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SUMMARY

The Savannah River Technology Center (SRTC) is investigating the viability of vitrification treatment of Argentine ion exchange material as part of a Department of Energy (DOE) - Office of Science and Technology Development Task Plan. Bench-scale studies were performed by the SRTC to define the necessary vitrification process for this material. However, the process had to be demonstrated in a melter system before vitrification could be considered a viable treatment option.

A vitrification demonstration with resin representative of the Argentine ion exchange material was performed at the Clemson Environmental Technologies Laboratory (CETL) under a South Carolina Universities Research and Education Foundation (SCUREF) contract. The demonstration was performed in the 1/4 square foot Stir-Melter using the iron-enriched borosilicate glass composition developed at the SRTC. The glass produced from the demonstration was determined to be homogeneous and durable. The vitrification process utilized represented a 59.5% volume reduction. The radioactive material retention was ~100% for Cs and Sr and ~43% for Co, which was based on glass retention calculations and demonstrated with surrogate chemical compounds. It is expected that the Co retention would be higher with actual spent resin because the Co would be bound on the resin matrix instead of loosely adsorbed as was the case with this test.
Offgas characterization did not include the surrogates used for the radioactive isotopes. Iron represented the most prominent particulate element characterized in the offgas system, while sodium was the most volatile element. Organic compounds emitted were not positively identified or quantified, but were believed to be high molecular

weight cyclic and heterocylclic nitrates and cynates and organosilicates. The nitrates and cynates were expected with amine resins, whereas the silicates were not. Changes to the offgas and melter system design would be necessary to help break-down these organic compounds into harmless species. In the identified form, the compounds would form tars in the offgas system and may be carcinogenic.

INTRODUCTION

The DOE has the responsibility for stabilizing the large volumes of radioactive and/or hazardous wastes it has generated in the approximately 50 years of nuclear weapons production. Under the Science and Technology Implementing Arrangement for Cooperation on Radioactive and Mixed Waste Management (JCCRM), the DOE is also helping to transfer waste treatment technology to international atomic energy commissions. As part of the JCCRM, DOE has established a collaborative research agreement with the Argentine Nuclear Energy Commission (CNEA). A primary mission of the CNEA is to direct waste management activities for Argentina's nuclear industry.[1]

In a JCCRM meeting in November 1996, several areas for collaborative research were identified; one being the immobilization of ion exchange materials. The CNEA is currently investigating treatment and disposal options for organic ion exchange resins that are being stored at the countries' nuclear power plants. Presently, two plants are storing large amounts of ion exchange resin that need to be disposed. The plants are the Atucha and the Embalse. The Atucha plant creates 2.83 m^3 of waste per year, while the Embalse plant creates 9.5 m^3 of waste per year. The current inventory in storage is approximately 42 m^3 for the Atucha plant, while the inventory at Embalse is approximately 130 m^3. The Atucha plant uses the resin to clarify water which is to be reused at the plant, while the Embalse Plant passes all solutions through the resins and, thus, creates larger volumes of waste.[1]

The resins were originally stored in two 15 m^3 capacity tanks at Atucha, but, due to the tanks being filled to capacity, the resins were transferred to a storage cistern. Presently, the spent resin in storage consists of the contents of the cistern and an additional tank full of material. The Embalse resins are stored in a large tank. Both resins have been in storage for about 10 years.[1] A treatment and disposal method is needed due to continued generation of the resins and limited storage capacity at both plants. Past work with the resins by CNEA has shown that acceptable grouts can be made. However, the resin loading was limited to about 10-15 wt%.[1] Vitrification studies with resins similar to the Argentine ion exchange materials have shown that ion exchange resins are suitable candidates for vitrification treatment. The DOE has an interest in the technology because ion exchange resins are used in several of their processes to remove both hazardous and radioactive constituents from solutions or sludges. Vitrification is a preferred technology because it is capable of consistently producing a durable, leach

resistant wasteform, while simultaneously minimizing disposal volumes through organic destruction, moisture evaporation, and porosity reduction. Due to the enhanced durability and leach resistance, the final waste forms have a very high potential for being delisted when Resource Conservation and Recovery Act (RCRA) metals are present in the waste stream. This avoids the cost of having to use expensive RCRA hazardous waste/mixed waste storage vaults, since direct disposal to a shallow landfill can be utilized instead.

