALLEY DEMONSTRATION PROJECT

At the WVDP, the SVS-III verification tests were conducted, at only one-seventh scale, between February and August 1995 as a supplemental means to support the vitrification process flowsheet (Jain et al., 1997). The principal reason for having minimelter tests was to optimize and develop techniques to control the vitrification process during radioactive operation. The need to operate the SVS-III prior to radioactive vitrification operations was a result of the changes in the vitrification process flowsheet that have occurred since the conclusion of the full-scale non-radioactive campaign.

The three primary areas of interest during the SVS-III testing were the redox state of the molten and solid glass, feed make-up strategy, and establishment of a statistical approach to the remote glass composition analysis. The amount of oxygen available to the glass melt, as reflected in the ferrous/ferric (Fe^{+2}/Fe^{+3}) or redox ratio, affects the melting process. Too much oxygen causes the melt to foam, at best slowing production, at worst plugging the offgas system. Too little oxygen causes oxides such as Fe_2O_3, NiO, and MnO to convert to metallic form and become suspended in the molten glass. The metal precipitate can eventually build-up to short out the electrodes, thus permanently damaging the melter. During nonradioactive operations and prior Scale Vitrification System runs, an empirical relationship was developed between the redox ratio and the amount of sugar, nitrates, and total solids in the feed. The SVS-III runs were designed to test that relationship and provide assurance that a similar relationship exists for the melter during radioactive operations. If it can be demonstrated that the redox ratio can be predicted from an analysis of the feed (i.e., sugar, nitrates, and total solids), then it will not be necessary to determine the redox ratio by converting feed into glass and analyzing for the Fe^{+2}/Fe^{+3} ratio prior to feeding the melter. This approach will significantly reduce feed make-up cycle time.

Various aspects of the feed preparation strategy were investigated during the SVS-III. These included the waste concentration cycle, the use of antifoaming agents in glass-formers, the addition of nitric acid either during glass-former preparation or directly to the waste, the addition of sodium metasilicate, and laboratory analysis of the feed materials.

For feed analyses, sampling is a critical operation. Because the chemical analysis of the feed slurry provides assurance in producing the target glass composition, the sampling process must provide a representative sample of the material being fed to the melter. It is known that foaming of the slurry and the design of the sampling system both affect the ability to obtain a representative sample. Resolving the problems in acquiring and analyzing representative samples was one of the goals of the SVS-III.

The SVS-III, the third Scale Vitrification System at the WVDP, is a pilot-scale, joule-heated, slurry-fed, nonradioactive vitrification system that is independent of the full-scale radioactive vitrification system. It incorporates several operational features of the full-scale system. The SVS-III includes its own slurry preparation system, offgas treatment system, and distributive control system, similar to those installed on the full-scale vitrification system (section 3.1).

The SVS-III vitrification process schematic is shown in figure 10-1. The process starts by mixing and preparing waste simulant using the slurry mix tank (SMT). The chemicals are added to the SMT using either the Vac-U-Max® system or a liquid pump. The Vac-U-Max® is a pneumatic device for transfer of granular materials. After simulant preparation is complete, it is sampled and analyzed. While the sample analysis is in progress, waste simulant is transferred via a grinder to the feed hold tank (FHT) where it is concentrated to maximize the percent of total solids (% TS) in the waste. The addition of sodium metasilicate to the waste simulant helps to maximize the % TS. The contents are concentrated at approximately 100 °C using steam coils. After concentration, the simulant is allowed to cool to room temperature.

Based on the waste simulant analysis, the amounts of glass-forming chemicals needed to produce a target glass composition are calculated. The glass formers are then added to the SMT using the Vac-U-Max® liquid pump. The completed glass-former batch is sampled and analyzed. After the waste and glass-former analyses are combined, and the results indicate a mix having the composition within the target region, the glass formers are transferred to the FHT using the grinder. The combined slurry is sampled in the FHT and analyzed for elements, NO_3^- , TOC, density, and % TS. Based on the TOC, NO_3^-, and % TS, sugar is added to the FHT and mixed. The mixture is again sampled to ensure the proper NO_3^-/TOC ratio. If the ratio is within the test parameters, the feed is transferred to the MFT. Slurry from the MFT is metered into the melter and processed into glass. Both glass and vapors exit the melter as a result of the processing. Glass is poured into a canister beneath the melter, and vapors go through the SVS-III offgas treatment system.

10.1.1 Feed Preparation System

All free-flowing powders were transferred to the SMT using the Vac-U-Max®. Powders were typically delivered in 0.21-m^3 (55-gal.) drums. These drums were positioned on a calibrated scale that controlled the amount of feed to the SMT based on loss in weight. A pneumatic conveyor pickup wand placed in the drums provides the means of transport. The powder was picked up by the vacuum in the wand and discharged by a solid separator stationed immediately above the SMT. The collection hopper, transfer lines, and filter are made of stainless steel to ensure chemical purity and to make cleaning easier. The flexible portion of the wand is made of polyethylene.

Liquid chemicals were handled using a similar drum and wand system set on calibrated weighing scales. Chemical resistant pumps are employed to transport the liquids from the drums to the SMT. To prevent overflow, the SMT and the FHT have high-level alarms that are interlocked to the pumps feeding them. The SMT is a 1.89-m^3 (500-gal.), 304-L jacketed stainless steel tank equipped with a Chemineer® agitator and internal heating and cooling coils. The tank is vented by a separate offgas system that filters the offgas first before discharging it to the atmosphere via a 5-hp fan; it is capable of pushing 200 SCFM of air. The SMT ventilation system is skid-mounted and includes a filter and a slidegate damper to control airflow. The SMT fan maintains a slight vacuum on the SMT to aid in filling and in keeping dust and nuisance vapors in the immediate area to a minimum.

The feed preparation cycle is designed so that the only chemical reaction that takes place in the SMT is acid/base neutralization. Chilled water is run through the jacket to absorb the heat produced in the neutralization process. Chemical additions to the SMT are made through liquid transfer, dry powder transfer, or portable nitric acid 0.21-m^3 (55-gal.) drum transfer lines. Chemical transfers out of the SMT to the FHT are routed through a grinder to ensure a maximum particle diameter of just under 50 μm in the slurry. The FHT is a 2.8-m^3 (740-gal.), 304-L semi-jacketed, stainless steel tank equipped with a Chemineer® agitator and internal heating and cooling coils. The FHT is maintained under negative pressure controlled by the

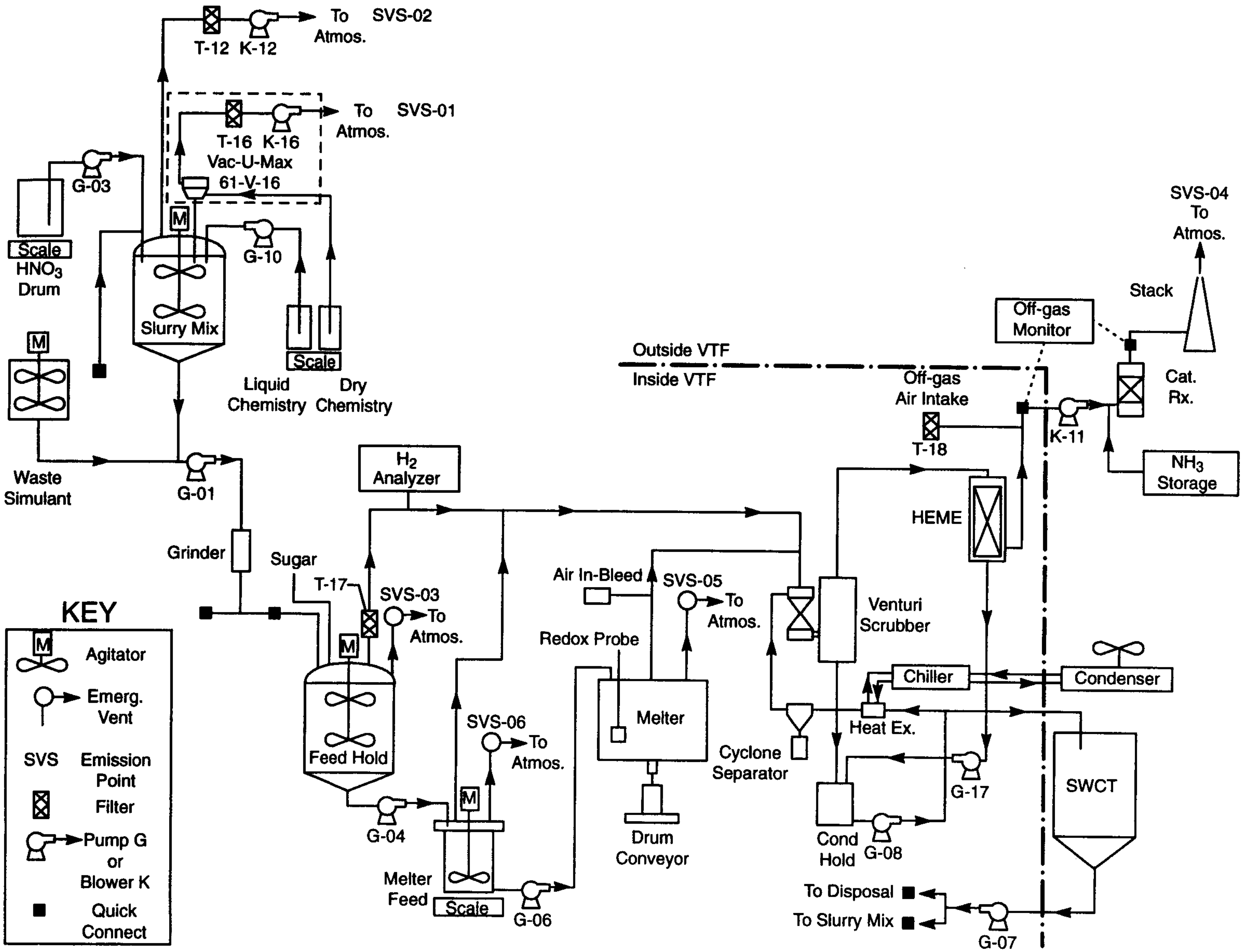

Figure 10-1. Scale Vitrification System III vitrification process schematic (Jain et al., 1997)

offgas system. This tank is utilized for boiling the waste simulant, mixing the waste simulant with the glass formers, and adding sugar to obtain the desired carbon-to-nitrate ratio. After verification and approval by sample analysis, the melter-fed slurry is transferred from the FHT to the MFT.

10.1.2 Vitrification System

The MFT is a 0.28-m^3 (74-gal.), 304-L stainless steel tank equipped with an agitator and a peristaltic pump. The peristaltic pump provides the feed to the melter at a constant flow rate through a water-cooled feed nozzle. The melter feed pump has a variable frequency drive that gives it the ability to manually control the feed rate to the melter. The SVS-III melter is capable of simulating the operations of the VF melter. It was built with one-seventh the surface area [0.325-m^2 (3.5-ft^2), 0.46-m (1.5-ft) by 0.71-m (2.3-ft), with a maximum pool depth of 0.2-m (0.6-ft)] and one-fourteenth the volume [62-L (16.4-gal.) maximum capacity] of the VF melter. This allows the SVS-III melter to reach steady state much faster and have a quicker volume changeout.

The SVS-III melter is a simple rectangular geometry tank, straddled by two paddle-shaped Inconel® alloy 690 electrodes. Above the glass pool is a set of four plenum or lid heaters. These heaters are silicon carbide resistance heaters centrally located within Inconel® alloy 690 sheaths. The plenum heaters are used during startup to raise the temperature of the glass surface until it becomes conductive enough for the electrodes to become productive. Once the glass is hot enough (~ 700 °C), an electric current is passed through the electrodes. The resistance to the electric flow by the contents of the melter creates the heat required to melt the glass. Glass is discharged from the melter through a single riser activated by an airlift lance. The glass flows down an Inconel® alloy 690 trough and into a 1.1-m^3 (290-gal.), stainless steel drum. The discharge chamber around the trough is heated by six silicon carbide elements. The molten pool of glass is contained by a Monofrax® K-3 (Cr/Al) refractory, backed by a Zirmul® (Al/Zr/Si type refractory), and an Al_2O_3 castable. A single discharge orifice exits the melter cavity into the Inconel® alloy 690 riser. Temperature in the melter is monitored in four primary areas: the discharge chamber, main pool, plenum area, and lid heater sheaths.

A 1.1-m^3 (290-gal.) drum is mounted on a chain-driven conveyor and moved under the melter discharge port. With a Fiberfrax gasket around the perimeter of the drum lip, the sealing bellows can be extended to press firmly around the drum, sealing it to the discharge chamber. The seal maintains the vacuum integrity of the melter. Glass is discharged into the drum in increments of approximately 7- to 8-L (1.8- to 2.1-gal.) each. The level of glass in the drum is monitored from the drum exterior using surface temperature indicators and an infrared pyrometer for backup. When full, the bellows is lifted from the drum, and the drum is moved out. Once the drum is out of the way of the bellows, a plate cover can be slid under the bellows to curb heat loss and air in-leakage.

10.1.3 Offgas Treatment System

The offgas treatment system provides a controlled negative gauge pressure for the FHT, MFT, and melter. It is operated in two distinct modes depending on whether feed is being prepared or the melter is processing slurry. The equipment is sized so that it will not support simultaneous operation. The volume of airflow is constant for both modes. An air in-bleed in the melter offgas line is used to control the pressure in the melter and the FHT while the offgas treatment system is operating.

Offgas treatment is required to mitigate the effects of temperature, NO_x formation, and particulate generation. A venturi scrubber with cyclonic separator quenches the offgas and removes large particulate matter. The offgas is then sent through the HEME to remove unwanted mist and particulates greater than submicron size. The water from the scrubber is collected in the condensate hold tank. It is cooled and filtered before being reused in the scrubber. Excess accumulations of scrubber water are stored in the scrubber water collection tank. This water is either used in the SMT during feed preparation activities or disposed of off site. A skid-mounted, offgas blower provides the vacuum necessary to pull the vapors from their origin to the NO_x reactor. The blower is a 10-hp, rotary positive displacement type made with stainless steel wetted parts. The selective catalytic reduction (SCR) process reduces NO_x in the offgas to nitrogen and water. The offgas is first heated to 300 °C using natural gas in a combustion chamber. NH_3 is then added to the offgas before it is passed through a fluidized bed of zeolite that has been treated with a catalyst. The effluent comes out the top of the SCR and enters the atmosphere from the stack. The offgas is sampled for NO_x concentration before and after the reactor in order to determine reactor efficiency and control NH_3 usage.

10.1.4 Process Issues and Upsets

Based on the results of this program, it was determined that there is a lower limit that separates a region of predictable oxidizing behavior in the glass melt from a region where small changes in the sugar/nitrates concentrations in the slurry have large effects on the redox state of the glass product. The SVS-III test series successfully demonstrated that a glass product with acceptable composition can be made consistently from a slurry recipe incorporating waste simulant and glass-former components. In addition, melter operation parameters such as feed rate, cold-cap coverage, glass melt and plenum temperatures, and melter power were controlled successfully to provide steady state operating conditions during the melter test runs.

The SVS-III melter exhibited irregularities in glass pours similar to the WVDP production melter, including erratic flow and glass buildup at the bottom of the discharge cavity. Unlike the WVDP production melter, SVS-III has only one discharge section. The glass leaked from the main melt chamber to the discharge section during the middle of the SVS-III test campaign. The melter was shut down several times to clear the glass blockage in the discharge section caused by the leak. Detailed examination revealed that the seal welds that held the pour spout to the dam (i.e., the vertical Inconel® alloy 690 wall that separates melting chamber and discharge chamber) had failed.

