

Vitrification of Ion-Exchange (IEX) Resins: Advantages and Technical Challenges

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VITRIFICATION OF ION-EXCHANGE (IEX) RESINS: ADVANTAGES AND TECHNICAL CHALLENGES†

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ABSTRACT

Technologies are being developed by the US Department of Energy's (DOE) Savannah River Site (SRS) in conjunction with the Electric Power Research Institute (EPRI)† and the commercial sector to convert low-level radioactive ion exchange (IEX) resin wastes from the nuclear utilities to solid stabilized waste forms for permanent disposal. One of the alternative waste stabilization technologies is vitrification of the resin into glass. Wastes can be vitrified at elevated temperatures by thermal treatment. One alternative thermal treatment is conventional Joule heated†† melting. Vitrification of wastes into glass is an attractive option because it atomistically bonds both hazardous and radioactive species in the glass structure, and volume reduces the waste by 70 - 80%. The large volume reductions allow for large associated savings in disposal and/or long term storage costs.

† Westinghouse Savannah River Cooperative Research and Development Agreement (CRADA) No. CR-94-002

†† Joule heated melters vitrify waste in a refractory-lined vessel containing diametrically opposed electrodes. The electrodes are used to heat the glass by passing an electric current through the material. This process is called Joule heating.

I. INTRODUCTION

Spent ion exchange (IEX) resin wastes are generated from a variety of waste treatment processes in the DOE complex and in commercial nuclear facilities. The spent IEX resins are generated during the decontamination of liquid or aqueous process streams. The contaminants which are removed from the aqueous streams and sorbed on the IEX resins can be radioactive, hazardous, or both. Thus, spent resins exist as High Level Waste (HLW),* Low Level Waste (LLW),** and Mixed Low Level Waste (MLLW).†††

* highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products in sufficient concentration (Nuclear Waste Policy Act of 1992)

** waste that is not high-level radioactive waste, spent nuclear fuel, transuranic waste, or by-product material as defined in section 11e(2) of the Atomic Energy Act of 1954 (Nuclear Waste Policy Act of 1992)

††† waste that contains source, special nuclear, or byproduct material subject to regulation under the Atomic Energy Act and hazardous waste species subject to regulation under the Resource Conservation and Recovery Act waste as defined in 40 CFR 261 (U.S. Code Title 42, Section 2011); if the hazardous species are on the U.S. Environmental Protection Agency (EPA) list of hazardous wastes as outlined in 40 CFR 261.31, .32, .33 then the waste is considered a "listed" MLLW

IEX resins are used in defense and commercial power reactors to remove hazardous anions and cations, particularly low levels of fission products such as Cs^{137} , Sr^{90} , Co^{60} , C^{14} and Tc^{99} . In addition, some tritium contamination or suspect tritium contamination is usually present. The IEX resin wastes from commercial power reactors typically use organic resins with sulfonated or chlorinated groups. The resin wastes, ashes or residues resulting from thermal treatment of such resins are, therefore, usually high in sulfur or chlorine.

The resin wastes from Boiling Water Reactors (BWR) are enriched in constituents such as Fe_3O_4 while wastes from Pressurized Water Reactors (PWR) are enriched in borate used as a homogeneous moderator and in Li^7 used for pH control. In addition, these wastes are usually contaminated with Cs^{137} and Co^{60} . Both dry and wet wastes from BWR/PWR reactors can be combined, e.g. IEX resins, waste sludges, filter aids, slurries, and other spent decontamination solutions.¹ Approximately, 100,000 lbs of BWR IEX waste and 30,000 lbs of PWR IEX waste are generated per reactor per year.[†] Large volumes of IEX waste must, therefore, be converted to a solid stabilized waste form for permanent disposal.