SRTC has performed previous vitrification studies with both a resorcinol based organic ion exchange resin, which was proposed for use in removing the Cs from High Level Waste (HLW) supernate, and Amberlite divinyl-benzene/styrene copolymer resins, which are used by reactor facilities to purify their basin water.[2,3,4] The proposed disposal method for the spent resorcinol resin was to feed it with the HLW sludge and glass frit to the Defense Waste Processing Facility (DWPF) melter, while the styrene resins did not have a defined disposal method. Using direct vitrification methods, early studies indicated that only low levels of resorcinol (5 grams of resin/100 grams of glass produced) and divinylbenzene/styrene resins (20 grams of resin/100 grams of glass produced) could be incorporated in the glass matrix. These loading were mainly bound by the redox (Fe^{2+}/ Fe) of the glass, since the presence of organics tends to cause more reduced glasses. An important finding in both of these studies was that the presence of nitrates helped lower the redox ratio, permitting greater amounts of organics to be treated per gram of glass produced.

In the bench-scale studies performed with the Argentine ion exchange materials, the benefits of using nitrates in the feed were exploited, as well as the use of iron oxide which behaves as a redox buffer. Using the iron-enriched borosilicate formulations that were formulated for the previous studies with divinylbenzene/styrene resins, acceptable glasses with waste loadings of up to 44 grams of the Argentine ion exchange materials per 100 grams of glass were produced.[5] This composition was used as the basis for the melter demonstrations.

While this formulation was shown to produce acceptable glasses in a crucible, the ability to produce larger quantities of glass and treatment of the material needed to be demonstrated in a melter in order for the process to be considered viable. The CETL at the Clemson Research Park was contracted under SCUREF Task Order 231 to perform the melter demonstrations. The CETL has been working cooperatively with the SRTC for over five years to demonstrate vitrification of simulated DOE wastes and had the necessary equipment and infrastructure to support the demonstrations. In addition, CETL had already demonstrated the feasibility of vitrifying resorcinol resins in the past for SRTC.

During the demonstration, processing problems could be determined and corrected in a cost effective manner before actual treatment of the waste. Potential offgas pollutants and glass inhomogeneities could also be identified.

During the demonstration, a SRTC run plan, WSRC-RP-97-0326[6], was used to provide objectives, necessary quality controls, glass composition, and sampling requirements.

WASTE DESCRIPTION

The use of ion exchange materials for purification of aqueous streams in the nuclear industry creates a waste stream that can be very high in both organic and radioactive constituents. Therefore, disposal often becomes an economic problem because of the large volumes of resin produced and the relatively few technologies that are capable of economically stabilizing this waste.

The major hazard of the ion exchange resins are the organics that compose the resins and the contaminants that are present on the resins after purification processes. Many of the organics resins are not considered characteristically hazardous in the un-used form. Principal contaminants are usually radioactive species removed from aqueous streams.

For this study, a resin representative of those used in Argentina's Embalse plant was tested. The Embalse plant currently uses or has historically used four different types of Amberlite divinlybenzene/ styrene ion exchange resins. These are IRN 77, IRN 78, IRN 150, and IRN 154. The IRN 77 is a strongly acidic cation resin, whereas the IRN 78 is a strongly basic anion resin. Both the IRN 150 and IRN 154 are 1:1 mixtures of IRN 77 and IRN 78, with the only difference being that IRN 154 is LiOH based. The properties of the IRN 77 and IRN 78 resins are shown in Table 1.

Table 1: Embalse Resin Properties[1]

Property	IRN 77	IRN 78
Ionic Form	H+	OH-
Functional Group	Sulphonic Acid	Quaternary Ammonium
Matrix	Cross Linked Polystyrene	Cross Linked Polystyrene
Structure	Gellular	Gellular
Particle Size	16 to 50 mesh	16 to 50 mesh
Density	1.26 g/ml	1.11 g/ml

The four resins were used in various combinations depending on the particular application. IRN 150 represents the largest volumetric portion of the resin in storage, approximately 49.4%, with IRN 154 having the next largest share, approximately 31.8%.[1] Since IRN 150 represents the largest portion of the waste in storage and since it is similar to IRN 154 and composed of IRN 77 and 78, it was used as the sole source of resin in the melter demonstration.