10.2 INTEGRATED DEFENSE WASTE PROCESSING FACILITY MELTER SYSTEM AT THE SAVANNAH RIVER SITE

The IDMS is a pilot-scale, non-radioactive VF designed to support the startup and operation of the HLW radioactive processing at the DWPF. The IDMS consists of a one-fifth scale feed preparation system and a one-ninth scale melter with its associated feeding and offgas treatment systems (Ritter et al., 1991). The IDMS operations were started in June 1990.

Part of the IDMS operating plan was to develop a process control strategy for the DWPF (Jantzen et al., 1993), study the behavior of noble metals in the melter (Hutson, 1994), and perform materials evaluation under processing conditions (Imrich and Jenkins, 1996). The IDMS consists of two major systems: the feed preparation system, and the melter and offgas treatment system.

10.2.1 Feed Preparation System

Figure 10-2 shows a schematic of the IDMS feed preparation system. The system consists of a SRAT, a process water condenser, a mercury decanter, and a chilled water condenser. The SRAT is equipped with an agitator, heating and cooling coils, and an air line that enters through a side port for purging the vapor space. Unlike DWPF, which has two tanks for processing feeds, IDMS uses only one tank (SRAT) to process feeds. The process water condenser operates between 25 and 50 °C. The condensate passes through the mercury decanter and then either back to the SRAT during total reflux or to a condensate tank during concentration. The mercury decanter is designed to collect elemental mercury in a sump for subsequent removal from the process. The noncondensible offgases, after leaving the process water condenser, pass through a chilled water condenser, which is designed to reduce the dew point of the offgas to 10 °C to minimize the release of mercury to the atmosphere. Prior to entering the chilled water condenser, vent streams from several other air-purged tanks also enter the offgas system.

10.2.2 Vitrification System

Figure 10-3 shows a schematic of the IDMS melter and offgas system. The melter system consists of the melter, MFT, and a melter offgas system. The IDMS melter, as shown in figure 10-4, is a refractory lined, cylindrical tank with an inner melt pool diameter of 0.61-m (2-ft) and melt pool depth of 0.69-m (2.3-ft). The melt pool surface area is one-ninth that of the DWPF melter. An upper and lower pair of diametrically opposed Inconel® alloy 690 electrodes provide a total of about 35 kW of power to maintain a glass pool temperature of 1,150 °C. Average glass production rate is approximately 11.3-kg/hr (24.9-lb/hr).

Melter feed is slowly fed through a narrow tube and is sprayed on top of the cold-cap. Due to the high temperature in the melter plenum (800 °C), most of the water is immediately evaporated. The more volatile organics are converted to CO, CO_2, and H_2O. Most of the nitrates and formic acid react in the cold-cap and define the redox condition in the melt. Eventually all reaction gases exit through the offgas tube.

10.2.3 Offgas Treatment System

The purpose of the offgas system is to maintain a slightly negative pressure in the melter plenum, provide an adequate airflow for combustion in the plenum (which is maintained at about 800 °C), treat offgases to remove condensibles and particulates, and provide vacuum required to initiate and control the pouring of glass. The offgas system has an offgas film cooler to reduce deposits at the entrance to the offgas system, a quencher (venturi scrubber) to cool offgas and remove large particulates, an OGCT to disengage the liquids and gases, a two-stage SAS to remove submicron particulates, a condenser to reduce the dew point to 10 °C, a HEME to remove mists and particulates, HEPA filters (including preheaters) to remove trace particulates, and a blower.

10.2.4 Process Issues and Upsets

In order to demonstrate the DWPF process control and product verification strategy, the IDMS was operated in three discrete batches using simulated waste streams (Jantzen et al., 1993). In these three test runs, all methodologies that were developed for use during radioactive operations for process control and product verification were followed. Results indicated that, by applying proper process control measures, DWPF can produce an acceptable glass product.

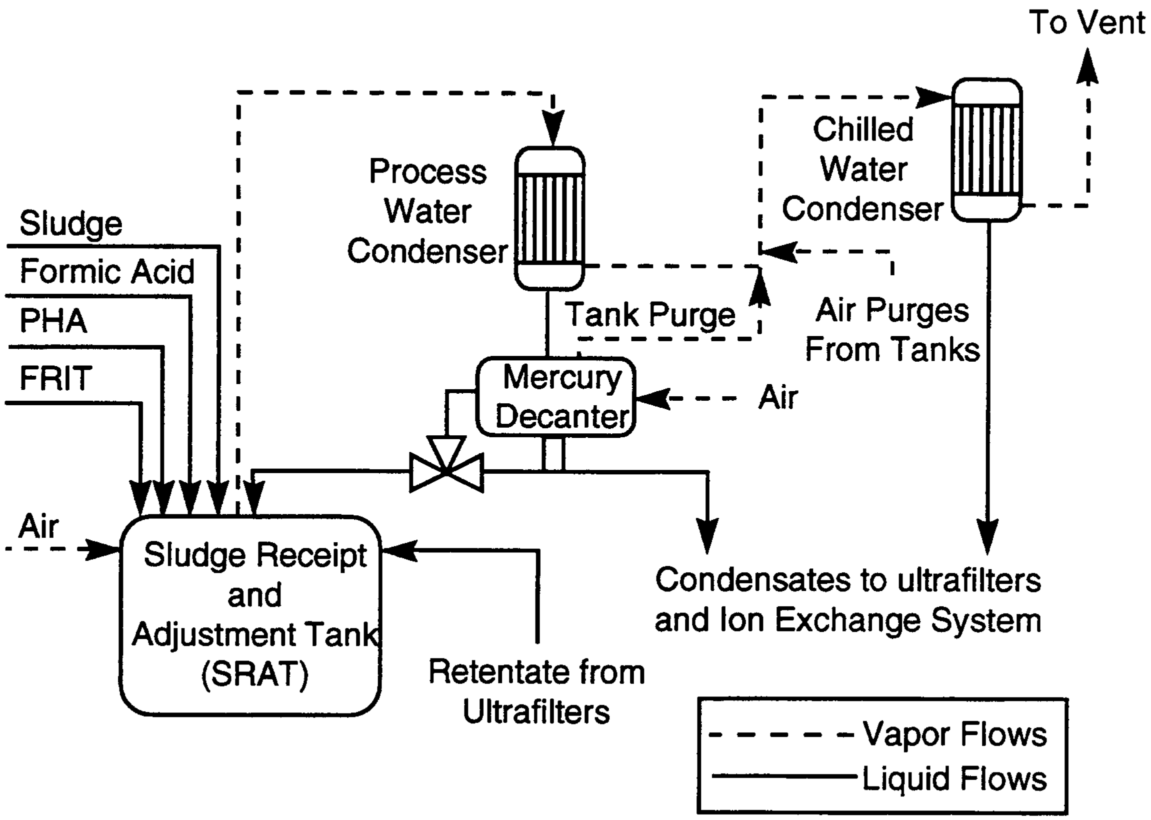

Figure 10-2. Integrated DWPF melter system and feed preparation flowsheet (Ritter et al., 1991)

Waste and waste simulants processed in the IDMS, as of March 31, 1993, included three types of SRS waste simulant [blend, HM (high aluminum waste at SRS), and PUREX], one type of Hanford waste simulant, and neutralized current acid waste containing noble metals (Hutson, 1994). A total 15.68-kg (34.5-lb) of Ru, 5.73-kg (12.6-lb) of Pd, and 3.12-kg (6.9-lbs) of Rh were introduced into the melter. The IDMS floor samples were routinely analyzed and monitored along with electrical characteristics. The analyses of the IDMS floor samples indicated the presence of large clusters of ruthenium oxide needles, Rh oxides, spinels, metallic Pd, and Pd tellurides. The electrical characteristics of the IDMS melter also showed a response to this deposition of conductive material. After about 550 hr of operations, the ratio of upper melt pool resistivity to that of lower melt pool resistivity quickly increased. This increase happened at about the same time that the melter floor samples revealed a significant accumulation of conductive material. This ratio could be used as an effective measure of conductive material on the melter floor.

In November 1994, test coupons were placed in the IDMS plenum and exposed to offgas components (Imrich and Jenkins, 1996). Fifteen different nickel and cobalt base alloys, including N06690 (this is the Inconel® alloy 690 without the trade name) were exposed for 5 mo to corrosive vapors and molten glass. During the 5 mo of testing, one melter feed/pour campaign was performed. Process conditions included temperatures exceeding 900 °C and processing of wastes containing formates, halides, sulfates, phosphates, nitrates, and mercury. Sulfates were less than 1,000 ppm and chlorides were less than 3,000 ppm. The results of the study indicated that the alloys with substantial cobalt content did not perform as well as nickel-based alloys. Results also indicated that alloys containing Cr concentrations greater than 25 percent with additions of Si or Al performed better than the N06690 reference material.

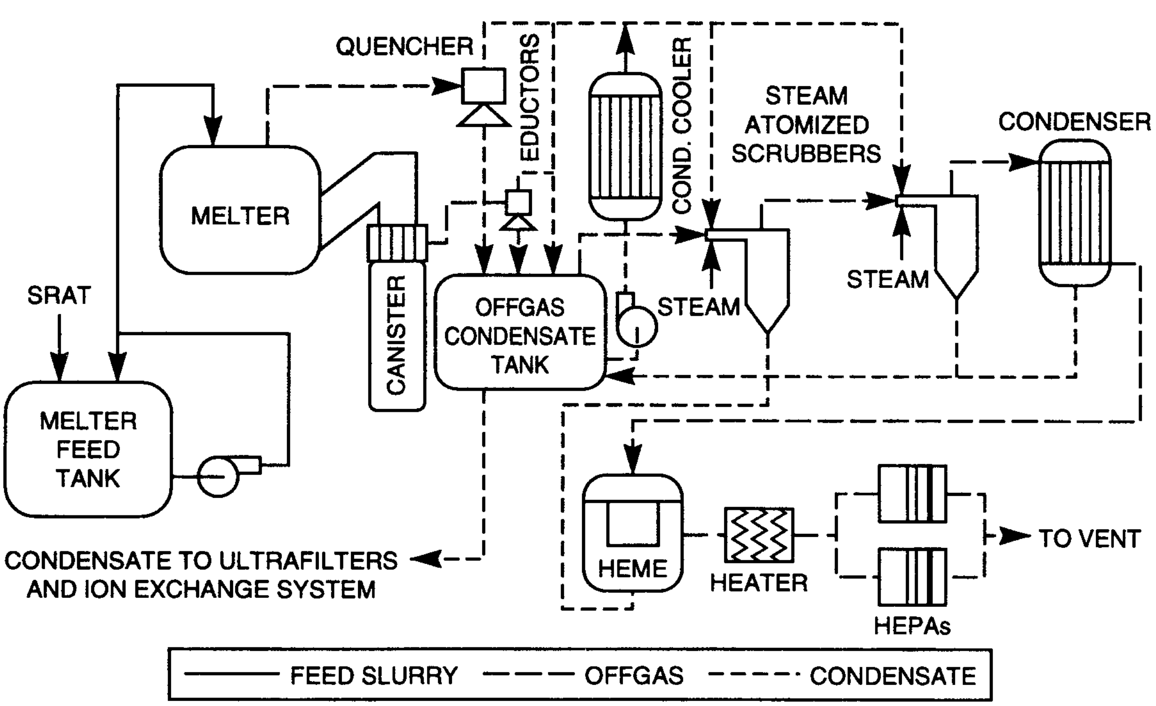

Figure 10-3. Integrated DWPF melter system and offgas flowsheet (Ritter et al., 1991)

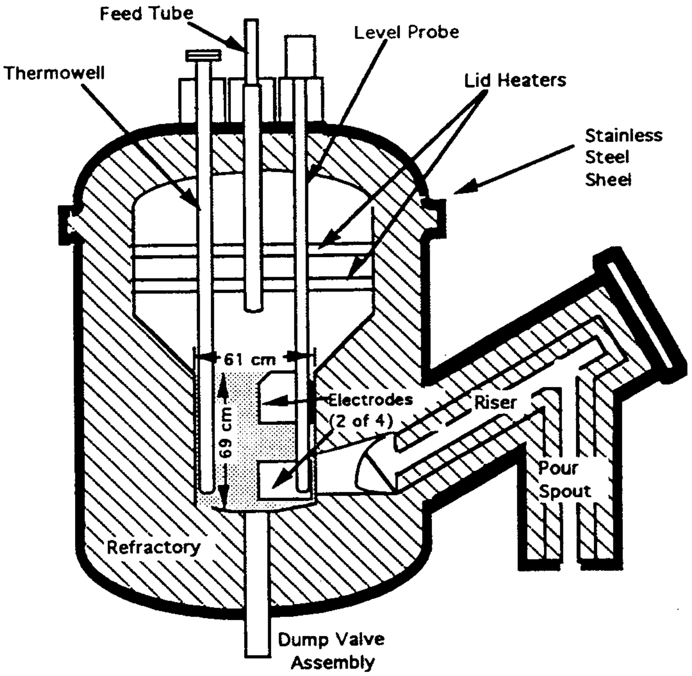

Figure 10.4 Integrated DWPF melter system (Hutson, 1994)

11 EMERGING SOLIDIFICATION TECHNOLOGIES

Technologies described in this section have been proven conceptually and are either at the end of the experimental stage or ready for pilot-scale testing. Among the technologies discussed below, cold-crucible melting technology is at the most advanced level for waste solidification.

11.1 COLD-CRUCIBLE MELTING TECHNOLOGY

The cold-crucible melting technology, also known as high-frequency induction melting technology, is an adaptation of the induction melting technology used in France for HLW vitrification. The cold-crucible skull melting technique was invented before World War II but never progressed beyond laboratory scale. In the cold-crucible concept, a solidified shell of the same material is used as a refractory interface with the melt. Formation of the solidified shell is accomplished by providing water-cooling jackets around the crucible (Jouan et al., 1996a,b; 1997). Figure 11-1 shows a schematic of the cold-crucible melter.

The design uses sectored layers of water-cooled jackets and induction coils around the crucible. The joule heating is provided by the induction coils while the water-cooling jacket forms a skull layer, 1 to 10-mm thick, inside the crucible walls. Figure 11-2 shows a typical temperature distribution map in the cold-crucible. The formation of a skull layer assures low corrosion and a longer life. The crucible could be used for melting wastes with a variety of corrosive components such as P_2O_5 and SO_3. The skull layer also allows the melter to operate at temperatures exceeding 2,500 °C and could be used to melt high refractory wastes.

The size of the crucible is limited by the ability of the induction coils to uniformly transmit induction frequencies to the center of the crucible. In large-diameter crucibles, attenuation of induction frequencies results in steep temperature gradients, as the current density diminishes exponentially from the outer wall to the core. In addition, if wastes have high resistivity, additional external heating sources may be required for startup.

There are three experimental cold-crucible melters currently operational at Marcoule in France (Jouan et al., 1998). The oldest is 10 yr old. The crucible is 0.55-m (1.8 ft) in diameter and 0.70-m (2.3-ft) in height. The crucible consists of rectangular solid stainless steel sectors with bored water passages. The crucible operates at 350 kHz by a power supply of 350 kW. Even after 5,000 hr of operations with a wide range of compositions, the crucible has not degraded. This facility has been used to demonstrate the feasibility of vitrifying HLW solutions from light water reactor fuel, using simulated "R7T7" glass. In addition, this facility was also used for vitrification tests with solutions simulating Hanford tank wastes. There are two other units, 0.30-m (1-ft) and 0.55-m (1.8-ft) diameter, that are being operated for nonnuclear testing. In addition, a 0.60-m (2-ft) diameter crucible is used for making special glasses at a production rate of over 50-kg/hr (110-lb/hr) by a commercial glass company in France.

A pilot facility for testing different waste streams is under construction at the Commissariat a l'Energie Atomique Marcoule center (site for HLW vitrification in France). The pilot plant will have a 0.30-m (1-ft) diameter cold-crucible with an offgas treatment system.