II. RATIONALE FOR VITRIFICATION

One alternative IEX resin waste stabilization option is to vitrify the hazardous and radioactive species into glass.² The rationale for the vitrification of IEX resin wastes are the following:

- glass is a very durable and environmentally acceptable waste form because both hazardous and radioactive species are atomistically bonded in the glass

[†] EPRI consultant, Jene N. Vance

- the Environmental Protection Agency (EPA) has declared vitrification the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste³
- the EPA has produced a Handbook of Vitrification Technologies for Treatment of Hazardous and Radioactive Waste⁴
- the DOE Office of Technology Development (OTD) has taken the position that MLLW should be stabilized to the highest level reasonably possible to ensure that the resulting waste form will meet both current and future regulatory specifications
- vitrification allows glass to have a high potential to meet the EPA characteristically hazardous and/or listed Land Disposal Restrictions (LDR's)^{††}
- glass formulations are flexible and easily accommodate process chemistry variation
- waste pretreatment is often minimal; waste can be dry or slurry fed to a melter
- high throughput melters which are low in cost, compact and have simple maintenance features are readily available from commercial vendors and can be made transportable
- commercially available melters have the ability to handle high concentrations of sulfate
- vitrification allows for large volume reductions, sometimes up to or greater than 97%⁵⁻⁶

^{††} vitrified waste forms have the highest probability of being "delisted"

- large reductions in volume minimize long-term storage or disposal costs
- minimization of long-term storage costs makes vitrification cost effective on a life cycle basis
- vitrification is a well developed technology
- vitrification and resin destruction avoid hydrogen generation of "resin only" storage or disposal in cement⁷

The US DOE Savannah River Site (SRS), which is operated by Westinghouse Savannah River Company (WSRC), is currently investigating vitrification for disposal of various low-level and mixed wastes.^{4-6, 8} The first hazardous/mixed wastes vitrified in laboratory studies at SRS have been (1) simulated incinerator wastes (ash and blowdown) and (2) actual listed nickel plating line (RCRA F006) waste water sludges admixed with spent filter aids. Additional studies have concentrated on sludges produced from various waste water treatment facilities at the Oak Ridge Reservation (ORR) and on cementitious waste forms that were incompletely stabilized. The current study investigates the use of vitrification for IEX resin wastes from commercial power reactors via Cooperative Research and Development Agreement (CRADA CR-94-002) between WSRC and the Electric Power Research Institute (EPRI).

III. VITRIFICATION PROCESS

Vitrification into simple glass compositions is achieved by tailoring a glass composition to take advantage of the common glass constituents in the waste. This allows for maximum waste loadings to be achieved, e.g. wastes high in borate and lithium, like the PWR wastes, would be stabilized in the alkali-boro-silicate glass forming system. Reactive additives are chosen or a glass-making frit is developed based on the "glass

forming potential" of the waste. Stabilization of heavy metals in glass has been shown to be enhanced by use of reactive additives* such as diatomaceous earth, perlite (perflo), rice husk ash, and/or precipitated silica.⁵⁻⁶ Use of highly reactive silica was determined to lower vitrification temperatures, increase waste loadings, maximize volume reductions, minimize melt line corrosion, and produce EPA acceptable glasses.

Vitrification via the Reactive Additive Stabilization Process (RASP) can be used to vitrify the following types of wastes:

- spent filter aids from waste water treatment
- waste sludges
- combinations of spent filter aids from waste water treatment and waste sludges
- combinations of supernate and waste sludges
- incinerator ash
- incinerator off-gas blowdown
- combinations of incinerator ash and off-gas blowdown
- cement formulations in need of remediation into glass
- inorganic filter media
- ion exchange (IEX) resins or zeolites
- asbestos or glass fiber filters
- radioactive materials including TRU wastes

* Reactive Additive Stabilization Process (RASP), U.S. Patent 5, 434,333

- contaminated soils, mill tailings, and other geologic media

Glass fluxing agents are added, if necessary, to lower melt temperatures and minimize volatilization of hazardous and/or radioactive species. The wastes plus additives are mixed and slurry fed to a melter where they are reacted at temperatures of 1150°C or greater.

IV. GLASS FORMING POTENTIAL OF A WASTE

In order to determine the "glass forming potential" of a waste, an approximate chemical composition should be determined by either a variety of wet chemical techniques,[†] by x-ray fluorescence (XRF), or by process history. For slurries or aqueous solutions a wt% solids should be determined after drying at 110°C. Additional information can be obtained about the species that will volatilize by analyzing the waste after drying at 110°C, 350°C, 650°C, and 1150°C. This allows determination of the waste composition on a dry calcine, e.g. glass forming, oxide basis. Dried sludge can also be analyzed by x-ray diffraction (XRD) to determine the major crystalline phases present.