The CNEA has not been able to completely characterize the Embalse resins in storage. However, experiments were performed to determine the current water concentrations and densities of the resins under various conditions. From these experiments, the parameters given in Table 2 were defined for the IRN 150 resin.

Table 2: IRN 150 Hypothesized Storage Parameters[1]

Condition	Total Water	Density
Slurry	79.9%	1.04 (g/ml)
Dewatered	71.3%	1.13 (g/ml)
Damp	56.6%	1.28 (g/ml)
As Received	57.9%	1.21 (g/ml)

No chemical or radiolytical characterizations of the Embalse resins have been performed to date. However, a radiolytical characterization of the Atucha resin was performed by the CNEA. The results of this characterization are shown in Table 3. A more recent radiolytical characterization was performed after the demonstration was completed. These results are also listed in Table 3.

Table 3: Radiolytical Characterization of the Atucha Resin

Radionuclide	Pre-Demonstration	After Demonstration
Co-60	10.27 µCi/ml	0.99 µCi/ml
Cs-137	27.84 µCi/ml	8.7 µCi/ml
Cs-134	1.89 µCi/ml	N/A
Total γ	40.54 µCi/ml	10 µCi/ml
Tritium	N/A	14 µCi/ml
Sr-90	N/A	0.2 µCi/ml

The more recent analyses also determined some of the chemical contaminants found on the Atucha resin. These are listed in Table 4. Once again, these were not known before the demonstration, so they could not be used to dope the resins during the demonstration.

Table 4: Chemical Contaminants on Atucha Resin

Contaminant	Amount (ppm)
Na	30.0
Ca	1.5
Si	4.0
B	0.5
NO_3^-	2.5
SO_4^{2-}	4.2
Cl^-	10.0

These contaminants were not tested with the glass compositions on a bench-scale or in the melter demonstration, but should not pose a problem because the cations are components of the glass composition. The anions are present in low enough concentrations that they will not affect the process and will be captured in the offgas system.

OPTIMUM GLASS COMPOSITION

Glass formulation studies have been performed at SRTC with resins representative of the Argentine ion exchange materials.[5] The information from these studies was used to perform the demonstrations at CETL. The only difference between the studies was that the SRTC tests used a combination of resins typical of all the resins used at

the Embalse plant, whereas, the CETL demonstrations only used IRN 150. This should not impact the processing or results. The targeted glass composition was an iron-enriched borosilicate glass. The target glass composition is given in Table 5. This composition has been submitted for a patent disclosure by Westinghouse Savannah River Company (WSRC).

Table 5: Target Glass Composition

Oxide	Wt%
B_2O_3	9.1
CaO	14.8
Fe_2O_3	22.2
Na_2O	8.1
SiO_2	45.8

This composition was used to obtain a resin loading of 44 grams of resin for every 100 grams of glass produced. This waste loading is approximately 31%.

MELTER SYSTEM DESCRIPTION

The Stir-Melter used for the demonstration is located at the CETL. The melter is a 1/4 square foot stirred tank melter, and is a lab-scale/ pilot-scale of the WV-9 melter currently owned by the Westinghouse Savannah River Company. The melter tank is constructed of Inconel$^®$ 690 and has dimensions of approximately 6" by 6" by 16" in depth. The optimal melt depth is usually controlled to 6 inches. The Stir-Melter vitrification strategy is unique due to the chamber design, electrode/heating concept, and its agitation method. The melter utilizes an Inconel$^®$ melt chamber, versus traditional refractory chambers. Inconel$^®$ is used because it serves as one of the two electrodes (the second is the Inconel$^®$ impeller), and less refractory contact decreases the amount of contaminated material generated during maintenance or dismantlement. The maximum temperature obtainable in the melter is approximately 1050°C because of the temperature limitations of the Inconel$^®$ components. The impeller is approximately 3" in diameter and is also fabricated from Inconel$^®$ 690. It provides a stirring action that results in much higher mixing and production rates than can be achieved by convective mixing alone. The height of the impeller in the melter can be adjusted to create a two-phase solution in the chamber; one phase consisting of dense molten glass, the second phase entrained with air and other gases from the melt. The gas-loaded glass has much lower viscosities and can be mixed very rapidly, which improves the rate at which solids can be melted into the glass. The impeller is powered by a half-horsepower variable-speed motor.