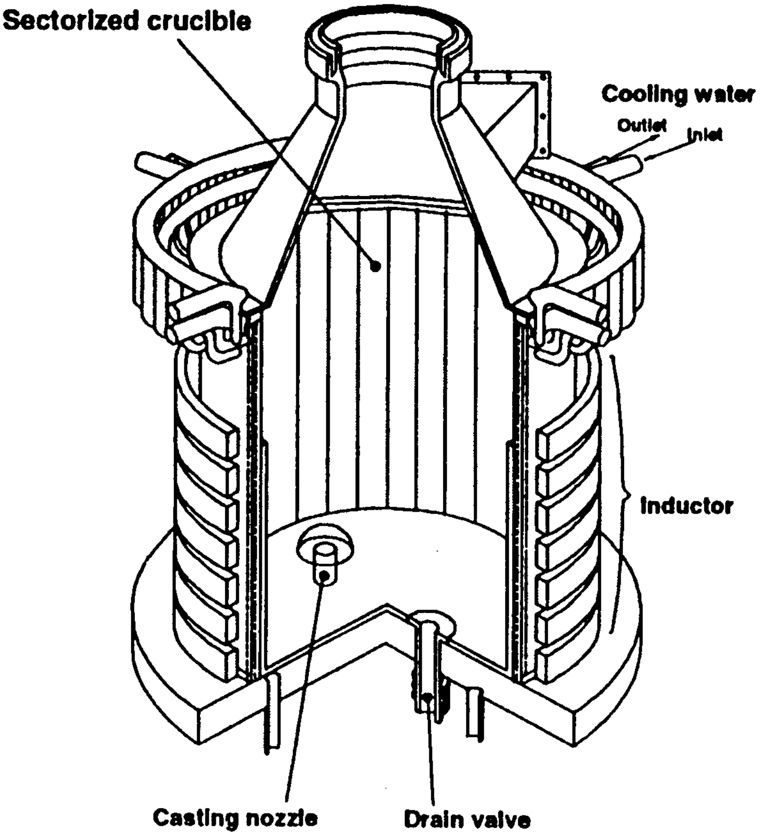

Figure 11-1. Cold-crucible, high-frequency induction melter schematic (Ladirat et al., 1995)

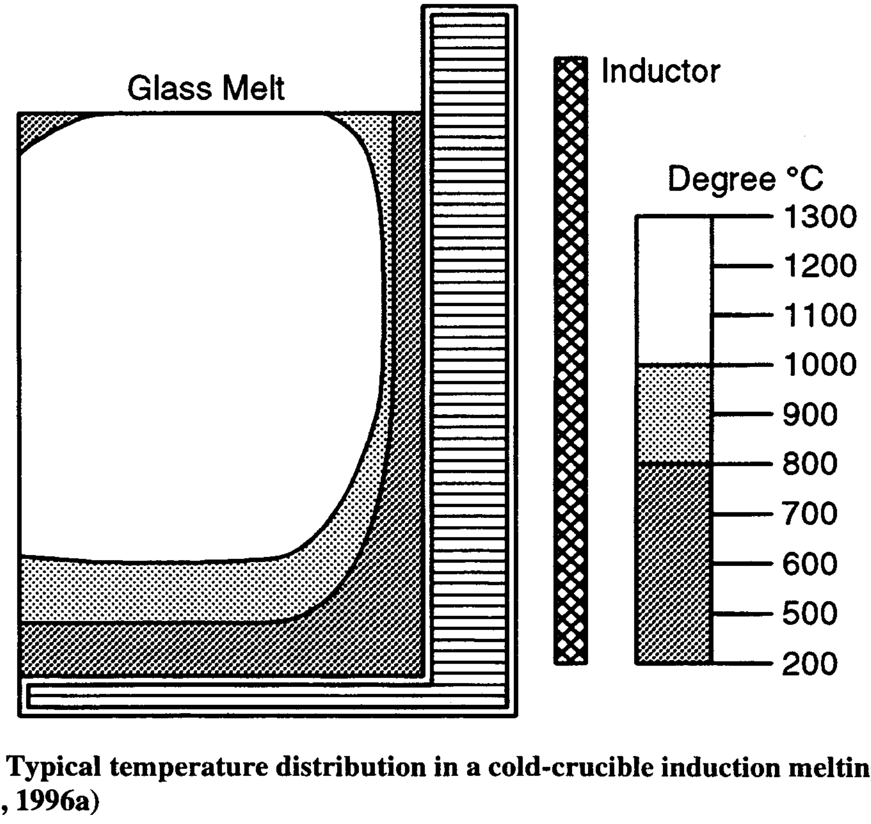

Figure 11-2. Typical temperature distribution in a cold-crucible induction melting (Jouan et al., 1996a)

The high-frequency induction melting (cold-crucible) technology is also being actively developed in Russia at the Mayak plant in Chelyabinsk to vitrify HLW solutions. The technology is jointly developed by the Moscow Institute for Research on Inorganic Materials and the RADON company at Zagorsk (Jouan et al., 1996a).

Even though the technology has not been tested with radioactive wastes, several projects are under way to develop the process for radioactive operations world-wide (Jouan, 1998). In addition to the development of a cold-crucible melter (CCM) for the Hanford wastes under the TWRS program, two CCMs are being designed for shipment to Saluggia, Italy, to vitrify HLWs at the Saluggia site, and to Taejon, Korea, to incinerate and vitrify LLW.

11.2 HYBRID, PLASMA-INDUCTION, COLD-CRUCIBLE MELTER

This technology was developed in Russia in the mid-1970's and was used for producing chemically active high purity metals such as zirconium, titanium, uranium, and rare-earth metal alloys. PICCM combines the advantages of plasma pyrolysis with temperature control aspects of induction heating. The cold-crucible eliminates concerns about refractory corrosion in metal/glass melts and eventual disposal of worn refractories. In addition, it provides a clean separation of glass from the metal phase. Because it is Russian proprietary technology, only a brief description of the process is available for discussion (Schumacher and Bickford, 1995).

A melter schematic is shown in figure 11-3. Induction heating in addition to plasma torch heating creates intense stirring within the metal portion of the melt. The metal melt is water cooled to allow formation of a skull layer. Separate taps allow the casting of metal from the bottom and the glassy phase from the side of the melter. This allows a clean separation between metal and glassy phase. A plasma torch is inserted from the top to supply enough energy to pyrolyze organics and melt glassy phase above the metal melt. The control of induction heating provides a balance between the formation of cold-cap above the metal phase and pyrolysis of organics, thus reducing volatilization of the radionuclides and other species.

Under a technology transfer program, a PICCM pilot test facility currently is being installed at the Georgia Institute of Technology by the Westinghouse Savannah River Center.

11.3 SUBMERGED COMBUSTION MELTER

The submerged combustion melter is a patented natural-gas fired technology (Olabin et al., 1996) and is proposed to be used for producing mineral wood and cement, roasting ores, melting glass and scrap, and vitrifying waste and ashes.

In submerged combustion melting, natural gas mixed with enriched air or oxygen is fired directly into and under the surface of the bath of the material being melted. Combustion products bubbling through the bath provide very effective heat transfer and mixing. Enriched air or oxygen help to combust organics in the feed stock.

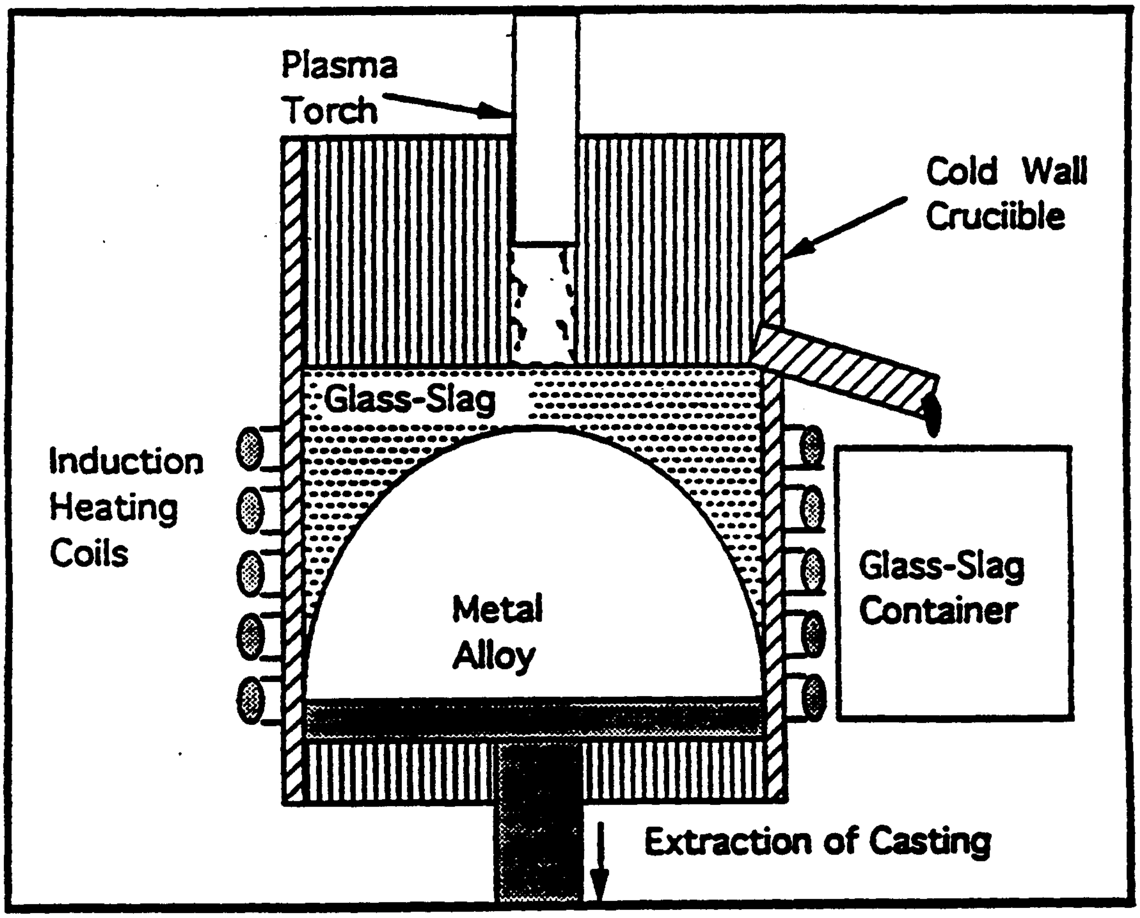

Figure 11-3. Hybrid plasma/induction cold-crucible melting system (Schumacher and Bickford, 1995)

A process schematic of the submerged combustion melter is shown in figure 11-4. Submerged combustion melters of 2.8 and 3.3-ton/hr (6,160- and 7,260-lb/hr) capacity using 315 °C preheated air are in commercial operation in Ukraine and Belarus for mineral wool production. An advanced pilot-scale submerged combustion melter test facility was built at the Institute of Gas Technology, Des Plaines, Illinois, and is being used to demonstrate the production of a number of mineral wool melts. However, to date no studies have been conducted to explore waste vitrification.

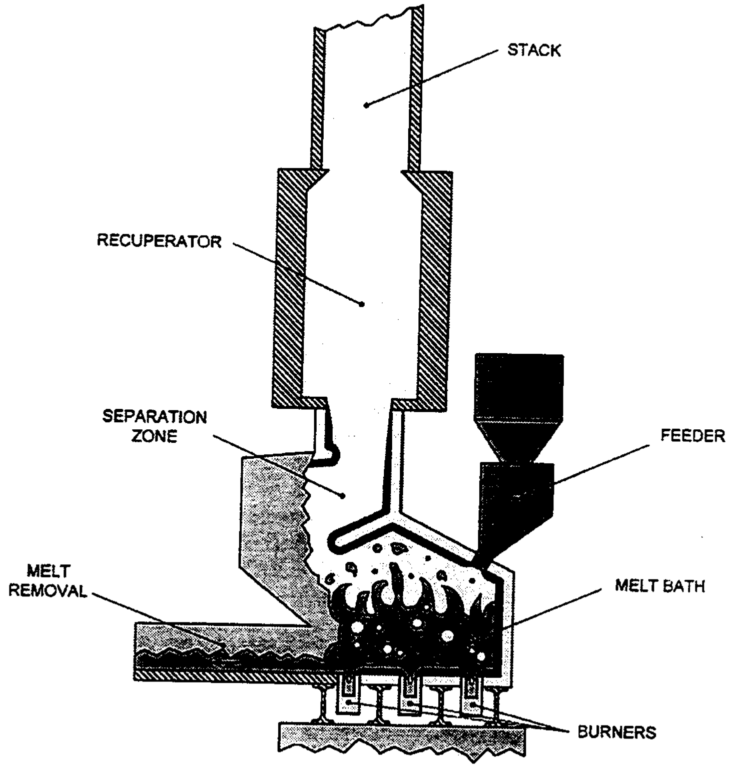

Figure 11-4. Submerged combustion melter schematic (Olabin et al., 1996)

12 NON-VITRIFICATION SOLIDIFICATION PROCESS EXPERIENCE

In 1979, the National High-Level Waste Technology Program initiated research and development on waste forms for solidifying HLW in the United States at fourteen laboratories, three universities, three industrial laboratories, and several DOE sites (U.S. Department of Energy, 1982; Hench, 1995; Hench and Clark, 1984). Between 1979 and 1981, seventeen different waste forms were evaluated and ranked. The peer review panel documented that borosilicate glass was the best developed and most viable waste form for both defense and commercial HLW. Synethic rock (Synroc) was selected as an alternative waste form. Other waste forms that reached semifinal stage included tailored ceramic, high-silica glass, (formed under elevated temperature and pressure), concrete-coated sol-gel particles, and glass marbles in a lead matrix. In the United States, most of the work on non-vitrified waste forms like glass ceramics, Synroc, and vitreous ceramics is being conducted at the INEEL and PNNL. At this time, research is focused on developing the waste form and not on designing the production facility.

The only production facility for the non-vitrified waste form for solidifying HLW into Synroc is located in Australia. This nonradioactive commercial-scale facility has a production capacity of 10-kg/hr (Jostsons, 1994). To date, a production plant for radioactive operations for non-vitrified waste forms has not been developed anywhere in the world. Review of cement/concrete solidification and polymer encapsulation are not included here because these waste forms are not suitable for Hanford waste. The Q-CEP by Molten Metal Technology Incorporated (MMT), is a new solidification process. Due to the proprietary nature of the technology, there is no information available in the literature on its performance. The following sections describe Synroc and Q-CEP solidification technologies.

12.1 SYNROC DEMONSTRATION PLANT, AUSTRALIA

Synroc was first proposed as a waste form for the HLW in 1978. After more than a decade of research and development on Synroc materials in Australia, Synroc production, using nonradioactive simulants, was demonstrated on a commercial scale in a 10-kg/hr production unit at the Synroc Demonstration Plant (SDP) in Australia (Jostsons, 1994). Construction of the plant was completed in 1987 and it has been operating in short programs to optimize processing and provide design input for the radioactive plant. As of 1996 (National Research Council, 1996), SDP has produced 6,000-kg (13,200-lb) of Synroc.

Synroc can be produced either by a conventional ceramic sintering process or by a hot-pressing process. The hot-pressing method was chosen for processing waste into Synroc. A Synroc process schematic is shown in figure 12-1. In a typical process, HLW solutions are mixed with Synroc precursor powders as shown in table 12-1. The mix is calcined at 700 °C for 1–2 hr in a rotary calciner (similar to one used in the AVM process in France). The calcination is done under a 3.5 percent H_2/N_2 reducing atmosphere. The calcined powder is blended with 2 percent Ti metal powder to control redox potential and loaded into stainless steel bellows containers. A powder mixing and filling is shown in figure 12-2. The steel containers are cold-pressed, followed by hot-pressing at 14–21 MPa (2,000–3,050 psi) for 2 hr between 1,150–1,200 °C. The bellows (with Synroc) are then cooled and loaded in standard disposal canisters. The space between the bellows is filled with a good heat transfer medium, (e.g., lead). Figure 12-3 shows the size of the bellows before and after hot-pressing.