The cation, anion, and XRD analyses are coupled together to determine if the various analyses are consistent, e.g. a mass balance analysis is calculated using the pooled waste analyses. Mass balance calculations are useful to verify the accuracy of the waste analyses. Mass balance analyses using the phases analyzed by XRD allows for a semi-quantitative determination of the species

expected to volatilize during vitrification, e.g. H₂O, CO₂, NO_x, organics, etc. This information assists in determining the amount and composition of the anticipated off-gas produced by a given waste stream.^{††}

The major cationic species left after calcining (drying at temperatures sufficient to drive off all anions except oxygen, e.g. > 800°C) are used to determine the "glass forming potential" of the waste. Wastes high in B₂O₃ would be formulated preferentially in the alkali-boro-silicate system, e.g. in the known region of durable homogeneous glasses formulated for HLW (Figure 1). Wastes high in CaO on a dry calcine oxide basis, would be formulated in the Soda-Lime-Silica (SLS) system due to the large known immiscibility gap in the CaO-B₂O₃-SiO₂ system.⁹ Wastes high in Fe₂O₃ could be formulated in either glass forming system. However, alkali-boro-silicate glasses

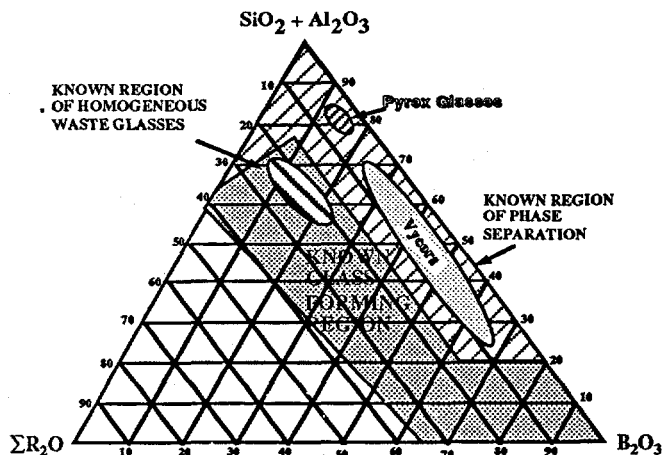


Figure 1. Composite diagram of the alkali-boro-silicate system indicating regions where homogeneous and inhomogeneous (phase separated) glasses form.¹⁰

[†] The EPA SW846 Method 3050 is not aggressive enough to determine the concentrations of major glass forming species such as Al₂O₃ and SiO₂ in wastes and use of this technique should be restricted to determination of the hazardous constituents of the waste; analysis by XRF or more aggressive chemical methodologies should be used to determine the major inorganic cationic species.

^{††} Volatiles can also be determined by Differential Thermal Analysis (DTA) coupled with Gas Chromatography and Mass Spectrometry (GCMS)

are preferred¹⁰ when volatilization of hazardous and radioactive constituents is a concern since the borosilicate glasses are known⁹ to melt at lower temperatures than SLS glasses.

V. SYSTEMS APPROACH

A systems approach to glass formulation is used to simultaneously evaluate product performance and processing considerations.¹⁰⁻

¹¹ Glass formulation includes the simultaneous optimization of the following process and product constraints:

- product control
 - chemical durability
 - homogeneity
 - thermal stability
- process control
 - viscosity
 - liquidus
 - volatility
 - melt temperature
 - melt corrosivity
 - waste solubility

This "systems approach" requires that parameters affecting product performance and processing considerations be optimized simultaneously. The "systems approach" ensures that the final product safeguards the public, and that the production process used is safe to operate.

First principles process and product quality models were developed at SRS¹¹ for vitrification of HLW in a borosilicate glass matrix. These process/product models directly relate process and product parameters to glass and/or feed composition.¹¹ This statistical process control methodology¹² provides for fabrication of durable waste glasses which are processable. This statistical process control methodology is direct applicable to vitrification of resin wastes in borosilicate glasses.