Pouring of the glass occurs through an overflow drain that ensures that the pour rate equals the feed rate. Flow through the drain is controlled by controlling the temperature of the spout, which has its own heater. The target production rate of the stirred-melter is about

2-3 pounds per hour of glass from a slurry feed. This rate can be increased when the melter is being dry fed.

Slurry feeding is accomplished through the use of a slurry feed port located at the top of the melter. The feed is dispersed over the melter surface and can be rapidly mixed in with the molten glass through the impeller stirring action. The Stir-Melter can also operate in a cold-top mode by using slower stirring motion to incorporate the new feed into the molten pool.   The slurry was fed from a continuously stirred feed vessel (approximately 5 gallon capacity). A peristaltic pump in the feed line directed the feed to the melter at a constant rate, which could be adjusted to accommodate the melt and pour rates of the melter.

Joule-heating in the melter is controlled by a 10 kVA SCR/transformer set that is controlled by an externally mounted thermocouple that monitors the melter side wall temperatures. Resistance heaters are also located around the outside of the tank to heat the tank during start-up and to assist in maintaining head-space temperatures during normal operation. The resistance heaters are powered by a 7 kVA SCR/ transformer set that is also controlled by the melter side wall temperature. An oxygen sparger is located at the bottom of the melt tank. Oxygen can be metered into the melt at a rate of 0.6 - 6.1 standard liters per minute to help maintain oxidizing conditions in the melt or to help break down organics in the feed.

For this run, the melter was connected to the input plenum of the laboratory exhaust system, since no pollutants of particular concern
were expected in the offgas. This system, which is designed for multiple inputs and radiological-level control, easily maintained a 0.5 inch of H_2O negative static pressure in the melt chamber. Laboratory exhaust is sent through a series of pre-filters and a final High Efficiency Particulate Air (HEPA) filter. A sampling manifold was installed between the melter and the laboratory exhaust system. This manifold enabled isokinetic sampling and it also held the necessary ports for temperature and Pitot tube measurements. Also, a separate port was available for non-isokinetic sampling of permanent gases, such as CO, CO_2, O_2, NO_x, and others.

OBJECTIVE

The primary objective of the test was to determine the feasibility of stabilizing Argentine ion exchange materials using vitrification technology. To meet this objective, the following were performed: a demonstration in the Stir-Melter with glass additives and resin and characterization of the glass and offgas products.

EXPERIMENTAL

Feed Fabrication
For the demonstrations at CETL, IRN 150 was used as the sole source of ion exchange resin. As mentioned above, this resin is made of IRN 77 and IRN 78 and is very similar to IRN 154.

No data was available from the CNEA on the types or amounts of contaminants contained on the resins from the Embalse plant. Therefore, the information available on the Atucha resin was used to determine the amount of surrogate radionuclides needed to dope the resin. The CNEA also requested that strontium be used in the demonstrations because they believed that it was also a contaminant on the resin, though none had been reported in their preliminary characterization. In this demonstration, non-radioactive cesium, strontium, and cobalt were used to simulate the radioactive contaminants. Each element was added at an amount equivalent to the total γ activity pre-demonstration value reported in Table 3. For the Co-60, an amount equal to roughly 6 times the value was used to spike the resin because the normal level would have been hard to detect in the glass.

Since the resin currently in storage at the Embalse plant is present as a slurry, the resin used at the CETL was also made into a slurry. To help with the adsorption of the surrogate radionuclides onto the resin, the radioactive surrogates were dissolved in water and then the resin was well mixed with the water containing the radioactive surrogates. An actual resin column was not used to adsorb the radioactive surrogates so they were probably not as bound as the actual resin material would be. An amount of water equivalent to that contained in the resin slurry at the Embalse plant (see Table 2) was used for dissolving the radionuclide surrogates and to create the slurry mixture.

For the melter demonstration, a little over a melter volume of feed was fabricated to be processed. The Stir-Melter can be started with very little glass in the melter tank, so very little turn-over of the melter contents is required before steady-state composition is obtained. The batch recipes used to fabricate the feed are shown in Table 6. This represented enough feed to produce a little over one melter volume of glass.