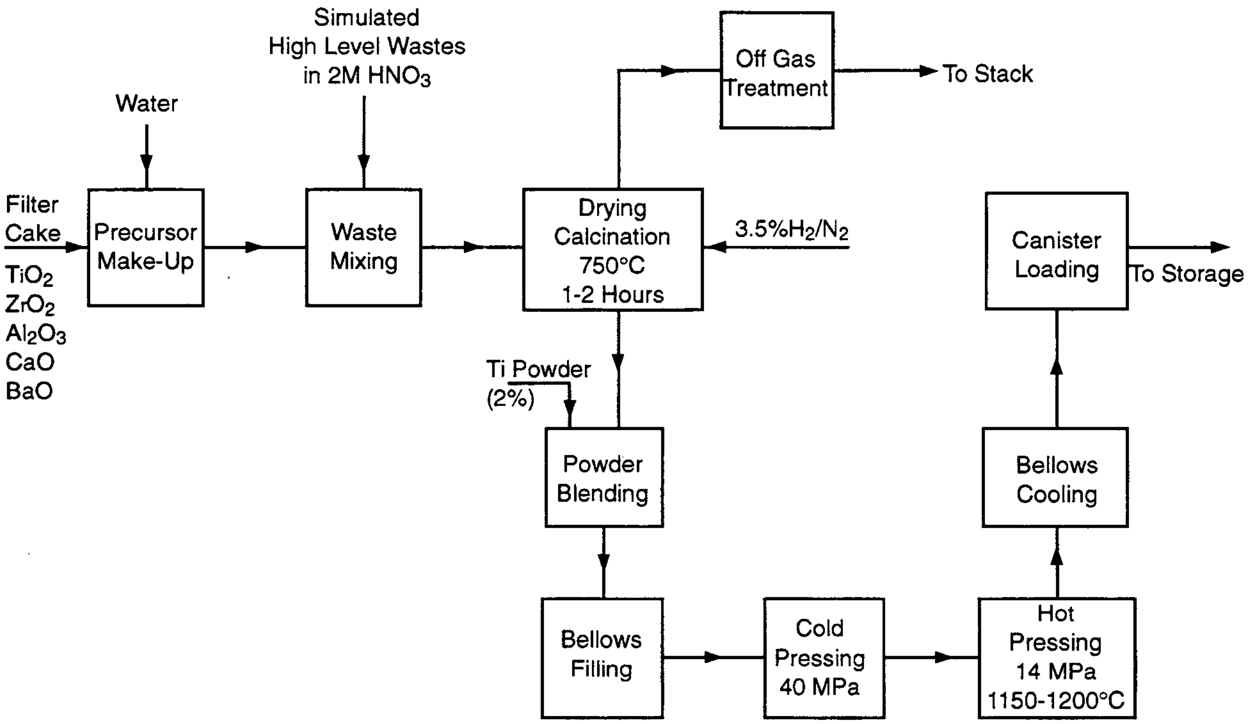

Figure 12-1. Synroc process flowsheet (Ringwood et al., 1988)

Table 12-1. Composition of Synroc-C (Jostons, 1994)

Composition	wt %
TIO_2	57.1
ZrO_2	5.3
Al_2O_3	4.3
BaO	4.5
CaO	8.8
HLW	20

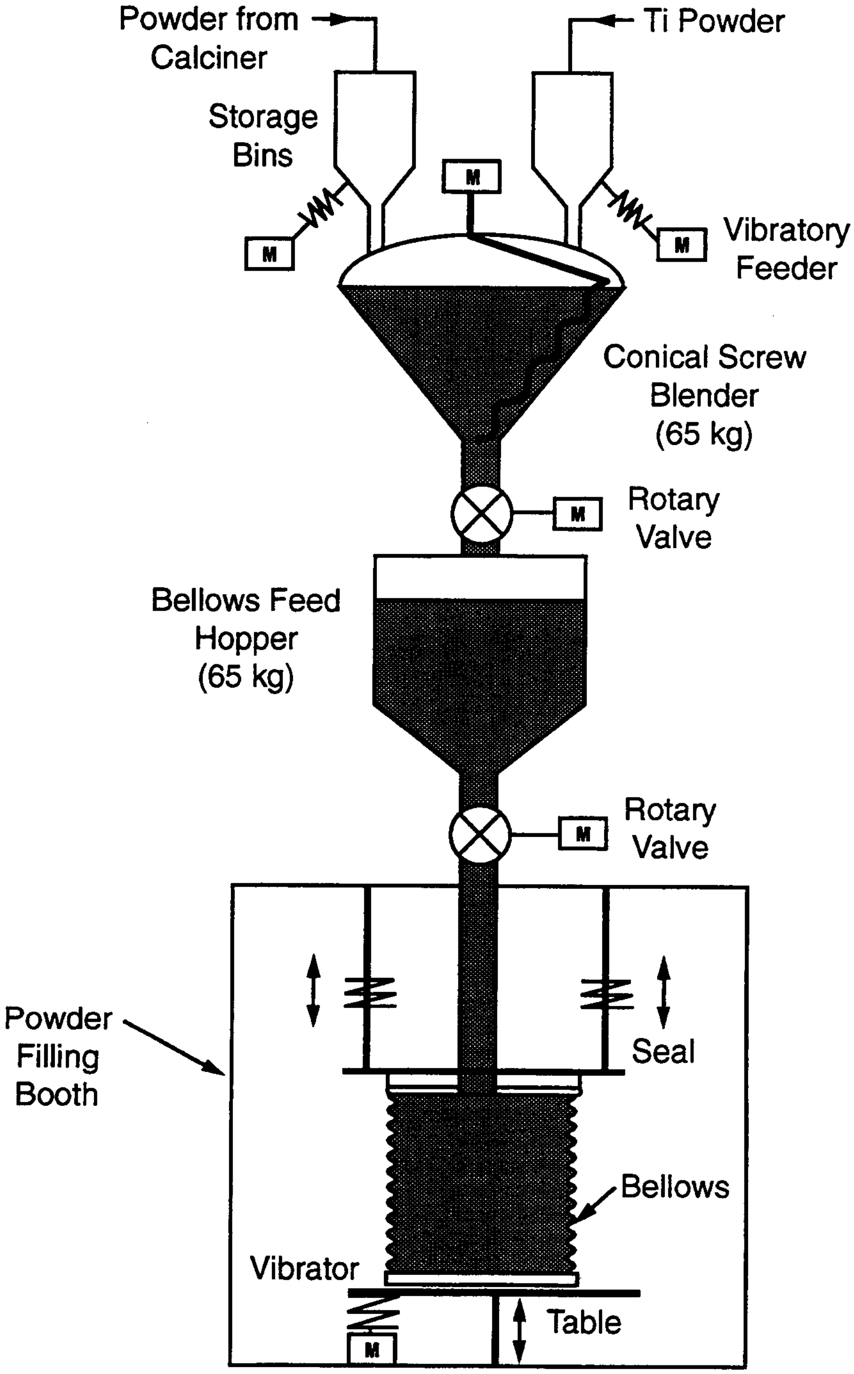

Figure 12-2. Powder mixing and filling process during Synroc manufacture (Ringwood et al., 1988)

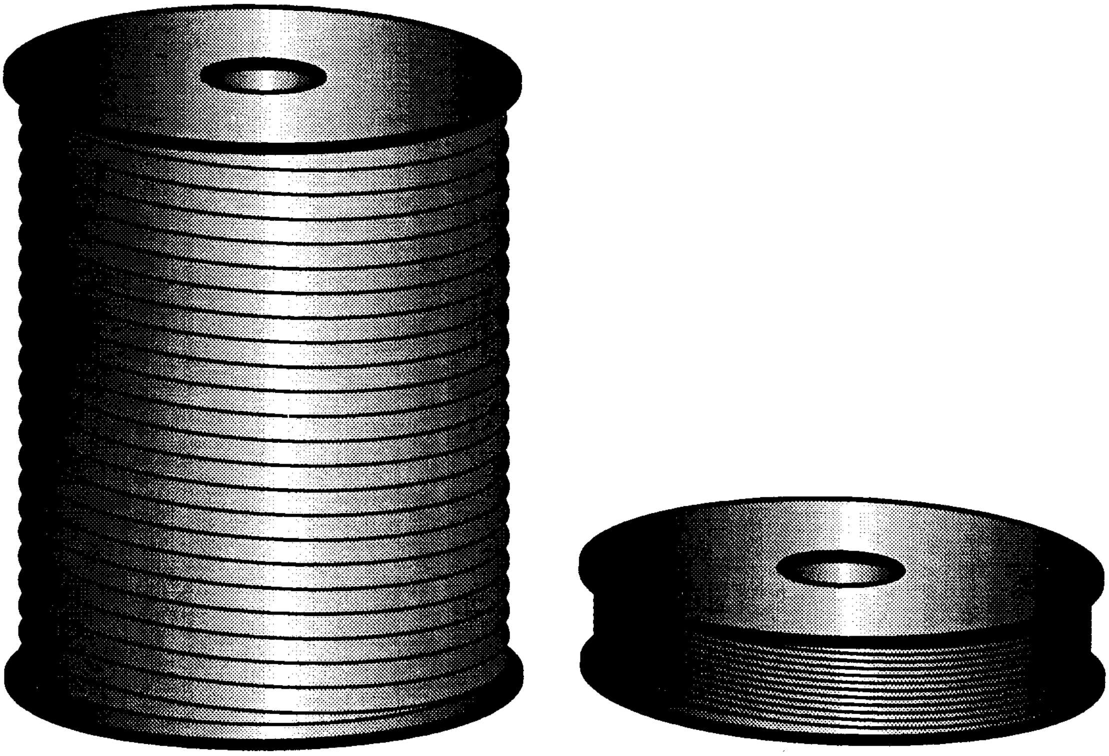

Figure 12-3. 400-mm-diameter Synroc bellows before and after hot pressing (Ringwood et al., 1988)

Major process improvements include using larger bellows and eliminating of the cold-pressing step. Bellows of 30–40 cm (1–1.3 ft) diameter have been successfully processed. In addition, development of a more reactive precursor has resulted in the elimination of the cold-pressing step prior to hot-pressing.

The operations have indicated Cs and Ru volatility below 0.15 percent of the inventory. Also the quality of the product was not influenced by large variations in HLW and precursor concentrations. However, at this time, there is not much information available on the processing and safety issues related to Synroc. A recent study (Vance et al., 1996), using simulated Hanford HLW liquid waste, has shown that Synroc will meet durability requirements for the Hanford HLW. In addition, Tc volatilization losses were less than with other solidification technologies.

Synroc is the most durable waste form but the technology has not reached a maturity and confidence level to be adopted for radioactive operations.

12.2 QUANTUM-CATALYTIC EXTRACTION PROCESS

The Catalytic Extraction Process (CEP) is a new, innovative, flexible, proprietary technology of MMT in Waltham, Massachusetts (Herbst et al., 1994; Valenti, 1996). This technology is used for processing hazardous waste streams, allowing the organic, organometallic, and inorganic waste streams to be recycled into useful resources. The Q-CEP is an adaption of the CEP technology for handling radioactive and mixed waste streams. The Q-CEP, in addition to destroying hazardous components, allows partitioning of radionuclides. The partitioning allows recycling of a large number of waste components into commercial products and solidification of radionuclides, either in glass/ceramics or metals.

In both CEP and Q-CEP, the molten bath (typically iron or nickel) acts as a homogeneous catalyst and as a solvent in dissociation of feeds, synthesis of products, and concentration of radionuclides in a desired phase. In the Q-CEP process, various radioactive mixed wastes are piped into a sealed bath of molten metal called a Catalytic Processing Unit, as schematically shown in figure 12-4. The bath is a sealed vessel lined with a ceramic refractory. Induction coils at the bottom of the bath are used to supply heat and keep the bath in the molten state. Proprietary chemicals are fed through tuyères at the bottom of the reactor with the waste streams to reconfigure elements from the bath into useable raw materials. The reactor can handle feeds of most physical forms such as gases, liquids, and slurries. The catalytic properties of the high-temperature metal breaks down the chemical compounds to their primary elements. The gases (i.e., H_2, CO_2, etc.) are sent to a hermetically sealed gas handling system. The elements (cations) are extracted as ceramics or alloys. The radionuclides from the wastes are encapsulated into ceramic or metal phases in the bath. The ceramic end product floats on the top of the molten metal and is skimmed off by tapping the bath. Metal byproducts remain in the bath as ferroalloy and are removed as needed.

According to the authors (Herbst et al., 1994), Q-CEP offers superior capabilities to those of melt refining. Q-CEP allows oxygen to be injected into the molten metal bath, greatly enhancing oxidation of the radioactive components. In addition, turbulence caused by gas injection into the metal bath facilitates mass and heat transfer, leading to active partitioning of radionuclides.

The Q-CEP plant at Scientific Ecology Group in Oak Ridge, Tennessee, is providing treatment for low-level radioactive ion-exchange resins from nuclear power plants. Other Q-CEP plants at the M4 Environmental facility at Oak Ridge are providing treatment for converting uranium hexafluoride to stable uranium compounds and commercial products, and for treatment of mixed wastes at DOE sites. In addition, several other plants are being constructed.

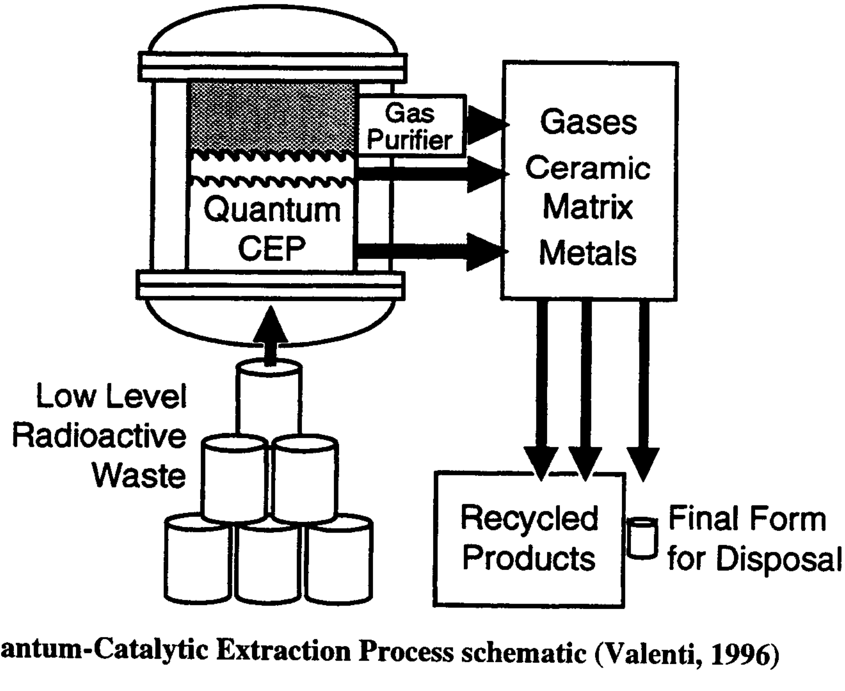

Figure 12-4. The Quantum-Catalytic Extraction Process schematic (Valenti, 1996)

13 TECHNOLOGICAL ASSESSMENTS

Solidification technologies presented in this survey can be broadly classified into the following categories: Inconel® based, joule-heated melters; high-temperature, joule-heated melters; induction melting, cold-crucible induction melters; plasma melters; combustion melters; microwave melters; molten metal technology, and Synroc technology. The following sections summarize strengths and weaknesses of each technology.