A. Product Control

The most important glass product property is the glass durability.¹⁰⁻¹¹ The durability of a waste glass is the single most important variable controlling release of radionuclides and/or hazardous constituents to the biosphere.

The chemical durability of glass is a complex phenomenon that depends on a variety of kinetic and thermodynamic parameters. However, the long-term durability of a wide variety of glasses has been determined to be a function of the glass composition. A model, the Thermodynamic Hydration Energy Reaction Model (THERMO) has been developed to relate glass composition to glass durability test response.^{11,13} THERMO is based on the calculation of the thermodynamic hydration free energy which is calculated from glass composition (including the redox) and/or the melter feed composition. The model expresses the thermodynamic tendency of species (components) in a glass to hydrate.

The reduction-oxidation (redox) equilibria of alkali borosilicate glasses used for waste disposal is important because glasses which have large concentrations of reduced iron are known to be poorly durable.¹³ In addition, glasses which are too reduced or too oxidizing can cause processing problems.

B. Glass Homogeneity

During the development of glass formulations for HLLW, known alkali borosilicate phase diagrams were compiled to determine the homogeneous glass composition envelope. The composite diagram is shown in Figure 1. Glasses in the region of phase separation form two separate glass phases, e.g. glass-in-glass phase separation. One phase is usually borate rich and is more soluble and the second phase is usually silicate rich and more insoluble. The durability of phase separated glasses is often poorer than that of homogeneous glasses because the durability test response is

dominated by whichever glass phase is more soluble.

The durability of waste glasses formulated in the region of known homogeneity give consistent durability test response. Glasses which phase separate give inconsistent durability test response unless the glass cooling rate is controlled. Controlled cooling rates are not employed during waste vitrification and so glass formulations are developed using models which avoid the composition regions in Figure 1 which are known to phase separate.

Glass durability can also be adversely affected by crystallization. Crystallization can sometimes cause accelerated leaching.¹⁴ However, some isometric crystals such as spinel do not disturb the glass matrix and do not cause accelerated leaching.¹⁴

C. Thermal Stability Considerations

Crystallization in glass can be eliminated, if desired, by defining the regions of thermal stability for the glass. This can be accomplished by determining the time-temperature-transformation (TTT) diagrams for the waste glass.¹⁴⁻¹⁵ Avoiding the time and temperature conditions that cause crystallization during processing and storage will eliminate concerns about the thermal stability and crystallization of the glass as well as any adversely effects on product performance.

VI. PROCESS CONTROL

A. Glass Viscosity (and Resistivity)¹¹

The viscosity of a glass melt, as a function of temperature, is the single most important variable affecting the melt rate and pourability of the glass. The viscosity determines the rate of melting of the raw feed, the rate of glass

bubble release (foaming and fining), the rate of homogenization, and thus, the quality of the final glass product. If the viscosity is too low, excessive convection currents can occur, increasing corrosion/erosion of the melter materials (refractories and electrodes) and making control of the melter more difficult. It is recommended that the lowest glass viscosities be conservatively set at ~20 poise at the melt temperature, T_{melt} .

Waste glasses are usually poured continuously into canisters or cans for ultimate storage. Glasses with viscosities above 500 poise at T_{melt} do not readily pour. Moreover, too high a viscosity can reduce product quality by causing voids in the final glass. A conservative range of 20-100 poise at T_{melt} is recommended as optimal.

Although, electrical resistivity of waste glasses is not a process model constraint, the electrical resistivity of a glass is highly correlated with its viscosity. The ability to predict the electrical resistivity of a glass from its composition, or alternatively from its viscosity, is important to startup and/or restart of Joule-heated electric melters. At low temperatures, glasses are good insulators, while at high temperatures they conduct electric current relatively well so that the glass melt may be heated by direct passage of electric current. The electrical resistivity is, therefore, the single most important variable affecting the establishment of Joule heating in an electric melter.

Models¹¹ exist for relating borosilicate glasses compositions to melting and establishment of Joule heating.