13.1 JOULE-HEATED INCONEL® MELTERS

Strengths

(i) Mature Technology: Two HLW plants are currently operating in the United States and one in Japan. The Pamela plant in Mol, Belgium, successfully completed operations. Numerous pilot-scale nonradioactive plants are in operation or have completed successful operations in the last 20 yr.

(ii) Low Volatility: This technology provides extremely low volatility for radioactive components such as Tc and Cs due to its operation in a cold-top mode.

(iii) Homogeneity: Due to the long residence time in the melter, the glass product is homogeneous.

(iv) Waste/Glass/Melter Component Interactions: The interactions between the waste, glass, and melter components have been well established for certain types of wastes.

Weaknesses

(i) Low Glass Production Rate: Glass production rates are limited by an upper operating temperature of 1,150 °C. The production rate for the DWPF melter is 100 kg/hr. Production rates depend upon the size of the melter but, for the same size melter, the production rates are significantly higher compared to the induction-melters but lower compared to the high-temperature, joule-heated melters and plasma melting systems. Production rate enhancements can be achieved by bubblers and stirrers, that may cause increased erosion of melter components.

(ii) Failure due to Noble Metal Accumulation: Several melters have experienced loss of electrical resistance in the melter due to the accumulation of noble metals. The melter at the Pamela plant in Mol, Belgium, failed due to noble metal accumulation on the melter floor. New sloped-wall designs, like those at the WVDP and at the TVP in Japan, and use of bottom drains, like those in the Duratek and Envitco melters, allow the noble metals to drain periodically, minimizing the probability of melter failure.

13.2 HIGH-TEMPERATURE, JOULE-HEATED MELTERS

Strengths

(i) High Glass Production Rate: Glass production rates are higher than those for most solidification systems but lower than those for plasma systems. Production rate enhancements can be achieved by bubblers and stirrers but may result in increased erosion of melter components.

Weaknesses

(i) Developed Technology but Not Mature: The transportable vitrification system and Fernald high-temperature melter have failed during operations. However, pilot scale plants at Clemson University (Envitco melter), CUA-VSL (Duratek melter), and PNNL are still operating.

(ii) High Volatility: Due to high operating temperatures, the volatility is higher compared to joule-heated Inconel® melters. No data was available on volatilization of radioactive components such as Tc and Cs.

(iii) Homogeneity: Because of high melting temperatures and high production rates, the melt has a short residence time in the melter and, therefore, the glass product may or may not be homogeneous.

(iv) Waste/Glass/Melter Components Interactions: a high-temperature melter system requires the use of molybdenum electrodes. These electrodes corrode in the presence of elements such as lead or nickel, which may cause premature melter failures. The melter at the Fernald site failed due to incompatible materials used in the melters. More research is needed to ensure waste material compatibility with the components of the high-temperature melter system.

(v) The issues are similar to the joule-heated Inconel® melters.

13.3 INDUCTION MELTING TECHNOLOGY

Strengths

(i) Mature Technology: Two HLW plants, T7 and R7, are operating in France and one in Sellafield, United Kingdom. The HLW Plant at Marcoule, France, successfully completed radioactive operations. The technology has been in existence for 20 yr.

(ii) Low Volatility: This technology provides extremely low volatility from the melter for radioactive components such as Tc and Cs, due to the use of calcined feed.

(iii) Homogeneity: The glass product is homogeneous, due to the long residence time and limited melting volume in the melter.

(iv) Waste/Glass/Melter Components Interactions: The interactions that may cause corrosion between the waste, glass, and the Inconel® crucible have been well established for certain types of wastes. The melter uses the Inconel® crucible as a melting pot. Due to corrosion, however, the pots should be replaced after 2,000 to 3,000 hrs of operations.

(v) Noble Metal Accumulation: The entire contents of the crucible are regularly drained, avoiding metal accumulation. In addition, a bottom drain helps to flush noble metals on a frequent basis. The alloying of the noble metals with the Inconel® crucible is a potential problem and crucible replacements are necessary every 2,000 to 3,000 hrs.

Weaknesses

(i) Low Glass Production Rate: Glass production rates are limited by the size of the melt crucible and the upper operating temperature of 1,150 °C. The size of the melter cannot be increased because attenuation of induction frequencies results in steep temperature gradients as the current density diminishes exponentially from the outer wall to the core in large-diameter crucibles. The production rate for the induction melter are lower, and production rate enhancements are not possible with current designs.

(ii) Feeding Mode: Due to the design of the system, only calcined feeds can be processed in the melter.

(iii) Crucible Life: Short crucible life and frequent replacement is an issue.

13.4 COLD-CRUCIBLE INDUCTION MELTING TECHNOLOGY

Strengths

(i) Waste/Glass/Melter Components Interactions: The interactions and consequent corrosion between the waste, glass, and the Inconel® crucible are significantly minimized by the formation of a skull layer at the glass-crucible interface by using sectored water-cooled jackets around the crucible.

(ii) Crucible Life: Due to the formation of the skull layer, crucible life is much longer than in induction melting systems.

(iii) Noble Metal Accumulation: The entire contents of the crucible are regularly drained, decreasing metal accumulation. In addition, a bottom drain helps to flush noble metals on a frequent basis. The alloying of noble metals with the Inconel® crucible is reduced due to the formation of the skull layer.

(iv) Glass Production Rate: Melting temperatures are not restricted by the operating temperatures for Inconel® crucibles. The formation of a skull layer allows for much higher operating temperatures. Glass production rates are higher compared to induction melting systems due to the higher operating temperatures in the melting chamber. The production rate could still be limited by the size of the melt crucible. The size of the melter cannot be increased due to the inability of the induction heating to reach a uniform temperature in large-diameter crucibles.

(v) Homogeneity: Due to a long residence time and limited melting volume in the melter, the glass product is homogeneous.

Weaknesses

(i) Developing Technology: This technology is an adaptation of the more mature induction-melting technology. Several pilot-scale tests are being conducted in France and Russia. There are no full-scale, cold-crucible induction melting systems in operation at this time.

(ii) Feeding Mode: Due to the design of the system, only calcined feeds can be processed in the melter.

(iii) Volatility: The volatility could be higher than with the induction melting systems due to higher operating temperatures.

13.5 PLASMA MELTING TECHNOLOGY

Strengths

(i) Glass Production Rate: Glass production rates are the highest among all solidification technologies.

(ii) Due to high operating temperatures of the plasma systems, this technology is well suited for hard-to-vitrify heterogeneous wastes.

Weaknesses

(i) Developing Technology: Even though this technology has been used in the commercial steel industry for a long time, its adoption to waste solidification is quite recent. Several pilot-scale plants are operating, and some testing has been performed using mixed low-level radioactive wastes. Full-scale radioactive testing has not been performed.

(ii) High Volatility: Due to high operating temperatures, the volatility is extremely high; it is the highest among all solidification technologies. Due to high volatilization, the final composition of the glass may not meet the target composition. Volatilization may be reduced if the system could be operated in a cold-top mode.

(iii) Homogeneity: Because of high melting temperatures and high production rates, the melt has a short residence time in the melter. As a consequence, glass homogeneity is a concern.

(iv) Waste/Glass/Melter Components Interactions: Plasma systems, due to their extremely high operating temperatures, cause extensive erosion on refractories and melter components. The formation of a skull layer at the glass-refractory interface, by using water-cooled jackets around the melter shell, can minimize refractory corrosion.

(v) Short Plasma Torch Life: Short plasma torch life is a major concern in the plasma systems for radioactive operations. Depending upon the conditions, the life of the torch could range from a few hours to a few days.

(vi) Failure due to Noble Metal Accumulation: This issue has not been evaluated for the plasma systems.

13.6 COMBUSTION MELTING TECHNOLOGY

Strengths

(i) Glass Production Rate: Glass production rates are high.

Weaknesses

(i) Developing Technology: Even though the technology has been used in the commercial glass, coal, and steel industries for a long time, its adoption to waste solidification is quite recent. Several pilot-scale plants are operating but radioactive testing has not been performed.

(ii) High Volatility: Due to high operating temperatures, the volatility is extremely high. Volatility is comparable to plasma melting technologies. Volatilization may be reduced if the system could be operated in a cold-top mode.

(iii) Homogeneity: Because of high melting temperatures and high production rates, the melt has a short residence time in the melter. As a consequence, glass homogeneity is a concern.

(iv) Waste/Glass/Melter Components Interactions: Combustion systems, due to their extremely high operating temperatures, cause extensive wear on refractories and melter components. The formation of a skull layer at the glass-refractory interface by the use of water-cooled jackets around the melter shell can minimize refractory corrosion. In addition, air/fuel interactions with wastes are unknown.

(v) Failure due to Noble Metal Accumulation: This issue has not been evaluated for the combustion melter systems.

13.7 MICROWAVE MELTING TECHNOLOGY

Strengths

(i) One-Step Process: The waste can be melted and disposed of in the same container.

(ii) Low Volatility: Due to low melting temperatures, volatility is low.

Weaknesses

(i) Experimental Technology: There are no full-scale radioactive operating microwave solidification systems. Some studies have been conducted using pilot-scale melter systems.

(ii) Low Glass Production Rate: Glass production rates are limited by the size of drums that could be placed in a microwave melter. The size of the drum is limited by the inability of the microwaves to uniformly heat large quantities. This is not a continuous process.

(iii) Homogeneity: Due to non-uniform melting, the glass product is not homogeneous.

(iv) Waste/Glass/Melter Components Interactions: The interactions and corrosion between the waste, glass, and container have not been established. In some instances, formation of hot spots has led to glass-flow from the containers.

(v) Failure due to Noble Metal Accumulation: This issue has not been evaluated for the microwave systems.

13.8 MOLTEN METAL TECHNOLOGY

Q-CEP technology is proprietary in nature, and not enough information is available to accurately evaluate its strengths or weaknesses.

13.9 SYNROC TECHNOLOGY

Strengths

(i) Excellent waste form for disposal.

(ii) Homogeneity: Hot-pressing makes the product homogeneous.

(iii) Low Volatility: Volatility during processing is low.

(iv) Waste/Glass/Melter Components Interactions: Since no melting is required, corrosion issues are minimal. The waste is hot-pressed in stainless steel bellows, which become a part of the waste form itself.

(v) Noble Metal Accumulation. This is not an issue. All components are retained in the Synroc. Each time, the process starts with a fresh batch.

Weaknesses

(i) Developing Technology: There are no operating Synroc radioactive materials solidification plants. A pilot plant has been operating in Australia for several years.

(ii) Low Production Rate: Synroc production rates are limited by the size of hot-presses. This is not a continuous process.

14 RADIOLOGICAL SAFETY AND HEALTH RISKS FROM SOLIDIFICATION OPERATIONS

The TWRS waste solidification plant should be designed to solidify wastes stored at the Hanford site without posing undue radiological safety and health risks to workers, the public, and the environment from solidification operations. Because of limited understanding of the composition, physical characteristics, and interactions among wastes in different tanks of the TWRS waste at the Hanford site, the task is challenging. However, incorporating lessons learned from the design and operations of commercial glass industries and existing waste vitrification plants should significantly reduce radiological safety and health risks. The review of key processing considerations related to radiological safety and health risks from operations can be broadly classified into four categories: (i) tank farms and feed preparation, (ii) waste solidification and storage, (iii) offgas treatment and release, and (iv) remote operations and human factors. The significance and ramifications of process parameters in each category are discussed in the following sections.

14.1 TANK FARMS AND FEED PREPARATION

The radioactive wastes stored at the Hanford site are complex mixtures of solids and liquids, incompletely characterized, consisting of liquids, slurries, saltcakes, and sludges. More than 99 percent of the waste volume and a majority of the total radionuclide inventory are contained in 149 SSTs and 28 DSTs. Summary descriptions of the wastes in SSTs and DSTs are provided in reports by Gephart and Lundgren (1995) and Cragnolino et al. (1997), and a detailed assessment of tank waste contents is provided by Agnew (1997).

The total volume of SST waste is approximately 132 million L (35 million gal.), of which 66 percent is wet saltcake consisting of crystallized nitrate and other salts, and 34 percent is sludge consisting of solids formed after waste neutralization with sodium hydroxide addition. The solids and dissolved constituents of the SSTs are ~90 percent sodium nitrates and nitrites, with the remainder consisting mostly of phosphates, carbonates, hydroxides, and sulfates. Radioactivity in the SSTs is dominated by Sr-90 (75 percent) and Cs-137 (24 percent); Sr is mostly in the sludge, whereas Cs is chiefly in the saltcake and interstitial liquids. The DST waste, with an approximate total volume of 76 million L (20 million gal.), is dominated by supernatant liquids transferred from SSTs and, thus, is 85 volume percent water. The constituents of the DST waste, like those of the SSTs, are dominated by sodium nitrate and nitrite (~70 percent), with ~20 percent metal hydroxides and the rest as phosphates, carbonates, oxides, and sulfates. The DST waste radioactivity is 72 percent from Cs-137, which is mostly in the slurry and interstitial liquid, and 27 percent from Sr-90, which is mostly in the sludge.

The storage of wastes at the Hanford site poses safety hazards of generation and combustion of flammable gases (Johnson et al., 1997) such as hydrogen or ammonia in the tanks, energetic reactions between organics and nitrates/nitrites (Turner et al., 1995) that could release radioactivity to the environment, and high heat loads from radionuclide decay (Wang, 1997) that could damage the waste tank concrete structures. These issues are unique to the TWRS and are being evaluated independent of the TWRS privatization program. In addition, several tanks that have potential for causing onsite or offsite radiation exposure to workers through uncontrolled release of fission products have been identified as watch list tanks in accordance with Public Law 101-510, Section 3137, Safety Measures for Waste Tanks at Hanford Nuclear Reservation (Hanlon, 1997) to ensure safety of the tanks is maintained during storage. The following discussion focuses on safety issues related to waste retrieval, transfer, homogenization, pretreatment, feed preparation, and reductant addition.

14.1.1 Waste Transfer Lines

Several safety issues are of potential concern during mixing and transfer of TWRS wastes. The foremost concern is rupture of transfer lines resulting from changes in waste slurry rheology. Depending on rheological behavior, the waste either could become more fluid or more viscous during mixing or transfer. High viscosity causes a potential for transfer line plugging that could result in accumulation of flammable radiolytically produced gases such as hydrogen. A rise in flammable gas concentration in a plugged transfer line above the LFL increases the probability of explosion, particularly in the presence of air or nitrous oxide in the waste. In a transfer line containing waste with high heat load due to radioactive decay of Sr-90 and Cs-137, plugging could result in a severe temperature excursion and problems such as thermal expansion and distortion or rupture of the line. Analogous problems could arise from waste that has a potential for energetic or exothermic reactions due to organic oxidation mechanisms.

14.1.2 Waste Transfer and Mixing

Precipitation of specific components, exothermic reactions, rheological changes, and flammable gas generation due to mixing of different wastes potentially could damage the mixing and transfer pumps. A transfer of waste to an empty tank poses no process safety hazard provided the tank material is compatible with the waste characteristics. In general, this is not the case for transfer to tanks that already contain other materials. For example, at the WVDP, a highly acidic THOREX waste was transferred to a carbon-steel tank containing an alkaline PUREX washed sludge. Prior to transfer, laboratory tests using both simulated and actual waste, coupled with fluid flow modeling to study mixing behavior, were conducted and a plan was developed to ensure proper tank safety during transfer (Gray and Westerman, 1995). A detailed analysis of waste compatibility prior to waste transfer should address potential problems and incidents relating to incompatibility of wastes and tank material.

14.1.3 Waste Homogeneity

Waste homogeneity during mixing and transfer is another important safety issue. While criticality is not an issue for the Hanford Site HLW tanks (Bratzel et al., 1997), potential for the accumulation of fissile material should be addressed during normal processing campaigns. The potential for criticality resulting from preferential segregation of fissile material or from failure of mixing pumps should be addressed before the retrieval and transfer of tank contents is initiated. In addition, waste inhomogeneities could result in waste batches that are unacceptable for processing, leading to production of nonconforming waste forms or to the return of these batches to the tank farm. Although production of nonconforming waste forms is not in itself a safety hazard, excessive concentrations of minor components, such as sulfates and phosphates, could result in increased corrosion of melter components, and accumulation of noble metals could cause formation of a conductive sludge on the melter floor and electrical shorting of the melter.

14.1.4 Waste Pretreatment

Waste pretreatment is an important part of the solidification process. Pretreatment allows separation of highly radioactive species, such as Sr-90, Tc-99, Cs-137, and transuranic waste (TRU), from the supernatant. Understanding the chemistry of the wastes and the separation media helps ensure a safe pretreatment process. Each component of the waste, before pretreatment to extract radionuclides, should be compatible with the pretreatment media. For example, in the WVDP pretreatment process, Pu solubility in the supernatant was found to increase due to dilution of the waste in the waste tank with time. This increase in Pu solubility resulted in Pu being released with the effluent into the evaporator (Dalton, 1992)[6]. Another example is the evolution of benzene during the ITP process at the SRS facility that caused TPB to precipitate Cs as Cesium TPB. This is a safety issue and currently is being addressed by the DOE as a result of the safety assessment of the ITP process by the Defense Nuclear Facilities Safety Board (1996).

14.1.5 Feed Preparation for Solidification

The feed preparation flowsheet, like the pretreatment flowsheet, should provide a safe operating environment. Each component of the glass-forming chemicals, before it is mixed with waste, should be compatible with waste. Chemicals added other than in an established sequence could result in temperature excursions due to exothermic heat of reaction, agglomeration, or the release of NO_x. As an example, in the WVDP flowsheet the addition of a polyglycol-based antifoam agent after nitric acid addition results in NO_x fumes and, therefore, it is added last to minimize NO_x generation (Firstenberg et al., 1995). In addition, the WVDP process flowsheet requires an acidic feed to ensure that proper rheology is maintained during mixing and feeding to a melter. When acidic glass formers are added to an alkaline waste, the rheology of the mix changes very rapidly. The mix rheology exhibits a maximum in slurry viscosity between a pH of 6 and 8 and decreases at lower or higher pH. Detailed laboratory studies on rheological behavior as a function of pH allowed the WVDP to prepare feed batches within processable bounds. In the DWPF feed preparation flowsheet, adjustments are made using frit and formic acid (Ramsey et al., 1994). The DWPF frit is much more erosive than the chemicals used at the WVDP, which has resulted in erosion of the DWPF feed tank components (Gee et al., 1996). These examples highlight the importance of using the proper chemicals to ensure that the design life of the components is attained. Other potential safety issues related to the feed preparation process include erosion and corrosion of on-line instruments that could result in the malfunction of on-line pressure, temperature, and level instruments. For example, erosion of level measurement tips could lead to erroneous reading and could result in overfill or underfill of the feed preparation tanks. Measures to mitigate such problems will help minimize any remote or hands-on maintenance work that needs to be done.

14.1.6 Selection of Reducing Agents

One of the major concerns in developing a feed preparation flowsheet is the selection of reducing agents and a proper understanding of noble metal-catalyzed reactions. For example, if a formic acid-based flowsheet is selected for TWRS waste (similar to the DWPF flowsheet), the potential for hydrogen generation due to catalyzed decomposition of formic acid by noble metals should be addressed to ensure hydrogen generation does not exceed the LFL. In addition, noble metal-catalyzed formic acid reduction of nitrite and/or nitrate to ammonia is a significant safety concern because of ammonium nitrate formation, which is an explosion hazard (King and Bhattacharya, 1996). For the TWRS waste feed preparation flowsheet, the effects of organics and organometallic compounds that are introduced from the waste should also be addressed to ensure that they do not result in formation of hazardous compounds.

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[6] Dalton, W.J. 1992. Qualification Testing of Titanium-Treated Zeolite for Sludge Wash Processing. White paper prepared for the U.S. Department of Energy. West Valley, NY: West Valley Nuclear Services.

14.2 WASTE SOLIDIFICATION AND STORAGE

Initial research on the development of vitrification processes for HLW started in the early 1960s. Since then, vitrification has gained wide acceptance as a viable technology for solidification and disposal of HLW stored around the world, and has also been recommended for disposal of LLW and mixed low-level radioactive and hazardous wastes in the United States. In a typical HLW vitrification process, waste is mixed with glass-forming chemicals and the resultant mixture is melted at temperatures greater than 1,100 °C in a melter inside a shielded cell. The melting process fuses the various components of the mixture into a glass melt that is poured and cast into stainless steel canisters. Since the operation of the first HLW vitrification plant at Marcoule, no catastrophic accident involving HLW vitrification technology (i.e., accidents that resulted in any significant radioactive dose exposure to the public or release to the environment) has occurred. This does not mean that vitrification technology is free from problems and issues that could result in failures. In fact, over the past 20 yr, several operational incidents such as breach of a melter vessel allowing molten glass to leak/drop out of the melter, uncontrolled release of offgas from the melter, failure of the joule-heating system, and plugging of the glass pour drain, have occurred at various HLW and LLW vitrification facilities. Table 14-1 provides a summary of some of the published melter-related incidents, corrective actions, and lessons learned from these incidents.

Table 14-1. Summary of melter-related incidents

Incident	Corrective Action	Lessons Learned
Joule-heated melter at the HLW vitrification facility at Pamela, Mol, Belgium, electrically shorted due to noble metal accumulation on the melter floor. (Elliott et al., 1994)	Facility was shut down and replaced by an identical melter.	Melters with sloped walls were designed at the WVDP and TVP to minimize the effect of noble metal accumulation. In addition, bottom drains are routinely provided to drain noble metals at regular intervals.
At the DWPF, wicking of the glass stream during pouring resulted in plugging of the discharge orifice on a regular basis. (Carter et al., 1997)	The discharge chute was modified to reduce wicking and, in addition, remote equipment was installed to clean a plugged orifice.	Future melter designs should account for wicking of glass pour streams.
At the Pamela facility in Mol, Belgium, high viscosity and crystallization of glass melt resulted in plugging of the discharge orifice. (Wiese, 1988)	Glass composition was modified to reduce liquidous temperature and viscosity.	Glass composition should be designed to meet both disposal and processing constraints.

Table 14-1. Summary of melter-related incidents (cont'd)

Incident	Corrective Action	Lessons Learned
At the TVP in Japan, radioactive glass accumulated in the coupling device between the melter and canister. This was attributed to extremely low temperatures at the discharge orifice due to the lack of proper temperature control in the region. (Tomikawa and Yoshioka, 1996)	The discharge orifice was remotely modified and the location of the thermocouples was changed to provide better control of temperature near the discharge section.	Melter design should evaluate the placement of measuring instruments.
At the WVDP, the transposition of a weld symbol at the dam and trough interface in engineering drawings was the root cause for glass seepage onto the discharge wall. The missing weld resulted in separation between the dam and trough. (Rowland, 1996)	Since the incident occurred during cold operations, hands-on repairs were conducted, and operations were subsequently resumed.	Rigorous design review checks and controls should be implemented.
At the WVDP, the ceramic nozzle liners failed due to insufficient thermal expansion allowance.	The nozzle liners were redesigned.	Selection of materials and design of components should undergo evaluation prior to radioactive operations.
At the WVDP, formation of glass fibers in the discharge section led to the blockage of the discharge orifice. This was a result of high air-inflow through the discharge orifice to the melter. (Hamel et al., 1998)	A flow-reducing orifice was installed to reduce airflow.	Operating limits for airflow rates, pressure, and temperature should be established prior to the start of the process.
At the Mayak vitrification facility in Russia, the HLW melter suffered an electrode failure due to excessive current load that caused accelerated corrosion and eventual failure of molybdenum electrodes. This was partially attributed to the failure of cooling systems for the electrodes. (Bradley, 1992)	The facility was shut down and a similar melter with improved electrode cooling system was installed.	Redundancy and stricter controls to operate within specification should be provided for critical systems. Performance of the melter should be continually assessed during operations via quality assurance programs and safety audits.

Table 14-1. Summary of melter-related incidents (cont'd)

Incident	Corrective Action	Lessons Learned
The mixed low-level radioactive vitrification facility in the M-area at the SRS site was shut down due to the formation of hot spots in the melter. The formation of hot spots was attributed to chemical additions that were made during the startup. (GTS Duratek, 1997)	The melter is in the process of being replaced.	Corrosivity of the melt and its compatibility with the components should be established before startup. Performance of the melter should be continually assessed during operations via quality assurance programs and safety audits.
At the Fernald site, a nonradioactive melter failed, spilling 6,000 kg of glass on the floor, due to degradation of the melter components caused by incompatible feed chemicals. (FERMCO, 1997)	The facility was shut down and no decision has been made to restart the facility.	Corrosivity of the melt and its compatibility with the components should be established before melter operations. Performance of the melter should be continually assessed during operations via quality assurance programs and safety audits.
At the LLW ISV plant at the ORNL, a release of offgas and an expulsion of 20,000 kg of glass caused glass fragments to be thrown up to 100 m from the melter site. In addition, several small fires resulted from escaping hot gases and molten glass. This event was a result of pressurized steam venting rapidly through the melt. (Oak Ridge National Laboratory, 1996)	The recommendations for corrective actions included diversion of standing water around the pit, installation of flow monitors and curved vent pipes beneath the melt to provide alternate paths for steam, sub-melt pressure measurement, and video monitoring of the melt surface.	Melters should have safeguards designed not only to account for normal operating conditions, but also for abnormal conditions such as steam explosion.

These examples clearly indicate that an in-depth understanding of melter design and of compatibility between melter and waste components is extremely important to minimize melter incidents. Even though the melter incidents that have occurred to date have not resulted in deaths or injuries, they did pose a threat to worker health and safety. In a robustly designed and built melter, control of the waste and glass chemistry under defined melter temperature and pressure ranges is a key to safe operations. Parameters such as chemical reactions, redox control, formation of conductive sludges, and glass properties such as viscosity, phase separation, and liquidous temperature should be addressed for safe operations. These parameters are discussed in the following sections.

14.2.1 Chemical Reactions

In a typical waste vitrification process, as slurry is fed to a melter, water evaporates and leaves behind a crusty layer of waste and glass-forming components. Organic and inorganic salts present in the slurry decompose in the crusty layer, releasing oxides of nitrogen, carbon, and sulfur. These reaction gases, along with water vapor, exit the melter through an offgas port. Knowledge of possible exothermic and endothermic chemical reactions that could occur within the crusty layer and formation of reaction gases such as ammonia, cyanides, and aromatic hydrocarbons is necessary to ensure that the process does not exceed safe concentration levels of flammable or explosive gases.

14.2.2 Glass Redox

The control of redox, defined as reduction-oxidation potential of the melt, is probably the most important process control parameter in the melter. The redox is dependent on both feed and melting systems, and is a result of the combined effects of reducing agents such as organics, oxidizing agents such as nitrates and nitrites; the waste concentrations of transition metal ions such as Fe, Cu, Mn, Ni, and Cr; and melter operating conditions such as bubbler flow rates, melter temperature, pressure, and air in-leakage into the melter. Both bubblers and air in-leakage introduce extra oxygen in the system and could potentially shift redox equilibrium. A redox response within a specified range is necessary to avoid process upsets that eventually could lead to permanent melter damage.

Because iron is abundant in most wastes, the redox response in most waste vitrification systems is measured by analyzing the Fe^{2+}/Fe^{3+} ratio. The melter environment is defined as being extremely reducing if the Fe^{2+}/Fe^{3+} ratio is greater than 1. Under such conditions, sufficient accumulation of conductive metals and metal sulfides could short-circuit the melter. If the Fe^{2+}/Fe^{3+} ratio is less than 0.01, the melter is defined as extremely oxidizing. The quantitative lower limit of Fe^{2+}/Fe^{3+} is not known; existing redox measurement equipment cannot analyze Fe^{2+}/Fe^{3+} less than 0.01 with confidence. Under extreme oxidizing conditions, foaming is observed in the melter. Foam creates an insulating layer of gas bubbles between the cold-cap and the melt, disrupting the thermal gradients in the melter. Typically, foaming, if controlled at its onset, slows the glass production rate but in most cases, is not an issue. However, if foaming is not controlled, conditions can arise that could lead to melter shutdown. For instance, the foam could fill the melter plenum, cause the melter offgas line to plug, and eventually pressurize the melter. If the melter pressure exceeds the pressure differential needed for glass pouring, a sudden uncontrolled discharge of the melt will occur. The discharge could result in complete blockage of the discharge chute with solid glass and lead to thermal shock of the melter due to a sudden loss of thermal mass in the melt chamber.

Because no on-line redox measurement tools are available, the redox response is usually forecast based on some empirical relationship between the feed characteristics and melter response. The WVDP and the DWPF use empirical models to forecast the redox state of the glass melt based on measured concentrations of the reducing and oxidizing components of the feed. The empirical models were developed based on extensive laboratory and pilot-scale testing of simulated feeds. At the WVDP, the redox is controlled by adding sugar to the feed, the amount of which is based on the nitrates, TOC, and % TS in the waste (Barnes and Jain, 1996). At the DWPF, the redox is controlled by addition of either formic acid or nitric acid to the feed using an empirical relationship based on the nitrate and formate analysis (Ramsey et al., 1994). Both the WVDP and DWPF melters operate at oxidizing conditions to avoid the formation of conductive sludges.

Redox monitoring of wastes containing high concentrations of MnO_2 and CuO is much more complex. Since both MnO_2 and CuO transitions occur at the oxidizing end of the Fe^{2+}/Fe^{3+} couple, the redox response cannot be correlated to the Fe^{2+}/Fe^{3+} ratio. In addition, reboiling occurs under oxidizing conditions. Reboiling is attributed to the shift in the redox state of the melt with a shift in temperature. The higher the temperature, the more reducing the melt becomes. Under reboiling conditions, MnO_2 is reduced to MnO, releasing significant amounts of oxygen. The reboil event behaves similarly to foaming, but is dependent on temperature changes in the melter.

The sensitivity of the redox response as a function of reductant concentration is extremely important in defining the redox range for any melter system. An acceptable range for redox response in the DWPF system is limited by the presence of CuO in the DWPF waste. In the melter, CuO could precipitate as Cu metal at moderately reducing conditions (e.g., at Fe^{2+}/Fe^{3+} greater than 0.5). On the other hand, an acceptable range for redox response in the WVDP system is very sensitive to the presence of nitrites. The operating range for redox is limited by the amount of nitrites present in the WVDP feed. Both DWPF and WVDP operations are limited to an extremely narrow redox range. The situation for TWRS waste is much more complex due to the presence of significant amounts of different types of organics. Melter incidents resulting from redox control problems for the TWRS waste should be addressed to determine the key parameters that will control the redox response.

14.2.3 Conductive Sludges and Noble Metals

Conductive sludges in the melter are defined as precipitated conductive metal sulfides or metals in the glass melt which are formed under reducing conditions. In addition, noble metals such as Rh, Pd and Ru, because of their very limited solubility in glass, tend to settle on the melter floor, forming highly electrically conductive paths. Most of these metals cannot be pretreated or extracted easily. Both formation of conductive sludges and settling of noble metals could potentially result in electrical shorting of a joule-heated melter. The melter design and feed composition should address the risk of premature melter failure, such as the one that occurred at the Pamela melter, due to settling of noble metals. An example of these studies is the extensive testing that was done at the PNNL to determine the influence of noble metals on the operational life of a reference Hanford Waste Vitrification Plant melter (Elliott et al., 1994).