B. Glass Liquidus¹¹

Formation of crystals in the melt during processing in a Joule heated melter can cause problems with processing and discharging of the glass. If a waste glass is not properly formulated, the insoluble species can form crystals during melting which settle to the

floor of the melter and form viscous layers. Formation of a viscous layer is highly undesirable because the viscosity of the melt increases sharply and this can cause difficulty in melting and discharging the glass.

C. Species Volatility/Melt Temperature

Waste glasses formulated for wastes containing radioactive or hazardous volatile species should be optimized at melt temperatures of $\sim 1150^{\circ}\text{C}$ or below in order to minimize volatility.

D. Melt Corrosivity and Waste Solubility Considerations

For HLLW vitrification, finely reactive glass forming "frits" have been developed as the glass forming additives in order to maximize glass homogeneity, simplify process control, and lower melt temperatures which minimize volatility. For LLMW wastes, the RASP process defined previously can be used to enhance the solubility and retention of hazardous, radioactive, and heavy metal species in glass.⁵⁻⁶

The RASP process was also determined to minimize accelerated melt line corrosion.⁵⁻⁶ In addition, melt line corrosion and general refractory corrosion can be minimized by formulating glasses with viscosities >20 poise.

VII. TECHNICAL ADVANTAGES

A. Optimization of Vitrification Advantages

As discussed in Section II and summarized in Table 1, there are many advantages to support vitrification as a means of IEX resin waste stabilization. Although glass formulations are flexible and will easily accommodate a wide chemistry variation of feed material, a systems approach should be utilized to optimize parameters that affect both product performance and processing considerations. Optimization leads to maximum waste loading (or volume reduction) which translates into minimized storage volumes and life cycle costs.

Table 1. Vitrification Advantages of Ion Exchange Resins.

Vitrification Advantages	Processing Solution(s)
Volume Reduction (minimize storage volume)	Maximize waste loading
Cost Savings (storage costs, lower life cycle costs, etc.)	Maximize waste loading
High Durability	Known glass formulating region of high durability
Radionuclides Atomistically Stabilized	Low temperature glass formulation for volatiles, SPC and/or models
Flexible and easily accommodate process chemistry variation	SPC and/or models
Developed Technology (processing and product performance)	Not Applicable
Avoid Hydrogen Generation of "Resin Only" Storage and/or Cement	Not Applicable

VIII. TECHNICAL CHALLENGES

Although vitrification of IEX resin wastes offers many advantages, it is not without technical challenges that must be addressed

when thermally treating organic-based resins. Table 2 lists some of the major technical challenges and potential processing solutions.

Table 2. Technical Challenges of Vitrification of Ion Exchange Resins.

Technical Challenges	Processing Solution(s)
Redox	Pretreatment, Bubbler, Oxidizers
Accumulation in cold cap	Mechanical Stirring
Cesium Volatility/Retention	Low Temperature Glass Formulation (1150°C), Moderate Cold Cap Coverage, Fairly Viscous Melt, No Excessive Bubbling
Off-Gas Emissions	Resin Pretreatment and Glass Formulation
Salt Solubility Limits	Glass Formulation, Off-gas System, and "Salt Drain"
Materials Corrosion	Glass Formulation
Containment of tritium	-

A. Redox

A primary processing and product performance issue is redox equilibria. The redox equilibria of a glass is a function of any oxidizers (nitrates, oxygen), or reductants (formic acid, resorcinol or other organic resins, coal, charcoal) present in the waste or added during processing. In the absence of excess oxidizers or reductants, the prevailing oxygen fugacity of a melt is a function of melt temperature.¹⁶ The experimental data indicate that oxygen fugacities in melter at 1150°C should be maintained at oxygen fugacities between 10^{-2} and 10^{-9} to simultaneously avoid foaming and metal precipitation. Due to the

high organic content of these IEX resin wastes, transition metals in the glass could precipitate as metallic species. Conductive, metallic species have the potential to electrically short melter electrodes if settling occurs in a flat bottom, Joule heated melter. Precipitated metals can be drained if the Joule heated melter employed has a sloped bottom and a bottom metals drain.