14.2.4 Glass Properties

The proper design of glass composition is important to ensure that the glass can be processed within the operating range of the melter and will not degrade the melter design life. The properties that dictate glass processing include glass viscosity, electrical resistivity, liquidous temperature, and phase separation. These properties are discussed in the following sections.

14.2.4.1 Viscosity

Control of glass viscosity, similar to control of waste rheology, is extremely important for continuous and safe melter operations. HLW glass melters operate between a viscosity of 20 and 100 poise at their operating temperatures. The convective currents in the melt, due to the thermal gradients in the melter, are responsible for homogenization of waste and glass-forming chemicals. At a viscosity higher than 100 poise, homogenization of the waste components is delayed because higher viscosity slows the kinetics of convective mixing. In addition, high viscosity makes the flow of glass from the melter into the canister slow and difficult. Also, an extremely high viscosity could result in the formation of a glass plug at the discharge section. On the other hand, a viscosity less than 20 poise results in increased volatilization of radioactive components, such as Tc-99 and Cs-137, and of alkali oxides such as Na_2O, Li_2O, and K_2O and boron oxide. This could result in accumulation of radionuclides in the offgas filters instead of encapsulating in glass. The filters may need frequent replacement to avoid plugging. In addition, low glass viscosity increases refractory erosion.

14.2.4.2 Electrical Resistivity

The control of electrical resistivity of the glass melt is extremely important for joule-heated melter operations. The electrical resistivity is mostly due to ionic conductivity and is a function of glass composition, largely the concentrations of alkali oxides such as Na_2O, Li_2O, and K_2O. Joule-heated HLW glass melters operate at electrical resistivities between 5 and 10 ohm-cm at melter operating temperatures. High resistivity of the glass melt results in high voltage potential across the electrodes that allows conduction to occur within the refractory walls that could cause dissipation of heat in refractory walls and increase power requirements. On the other hand, low resistivity of the glass melt results in high current density that could exceed the current carrying capacity of the electrodes required to maintain the melt at the desired temperature and, thus, result in electrode failure.

14.2.4.3 Liquidous Temperature

Whenever a glass melt is cooled below the liquidous temperature, crystal formation occurs in the melt. The crystals that are formed could settle on the melter floor as do noble metals. However, unlike noble metals, the crystals may not be conductive. If the melter is maintained below the liquidous temperature for an extended period of time, these crystals could continue to form and eventually block the glass pour drains and make the melter non-functional. Depending upon the nature of these crystals, they may or may not redissolve in the melt upon reheating to above liquidous temperatures.

14.2.4.4 Phase Separation

Phase separation occurs whenever a component exceeds its solubility limit in the glass melt. The glass melts have very limited solubility for components such as noble metals and sulfur. The issues related to noble metals have been discussed in a previous section. The issues related to sulfur solubility are discussed next.

At the WVDP, the sludge was washed several times to reduce the concentration of sulfates, measured as SO_3, below 0.25 weight percent. The SO_3 solubility in WVDP reference glass is 0.25 weight percent; SO_3 concentrations above this value may result in formation of an immiscible molten sulfate (gall) layer on top of the cold-cap. This gall behaves like a foam. Also, at the Pamela vitrification facility, the amount of waste that could be processed into the glass was limited by the amount of sulfur in the waste (Wiese et al., 1988). In addition, the sulfates, in the presence of chlorides in the waste, dramatically corrode stainless steel and Inconel® between 500 and 900 °C. Glass composition should address the phase separation issues during melting. Potential for molten sulfate formation in Hanford waste is discussed in a paper by Sullivan (1995).

14.3 OFFGAS TREATMENT AND RELEASE

There are two major functions of the offgas treatment system: first, to ensure that offgas released to the atmosphere meets local, state, and federal guidelines; and second, to maintain a negative pressure in the vitrification facility. A typical offgas exiting the melter contains water vapor and oxides of nitrogen, carbon, and sulfur, along with entrained feed particles and volatile components. As the offgas is cooled, the entrained feed particles and volatile components deposit along the offgas pipeline. A robust design allows the entrained particles to either drop back into the melter or be carried over into another vessel without depositing along the offgas pipeline. If the design is not capable of meeting functional requirements, the deposits eventually build up, blocking the offgas flow. Under such conditions, the offgas released from the cold cap in the melter will pressurize the melting chamber. If the melter pressure exceeds the pressure differential needed for glass pouring, a sudden uncontrolled discharge of the melt similar to foaming events could occur. The discharge could result in a complete blocking of the discharge chamber with solid glass that would cause thermal shock of the melter due to a sudden loss of thermal mass in the melt chamber. In addition, overpressurization may cause the melter to release offgas outside the cell.

A generic offgas treatment consists of a quencher to cool the offgas, a series of scrubbers to remove NO_x and entrained particles, a HEME for removing mist, and HEPA filters for containment of radioactive particulates. In addition, the offgas system could include specific treatment components depending upon the nature of the offgas.

In most vitrification facilities, the offgas system controls the pressure in all the feed vessels and the melter. A slightly negative pressure is required to contain radioactivity within the system. Failure of the offgas blower or process upsets such as foaming, plugging of offgas lines, or plugging of the glass discharge chamber, could disrupt the offgas pressure control. During such upsets, it is likely that certain parts of the system could go slightly positive and release radioactivity outside the cell.

14.4 REMOTE OPERATIONS AND HUMAN FACTORS

In a HLW vitrification facility, all process components and equipment are enclosed within heavily shielded concrete walls because of the highly radioactive environment. A large amount of equipment is operated and maintained using MSMs and in-cell cranes. The complexity of the in-cell layout of equipment requires long hours of activity for expert MSM and in-cell crane operators. Human factors therefore, are an integral part of safe operations. Designing low-maintenance, MSM-friendly equipment and training operators to efficiently and effectively operate the MSMs will significantly reduce human errors, such as misalignments of pipes and hoses and incomplete closure of valves, that could lead to offgas releases or slurry leaks. Training of operators using mock-ups would also reduce downtime and incidents involving human error. An example of the use of MSM-friendly equipment is the redesign of a slurry sample station at the WVDP to simplify valve operations. This redesign reduced the sampling time and minimized radioactive slurry drips on the sample station floor (Hamel et al., 1998). Similarly, at the WVP at Sellafield, improvements to in-cell cranes and MSMs alleviated most of the in-cell operating problems and dramatically reduced downtime (Millington, 1995).

15 SUMMARY AND RECOMMENDATIONS

This report provides a current status of high-temperature solidification technologies that have been used or proposed throughout the world. The report includes a survey of technologies used or proposed in the waste management (chemical and nuclear materials) industries, and relevant information on commercial technologies used in the ceramic and glass industries. This report has been prepared to assist the NRC in:

- determining whether sufficient information exists to assess safety considerations regarding the Hanford TWRS,
- determining whether current regulatory guidelines are adequate for controlling implementation of the technology to solidify Hanford waste,
- identifying the existence of technical uncertainties,
- assessing where future guidance may be warranted, and
- evaluating a "first-of-a-kind" process that is being proposed or utilized.

The survey of waste solidification processes used in the United States and abroad indicates that, although major accomplishments have occurred in the area of vitrification in the last 20 yr, developments are continuing in other solidification technologies such as glass-ceramics, Synroc and, more recently, in molten metal processes. The technologies can be broadly classified into the following categories: Inconel®-based, joule-heated melters; high-temperature, joule-heated melters; induction melters; cold-crucible induction melters; plasma melters; combustion melters; microwave melters; molten metal technology; and Synroc technology. The development of a successful solidification process requires a reasonable level of characterization of the wastes that need to be solidified before a technology can be selected. This selection should be based on the nature of the waste and the final waste form that will provide effective encapsulation.

The joule-heated Inconel® melter technology and induction melting technology are the two most widely accepted and mature technologies for vitrifying HLW. Glass melting via joule heating is used in the United States, Japan, Russia, and Belgium, while glass melting via induction-type heating is used in France, England, and India for vitrifying HLW. Both technologies have successfully encapsulated HLW into glass and provide extremely low volatility for alkalis, boron, and radioactive components such as Tc and Cs, and a homogeneous product due to long residence time in the melter. While the joule-heated melter can be designed to meet production rate requirements [vitrification plant in Mayak, Russia, has a production capacity of 1,200-kg/hr (2,640-lb/hr) while the vitrification plant in Tokai, Japan, has a production capacity of 9-kg/hr (19.8-lb/hr)], the size of the induction melter cannot be increased due to the attenuation of induction frequencies in large-diameter crucibles. In addition, the life of a joule-heated melter ranges from 3 to 5 yr, while the melting crucible for the induction melting is considered a disposable item with replacement time ranging from 1,500 to 4,000 hr. Due to the design of the induction melting system, only calcined feeds can be processed in the melter while the joule-heated melter can easily adopt to wet or dry feeding. Other technologies that are discussed in the report are either in the development stage or have never demonstrated solidification of radioactive wastes.

Initial research on the development of the joule-heated vitrification process for HLW started in the early 1960s. The first vitrification plant that was operational in the United States was commissioned for radioactive operations in December 1985 to produce 32 heat and radiation source canisters for the FRG. This facility was shut down in March 1987. The melter was developed at the PNNL as a part of a bilateral agreement between the Bundesminiterium fur Forschung und Technologie and the DOE. The first joule-heated radioactive vitrification plant, the Pamela vitrification facility in Mol, Belgium, was commissioned in 1985. In the United States, vitrification plants at the WVDP and the DWPF were commissioned in 1996. The TVP in Japan was commissioned in December 1995 and employs a joule-heated melter system similar to the WVDP, West Valley, NY and the DWPF at the SRS. Major differences exist in the capacity of the TVP melter, which is only 0.3-m^3 (10.6-ft^3), compared to 0.9-m^3 (31.8-ft^3) at the WVDP and 2.2-m^3 (77.7-ft^3) at the DWPF, and the canister size, which is 300-kg (660-lb) for the TVP, and 2,000-kg (4,400-lb) for the WVDP and the DWPF. In addition, the average melt rate for the TVP is 9-kg/hr (19.8-lb/hr), compared to 30-kg/hr (66-lb/hr) for the WVDP and 100 kg/hr for the DWPF.

Induction melting technology using calcined wastes for encapsulating HLW was first developed in France. The AVM in Marcoule, France, was commissioned in 1978 to vitrify fission product solutions from the UP1 reprocessing plant in France. The success of the AVM led to the startup of two similar facilities, R7 and T7. The R7 and the T7 facilities were commissioned in 1989 and 1992, respectively, at the La Hague reprocessing plant. The R7 and the T7 are identical plants, each having three vitrification lines and are being used to vitrify UP2 and UP3 reprocessing plant wastes, respectively. Each vitrification line is designed for a production rate of 30-kg/hr (66-lb/hr). Furthermore, the United Kingdom adopted this technology at the Sellafield site in 1981. The WVP at Sellafield was commissioned in 1991. The WVP consists of two vitrification lines and has a higher production rate than the AVM.

Cold-crucible induction melting technology is an adaptation of the mature induction melting technology. Several pilot-scale tests are being conducted in France and Russia. Even though the technology has not been tested with radioactive wastes, several projects are under way to develop the process for radioactive operations worldwide (Jouan et al., 1998). In addition to the development of a CCM for the Hanford wastes under the TWRS program, two CCMs are being designed for shipment to Saluggia, Italy, to vitrify HLWs at the Saluggia site, and to Taejon, Korea, to incinerate and vitrify low-level reactor wastes. The interactions and corrosion between the waste, the glass, and the Inconel® crucible are significantly minimized by the formation of a skull layer at the glass-crucible interface, which provides a longer crucible life compared to induction melting systems. In addition, melting temperatures are not restricted by the operating temperatures for the Inconel® crucibles, which results in higher glass production rates.

The Hanford low-level vitrification test program was initiated to test and evaluate promising commercial vitrification technologies to support selection of reference technologies for the Hanford site LLW vitrification. This program evaluated seven different technologies: the cyclone combustion melter; the joule-heated Inconel® electrode melter; the carbon electrode melter; the plasma torch-fired cupola furnace; and three different types of high-temperature, joule-heated melters. The evaluation and assessment of the technologies determined that the joule-heated melter technology operating in a cold-top mode is the most reliable.

The MWFA was established by the DOE to develop and facilitate implementation of technologies required to meet DOE commitments for characterization, treatment, and disposal of mixed wastes. Under MWFA sponsorship, a number of thermal treatment technologies to stabilize mixed wastes have evolved. Several technologies such as the plasma hearth process, plasma arc process, high-temperature, joule-heated melters, alternating current arc melters, microwave melters, and combustion melting systems are extensions of the existing commercial technologies, while cold-crucible technology and the Q-CEP are new technologies that were evaluated by the MWFA.

The CEP is an innovative, flexible, proprietary technology of MMT, Incorporated, in Waltham, Massachusetts. This technology is used for processing hazardous waste streams. It allows the organic, organometallic, and inorganic waste streams to be recycled into useful resources. The Q-CEP is an adaption of the CEP technology for radioactive and mixed waste streams. In addition to the destruction of hazardous components, the Q-CEP allows partitioning of radionuclides. The partitioning allows recycling of large numbers of waste components into commercial products and the solidification of radionuclides, either in glass/ceramics or metal. In both the CEP and the Q-CEP, the molten bath (typically iron or nickel) acts as a homogeneous catalyst and as a solvent in dissociation of feeds, synthesis of products, and concentration of radionuclides in the desired phase. The Q-CEP was selected by the DOE as the alternative to joule-heated melter technology for the Phase I TWRS privatization program. Unfortunately, due to the proprietary nature of the process, not much information is available regarding operating experience with Q-CEP technology.

The high-temperature, joule-heated melter technology offers glass production rates higher than all other solidification technologies except for plasma and combustion melting systems. The production rate can be further enhanced by the use of bubblers and stirrers. Both the TVS and the Fernald high-temperature melter have failed during operations. The TVS failed due to thermal shock resulting from the heatup and cool-down cycles that the melter underwent during its operating life while the melter at Fernald failed as a result of excessive high-temperature corrosion of melter components and refractory erosion. More research is needed to ensure waste material compatibility with the components of the high-temperature, joule-heated melter.

The only operational, joule-heated, low-level radioactive mixed waste vitrification plant is situated in the M-Area at the SRS. The plant is in the process of vitrifying approximately 2,500 m^3 (660,500 gal.) of low-level radioactive mixed waste stored at the M-area. GTS Duratek completed the construction of the vitrification plant in January 1996, and commissioned it to process low-level radioactive mixed wastes in October 1996. The, Duramelter® 5000 is currently the largest low-level radioactive melter system operating in the world. This is also a one-third size prototype of the melter system to be built for the TWRS in Richland, Washington. On March 31, 1997, waste processing was temporarily suspended after observing possible signs of erosion and corrosion on the melter components. Visual inspections indicated the formation of hot spots in the melter due to refractory corrosion by molten glass, especially at the refractory joints. The facility was restarted after installation of a new melter.

Plasma melting technology has been widely used in the commercial steel industry for a long time, and its adoption to waste solidification is quite recent. Several pilot-scale plants are operating and some testing has been performed using low-level radioactive mixed wastes. Full-scale radioactive testing has not been performed. The technology is well suited for hard-to-vitrify heterogeneous wastes due to high operating temperatures. Short plasma torch life is a major concern in plasma systems for radioactive operations that, depending upon operating conditions, could range from a few hours to a few days.

Combustion melting technology, like plasma melting technology, is a developing technology. Even though this technology has been used in the commercial glass, coal, and steel industries for a long time, its adoption to waste solidification is quite recent. Several pilot-scale plants are operating, but radioactive testing has not been performed. In both plasma melting and combustion melting technology, glass production rates are high, but volatility due to high operating temperatures and inhomogeneity resulting from short residence time are a concern. In addition, extremely high operating temperatures cause extensive erosion and corrosion of refractories and melter components.

Microwave melting is an experimental technology. There are no full-scale radioactive operating microwave solidification systems. Some radioactive waste vitrification studies have been conducted using pilot-scale melter systems. Microwave melting is a one-step process. The waste can be melted and disposed in the same container. Due to low melting temperatures, volatility is low. Glass production rates are limited by the size of drums that can be placed in a microwave melter. The size of the drum is limited by the inability of the microwaves to uniformly heat large quantities and due to nonuniform melting, and the glass product is inhomogeneous. The interactions and corrosion between the waste, the glass, and the container have not been established. In some instances, the formation of hot-spots has led to glass flow from the containers.

Synroc technology has been around for a long time, but it is still a developing technology. There are no operating Synroc solidification plants processing radioactive materials. A pilot plant has been operating in Australia for several years with nonradioactive feed. Synroc is an excellent waste form for disposal. Hot-pressing makes the product homogeneous and reduces volatility during processing. Since no melting is required, corrosion issues are minimal. The waste is hot-pressed in stainless steel bellows, that become a part of the waste form. Noble metal accumulation is not an issue. All components are retained in the Synroc: each time, the process starts with a fresh batch. Synroc production is a batch process. The production rates are limited by the size of hot-presses.

Based on the review of the solidification technologies, technological assessments, and evaluation of the process and operational safety issues, a number of areas associated with the solidification options for TWRS activities that will require evaluation have been identified. These include:

- Explosion hazard due to flammable gas (hydrogen and ammonia) generation.
- Criticality hazard from plugging and accumulation of radionuclides in transfer and offgas pipes.
- Uncontrolled chemical reactions, leading to radionuclide release, due to mixing of incompatible wastes and chemicals.
- Corrosion of melter components, leading to melter failure, due to processing of wastes containing corrosive chemicals.
- Gap formation in the melter, due to thermal stresses and thermal shock during heatup and cool-down cycles.
- Precipitation of metals, leading to electrical shorting of the melter, due to improper redox control methodology or settling of noble metals.
- Failure of the process components, leading to radionuclide release, due to incompatibility of the materials-of-construction with waste and feed chemistry.

In summary, it is important that the plant be designed to accommodate possible variables in the wastes to ensure safe operations. Because of limited knowledge regarding waste compositions at the Hanford site, that task is challenging, but lessons learned from the design and operations of commercial industries and the radioactive and nonradioactive plants in operation around the world will be useful in minimizing process and safety risks.

16 GLOSSARY

Calcined Waste—Powdered waste in which the salts such as nitrates, carbonates and hydroxides, have decomposed to their oxide form.

Cold-Cap—A semi-solid crusty layer of waste components floating on top of the molten glass in a melter. Cold-cap is responsible for minimizing volatilization of components such as Tc, Cs, Na, Li, K and B.

Decontamination Factor—The factor by which the concentration of radioactive contaminants is reduced, measured by the ratio of initial radioactivity to that after decontamination.

Double-Shell Tank—The newer one-million-gallon underground waste storage tanks consisting of a concrete shell and two concentric carbon steel liners with an annular space between the liners.

Float-glass—Flat glass that has been formed on molten metal.

High-Efficiency Particulate **Air**—A filter designed to achieve 99.995 percent minimum efficiency in the containment of radioactive particulates greater than 0.3 micrometer in size.

High Level **Waste**—HLW means: (i) irradiated reactor fuel, (ii) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated fuel, and (iii) solids into which such liquid wastes have been converted.

Neutralized Current Acid Waste—The primary HLW stream from the PUREX process. It is a liquid waste, high in Cs, Sr, and **TRU** content, and is the most radioactive of the waste streams from the reprocessing facility.

Salt Cake—At DWPF, the HLW supernatant is concentrated by evaporation beyond saturation. The concentrate is then transferred to the tank and is called salt cake. The salt cake and its saturated solution contain most of the radioactive Cs-137 and traces of Sr-90.

> —At Hanford, crystallized nitrate and other salts deposited in HLW tanks, usually after active measures are taken to remove moisture.

Skull Layer—Layer of cold glass formed between crucible and molten glass in a cold crucible melter.

Sludge—Solids consisting mostly of precipitated metal hydroxides except alkali metals. These are formed after waste neutralization with sodium hydroxide solution.

Transurauic Waste—Wastes containing elements with atomic numbers greater than that of uranium.

17 ACRONYMS

% TS—Percent of Total Solids

AVM—Atelier de Vitrification de Marcoule (Marcoule Vitrification Facility), Marcoule, France

AZS—Alumina-Zirconia-Silicate

B&W—Babcock & Wilcox, Alliance, Ohio

CCM—Cold-Crucible Melter

CEP—Catalytic Extraction Process

CFMT—Concentrator Feed Makeup Tank

CMM—Canister Manipulating Mechanism

CMS—Combustion and Melting System

CRV—Counter-Rotating Vortex

CUA—Catholic University of America

DC—Direct Current

DNFSB—Defense Nuclear Facilities Safety Board

DOE—U.S. Department of Energy

DWPF—Defense Waste Processing Facility

EPA—U.S. Environmental Protection Agency

EPI—Electro-Pyrolysis, Inc.

FACTS—Functional and Checkout Testing of Systems

FHT—Feed Hold Tank

FRG—Federal Republic of Germany

GTAW—Gas Tungsten Arc Welder

HEME—High-Efficiency Mist Eliminator

HEPA—High-Efficiency Particulate Air

HEWC—High-Enriched Waste Concentrate

HLLW—High-Level Liquid Waste

HLW—High-Level Waste

ICC—Inner Canister Closure

IDMS—Integrated DWPF Melter System

IFO—Index of Feed Oxidation

ILDS—Infrared Level Detection System

INEEL—Idaho National Engineering Laboratory

ISPV—*In Situ* Plasma Vitrification

ISV—*In Situ* Vitrification

ITP—In-tank Precipitation Process

IWDV—*In Situ* Waste Destruction and Vitrification

LEWC—Low-Enriched Waste Concentrate

LFCM—Liquid-Fed Ceramic Melter

LLW—Low-Level Radioactive Waste

LSFM—Large Slurry-Fed Melter

MAWS—Minimum Additive Waste Stabilization

MFHT—Melter Feed Hold Tank

MFT—Melter Feed Tank

MIT—Massachusetts Institute of Technology

MMT—Molten Metal Technology

MSM—Master Slave Manipulators

MTU—Metric Ton Uranium

MWFA—Mixed Waste Focus Area

NRC—Nuclear Regulatory Commission

OGCT—Offgas Condensate Tank

OU-4—Operable Unit 4

ORNL—Oak Ridge National Laboratory

PACT—Plasma Arc Centrifugal Treatment System

PCCS—Product Composition Control System

PCT—Product Consistency Test

PEI—Penberthy Electromelt International, Inc., Seattle, Washington

PHA—Precipitate Hydrolysis Aqueous

PHP—Plasma Hearth Process

PICCM—Plasma-Induction Cold-Crucible Melter

PNC—Power Reactor and Nuclear Fuel Development Corporation

PNNL—Pacific Northwest National Laboratories [originally called Pacific Northwest Laboratories (PNL)]

PSCM—Pilot-Scale Ceramic Melter

PUREX—Plutonium-Uranium Recovery Extraction

Q-CEP—Quantum-Catalytic Extraction Process

RASP—Reactive Additive Stabilization Process

RFP—Rocky Flats Plant

RLFCM—Radioactive Liquid-Fed Ceramic Melter

SAIC—Science Applications International Corporation

SAS—Steam Atomizing Scrubber

SBS—Submerged Bed Scrubber

SCR—Selective Catalytic Reduction

SDP—Synroc Demonstration Plant

SFCM—Slurry-Fed Ceramic Melter

SME—Slurry Mix Evaporator

SMT—Slurry Mix Tank

SRAT—Sludge Receipt and Adjustment Tank

SRS—Savannah River Site

SST—Single-Shell Tank

STAR—Science and Technology Applications Research Center, Science Applications International Corporation

SVS-III—Scale Vitrification System III

Synroc—Synthetic Rock

TECO—Toledo Engineering Company

THOREX—Thorium Recovery Extraction

TOC—Total Organic Carbon

TPB—Tetraphenyl Borate

TRM—Telerobotic Manipulator

TRP—Tokai Reprocessing Plant

TRU—Transuranic Waste

TVP—Tokai Vitrification Plant

TVS—Transportable Vitrification System

TWRS—Tank Waste Remediation System

USBM—U.S. Bureau of Mines, Albany, Oregon

VF—Vitrification Facility

VPPS—Fernald Vitrification Pilot Plant System

VPS—Vitrified Product Store

VRL—Vitrification Research Laboratory

VSL—Vitreous State Laboratory, Catholic University of America

WHC—Westinghouse Hanford Company

WIP—Waste Immobilization Plant

WQR—Waste Form Qualification Report

WSTC—Westinghouse Science and Technology Center, Pittsburgh, Pennsylvania

WVDP—West Valley Demonstration Project

WVP—Waste Vitrification Plant, Sellafield, United Kingdom

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APPENDIX A

PRIMER ON GLASS PRODUCTION

A.1 Introduction

Radioactive wastes can be encapsulated into several solid forms such as cement, mortar, concrete, crystalline ceramics, glass and metals. Glass has developed as a preferred waste form among all available waste forms for encapsulation of high level waste (Hench, 1995). The sections below define glass as a waste form and discuss basic technologies involved in transforming radioactive waste into glass.

A.2 Glass

Glasses are generally considered as solids with liquid like structure, noncrystalline solids or simply as amorphous solids (Varshneya, 1994) and are broadly categorized into inorganic, organic or metallic glasses. The discussion on the formation of organic and metallic glasses is beyond the scope of this review. The inorganic glasses are further classified into oxide and nonoxide glasses. The oxide glasses are predominantly used for encapsulating radioactive wastes.

Oxide glasses are either single component or multi-component. In most multi-component oxide glass forming systems, silica is a major component. Depending on the remaining components, oxide glasses relevant to radioactive waste vitrification can be classified as alkali silicates (glasses containing a mixture of alkali oxides and silica), alkali borosilicates (glasses containing a mixture of alkali oxides, boron oxide and silica), alkali aluminosilicates (glasses containing a mixture of alkali oxides, aluminum oxide and silica), and alkali boroaluminosilicates (glasses containing a mixture of alkali oxides, boron oxide, aluminum oxide and silica). The non-silica based oxide glasses include phosphates glasses. The glass compositions most widely used for the LLW and HLW vitrification fall into the category of alkali boroaluminosilicates. These glasses offer excellent durability and thermal stability for long-term storage.

A.3 Glass Properties

The control of glass properties, such as viscosity, electrical resistivity, and liquidous temperature, within the range shown in Table A-1, is extremely important in encapsulating waste into glass. The electrical resistivity determines weather joule heating will be effective in dissipating heat while viscosity ensures that the glass will easily flow and homogenize in the melter. The liquidous temperature establishes the lowest temperature below which melter operations for extended time will crystallize the melt.

A.4 Vitrification

The process of fusing components of the waste and glass forming oxides into a glassy structure is called "vitrification." Even though glasses have an ability to incorporate most of the elemental constituents of the radioactive waste into a glassy matrix, it requires temperatures in excess of 1,100 °C. The upper operating temperature depends upon the choice of electrodes. In melters having Inconel® electrodes, the maximum operating temperature is 1,150 °C to avoid creep in the electrodes while for molybdenum electrodes, the maximum operating temperature is 1,500 °C.

The vitrification temperature depends upon amount of flux present in the composition. Fluxes are defined as the components, such as alkali oxides and boron oxide, that lower the fusing temperature of the glass. It should be noted that the higher the amount of fluxes, the lower the durability of the waste form. The solubility of various components in glass depends on the composition of the glass as well as the chemical composition of the radioactive waste. Special consideration is required for low solubility components such as sulfates and noble metals, and volatile components such as halides during process flowsheet development.

Table A-1. Process constraints (Barnes and Jain, 1996)

Parameter	Lower Acceptance Bound	Upper Acceptance Bound
Viscosity at 1100 °C (Poise)	20	100
Glass electrical resistivity at 1100 °C (ohm-cm)	5	10
Liquidous temperature	N/A	1,050

A.5 Process Chemistry

In a typical radioactive waste vitrification process, a liquid slurry (in INEEL case, calcined waste mixed with dry or wet glass formers) containing radioactive wastes mixed with glass forming chemicals is fed into a melting vessel. As the slurry falls on the top of the molten glass melt contained in the melter, water evaporates leaving behind a crusty layer of salts. This crusty layer of salts is called "cold-cap". The formation of stable cold-cap is extremely important to minimize volatilization of radioactive species such as Cs-137. The components of the cold-cap decompose as the heat from the molten glass pool is transferred into the cold-cap. The inorganic salts, which are predominantly a mixture of nitrates, nitrites, and sulfates, and organic compounds such as sugar and/or formic acid decompose leaving behind calcined metal oxides. The decomposition gases, consisting mostly of NO_x from nitrates and nitrites, CO/CO_2 from organics and SO_x from sulfates, exit the melter through an offgas line and are treated to remove entrained solids, volatile components such as Cs-137 and hazardous components prior to releasing to the atmosphere. The calcined oxides fuse together to form a glassy melt. Process is optimized by controlling the parameters such as melt temperature, melter pressure, slurry feed rate, redox chemistry and glass pour rate.

A.6 Vitrification Technology

Fossil fuel combustion and electric heating are the primary sources of thermal energy used for vitrification. While fossil fuel combustion is a primary mechanism for making glass in the traditional glass industry, the radioactive waste industry depends largely on electric heating for vitrification. The electric heating mechanisms that are currently used or are being developed include joule heating, induction heating, microwave heating, plasma heating, and electric arc heating.

In joule heating, a liquid slurry is fed to a refractory lined ceramic melter and a set of Inconel® or molybdenum electrodes supplies electric current through a melt. The internal resistance offered by the melt dissipates energy in the form of heat energy. The joule heating is most effective when the resistivity of the melt is between 5 and 10 ohm-cm at 1,100 °C.

In induction heating, calcined waste and glass forming oxides are placed in an induction-coil-lined Inconel® melter and subjected to an alternating electromagnetic field. The induced currents produced in the calcined waste dissipate electric energy in the form of heat by the joule effect. Note that in the induction melters an additional pretreatment process step to calcine the slurry is required prior to vitrification. Induction melters are not suitable for water-based slurries. The high-frequency cold-crucible induction melters, in addition to normal induction heating has a series of sectored water cooling-coils that cools the surface of the melter and forms a skull-layer around the melter. A "skull layer" is defined as a frozen vitrified solid layer of the melt around the crucible-melt interface. This significantly prolongs the melter life.

Microwave heating is a form of dielectric heating in which waste and glass forming oxides are polarized in an alternating, microwave-frequency electric field. As the electric field alternates, distortion of the polarized molecules causes heat dissipation.

Plasma heating is accomplished by converting gases, such as nitrogen, oxygen, noble gases, air or mixtures of these gases, into plasma by an electric arc. An electric arc can either be generated by direct current or alternating current. In a non-transferred arc process, plasma is generated by passing gas between the electric arc that is generated between two internal electrodes within the plasma torch. In a transferred arc process there is only one electrode in the torch while the other electrode is the waste material itself. Plasma is generated as the gas passes through an electric arc between the torch and the waste material. In electric-arc heating, which is slightly different from plasma heating, heat is transferred to the waste and glass forming oxides by ionized gases generated by creating an electric discharge between two electrodes.

In summary, selection of glass composition, type of melting technology and pretreatment requirements depends largely on the chemical composition and the characteristics of the waste, and the final set of waste form properties required for disposal.

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