Glass durability can also be affected by redox.¹³ An increase in the glass Fe(II)/Fe(total) ratio can decrease durability because Fe(II) acts as a network modifier, while Fe(III) can be a network former. Processing solutions to mitigate potential negative redox issues include bubbling oxygen

through the melt,¹⁷ adding oxidizers such as nitrates to the melter feed which would react with the organic at melt temperatures,² mechanically stirring the melt to increase the oxygen exchange between the melt and vapors above the melt, and/or pretreatment of the resin to destroy carbaceous materials via chemical destruction or wet oxidation. A combination of these processing solutions may be utilized as well.

B. Volatilization

The volatilization of cesium and other semi-volatile radioactive metals sorbed onto the resin poses another processing concern.

Cs¹³⁷ is vaporized from borosilicate type glass melts as CsBO₂¹⁸ and/or gaseous Cs¹⁹⁻²¹ at temperatures between 800 - 1150°C.

Volatilized cesium must be removed by the off-gas system which generates (or increases) secondary contamination stream handling. Retention efficiencies vary with the type of radioactive metal being considered and are highly dependent upon processing temperature.

Cold cap coverage for Joule heated melters plays an integral role in controlling volatilization. Preliminary pilot-scale testing by Bibler showed a tendency of a resorcinol ion exchange resin to accumulate in the cold cap.²² This increased the time necessary for the feed to become incorporated in the melt. It also lengthened the time species, such as Cs and organics, were exposed in the melter plenum for volatilization. Mechanical stirring (via an impeller) and/or use of lid heaters in the melter plenum may eliminate or minimize accumulation of the resin within the cold cap as the crust is continuously drawn into the melt. As described previously, mechanical agitation can also mitigate negative redox effects of a reduced melt by increasing oxygen exchange. A more oxidized melt could also lower the amount of cesium volatilized as well as other metals.²³

Processing solutions that address volatilization concerns include minimizing processing temperature and maintaining moderate cold cap coverage. Proper glass formulation can minimize the required melting temperature while maintaining product performance criteria. Maintaining moderate cold cap coverage is more of a challenge since it is primarily a function of feed rate and melting rate.

C. Off-Gas Emissions

Vitrification of wet BWR/PWR type ion exchange resins causes the formation of NO_x, CO_x, and SO_x creating off-gas emissions concerns.¹⁷ Also mixed alkali salts, borates, and chromates are semi-volatile off-gas species at 1150°C which can vaporize from borosilicate glass melts.²⁴⁻²⁶ Destruction of organics in a melt forms volatile CO and CO₂ while nitrates, if added as melt oxidizers, cause formation of NO and NO₂. Low temperature glass formulations and/or pretreatment or destruction of the organic resins ex-situ of the melter will minimize off-gas emissions.

D. Salt Solubility Limits

Many common salts (sulfates, chlorides, phosphates, and chromates) have limited solubility in glass.²⁴⁻²⁸ Solubility limits may be optimized through proper glass formulation. However, if solubility limits are exceeded, both processing and product performance problems may arise. In particular, if molten salts are allowed to accumulate, steam explosions within the melter may occur. Removal of insoluble salt accumulation from the melter can occur by use of a "salt drain". Melters have been designed which have a separate drain to pour off alkali salts floating on top of the melt.²⁹ The salt phase becomes a secondary waste stream that can be immobilized via another alternative, e.g., sulfur polymer cement. Entrainment of the salt phases in the off-gas line should be

avoided by proper off-gas design.[†] Off-gas pluggage may occur if the off-gas design is incorrect, e.g., salts condense prior to reaching the quencher, scrubber, and filters.²⁴⁻²⁶ Deposition of unwanted alkali metabolates and salts in the off-gas line were found to be a function of off-gas velocity, off-gas line temperature, and off-gas speciation.

E. Materials Corrosion

Materials corrosion is another technical challenge to vitrification of IEX resin wastes. High sulfate and chloride containing wastes will form acidic off-gas as a result of pyrohydrolysis.³⁰ Therefore, materials used in the off-gas system should be acid resistant.

If molten salts form on the surface of the melt, refractory corrosion at the melt line could be excessive. Organics can be corrosive to both electrodes and the off-gas system. As the melt temperature increases, the severity of these corrosion mechanisms increase. Melter and off-gas materials of construction must be chosen with respect to these potentially corrosive conditions. In summary, predestruction of organics prior to vitrification, melter designs with salt drain capability, and low temperature glass formulations are potential processing solutions to minimize corrosion of melter and off-gas components.

IX. LABORATORY SCALE "PROOF-OF-PRINCIPLE STUDIES

Laboratory or bench scale "Proof-of-Principle" studies are presently being used in conjunction with Statistical Process Control (SPC) models previously discussed to evaluate vitrification of a suite of six ion exchange resins used in commercial BWR/PWR reactors. The following parameters will be evaluated during this bench scale testing:

- waste loading
- melt temperature
- waste solubility
- varying types of alkali additives
- varying types of silica additives, e.g. RASP vs. conventional vitrification (perlite, sand, precipitated silica, rice husk ash, etc.)
- melt line refractory corrosion
- general refractory corrosion

The Proof-of-Principle studies include analysis of the resins, analysis of the volatile species emitted by the resins during thermal treatment, determination of the glass forming potential of the resins and associated waste, optimization of glass formulations, and evaluation of the durability of the product using both the EPA Toxic Characteristic Leaching Procedure (TCLP) and the high-level waste durability test, the Product Consistency Test (PCT; ASTM C1285-94).

The glass compositions developed will maximize glass durability and waste loading while optimizing melt properties which affect melter operation, such as melt viscosity and melter refractory corrosion. Maximum waste loadings minimize storage volume of the final waste form providing considerable cost savings.

X. PILOT SCALE TREATABILITY STUDIES

"Proof-of-scale-up" or pilot scale studies with at least one the BWR/PWR IEX resins or a mixture of resins will be performed to provide data to assess the processing concerns addressed above. In particular, pilot scale studies will address the following:

[†] Jantzen patent pending

- confirmation of the processability of glass compositions optimized in crucible studies
- determination of off-gas emissions as a function of melt temperature
- verification of melter behavior as a Continuously Stirred Tank Reactor (CSTR) to ensure that waste and glass formers are homogenized during melting
- demonstration of recycle of secondary waste condensate produced
- predictability of process/product models
- evaluation of melter refractory and electrode corrosion

XI. VOLUME REDUCTIONS

Preliminary "proof-of-principle" testing with wet PWR/BWR resin wastes indicates that waste loadings of ~50 wt% PWR and 35 wt% BWR wet resin are achievable in homogeneous borosilicate type glasses (Figure 1). The reduced waste loadings of the BWR resins occurs because Fe_3O_4 crystals form during melting, e.g. the liquidus is violated, at the melt temperature of 1150°C for the higher waste loadings.

Waste loadings of 50% for PWR resin wastes and 35% for BWR resin wastes convert to volume reductions of 77 and 66 volume percent, respectively. For calculational purposes the volume reduction calculations are based on several assumptions. These include the following:

- wet resin wastes are 50% solids and 50% water
- specific gravity of the resin wastes is ~1.26 kg/liter
- density of the glass is 2.7 kg/liter

- once dried at 110°C, 50% of the resin waste is volatile, e.g. lost on ignition at the melt temperature

XII. CONCLUSIONS

Vitrification of ion-exchange resins to stabilize a wide variety of PWR/BWR wet resin wastes and sludges is feasible. Although vitrification of IEX resin wastes poses many potential technical challenges, viable processing solutions exist. These include proper compositional development, resin pretreatment (chemical destruction or wet oxidation), melter design (bubblers, stirrers, salt tap, etc.), and/or batch additives (oxidizers).

Glass compositions can be designed to accommodate both the hazardous and radioactive species in the wastes. The wastes appear to be soluble in borosilicate glass which takes advantage of the glass forming potential of high borate and lithium containing PWR wastes. Therefore, the Statistical Process Control (SPC) system developed for high-level waste borosilicate glasses is applicable. The glass compositions for IEX wastes can, therefore, be designed to be both durable and processable. Waste loadings of 35-50 wt% provide volume reductions of 66-77 volume percent.

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