Table 6: Batch Recipes for Argentine Resin Glass Feed

Additive	Batch #1	Batch #2	Batch #3
Borax	1.98 lbs	1.97 lbs	1.48 lbs
$CaCO_3$	2.75 lbs	2.75 lbs	2.05 lbs
$Fe(NO_3)_3 \cdot 9H_2O$	10.65 lbs	10.75 lbs	7.96 lbs
$NaNO_3$	1.16 lbs	1.17 lbs	1.37 lbs
SiO_2	4.76 lbs	4.76 lbs	3.55 lbs
$Sr(NO_3)_2$	3.10 g	3.13 g	2.34 g
$CsNO_3$	2.89 g	2.86 g	2.20 g
$Co(NO_3)_2 * 6H_2O$	4.25 g	4.27 g	3.19 g
IRN 150	4.67 lbs	4.66 lbs	3.50 lbs
Water	7.67 gal	7.68 gal	5.76 gal

Ferric nitrate was used because the nitrates were needed to help with the oxidation of the organics in the resin. This information is also a part of the WSRC patent disclosure. The third batch of feed was slightly different because more Na_2O was needed in the glass to help

lower glass viscosity. After initial feeding to the melter, the glass appeared to be very viscous, so 544 g of $NaNO_3$ were added directly to the melter through the dry batch feed port and 22.63 g of $NaNO_3$ were added to the pour riser. Approximately 189 g of $NaNO_3$ were added to the Batch 2 feed in the feed vessel. These additions equated to an increase in Na_2O content of approximately 4 wt% in the glass.

Since slurry feeding was used in the demonstration, excess water was added to the batches. This water is included in the totals given in Table 6. The feed fabrication procedure involved mixing the glass additives, with the exception of the ferric nitrate, and excess water together. The ferric nitrate was then added alternately with the resin slurry to the glass additive slurry. This was done so the resin would not start reacting with the nitrates until the melter was ready for feeding. In bench-scale studies, foaming occurred in the batch as soon as these components were added.

Several samples of the fabricated feed material were taken during the demonstration for analyses and archival. These analyses included weight percent solids, calcined solids, pH, specific gravity, and feed chemistry. These analyses were needed to verify the representativeness of the feed, as well as to calculate the total volume reduction obtained from vitrification.

Melter Operation
Visual observations of the operating behavior of the melter were very important during the trials, including the presence of foam or salt layers. Corrosion of the melter components was also an important consideration. Accurate records of feed rate were taken so reaction times could be determined. The following data was also recorded:
- volume of feed processed;
- glass pour rates;
- mass of glass produced;
- power requirements needed;
- offgas operating conditions (pressures, any pluggages, etc.);
- melt tank and drain temperatures; and
- any processing problems identified.

This data was taken throughout the trials, as applicable, to ensure that the behavior of the ion exchange material in the melter was well characterized.

At the completion of the tests, the melter was shut-down according to CETL procedures. The containers of glass produced were examined for any signs of devitrification. The melter tank and the impeller, other melter components, and the offgas system were examined for any wear, pitting, or corrosion. During the demonstration, an optimum feed rate was determined based on the slurry properties and the feed melt rate. The optimum feed rate is defined to ensure that the melt surface is evenly covered and that no unnecessary build-up of glass or cold-cap material occurs. Feed rates were monitored and manually recorded throughout the demonstration. In addition to monitoring the feed rate, the following were also recorded: the power, voltage, and current being used by the auxiliary heaters and melt circuit; impeller power and frequency; and

the setpoint and actual melter temperatures. Monitoring of this information helped to ensure that the temperature in the melter remained reasonably constant. Power to the melter was adjusted during actual operation to help maintain the desired temperature and melt rates.

When the melter had been fed enough of the slurry to provide sufficient glass build up, the drain power was increased to increase the drain temperature and to initiate pouring. The glass was poured from the melter into graphite crucibles for storage. The pour rate was also monitored and manually recorded during the demonstration to determine the production capacity with this feed. Any problems related to pouring, such as drain pluggages or slow pouring, were recorded in notebooks specified for the CETL demonstration so an accurate record could be maintained.

The laboratory offgas system was operated throughout the demonstration. Samples of the offgas were taken near the end of the campaign when the melter was believed to be at steady-state operating conditions. A Multiple Metals Sampling Train was performed to determine the distribution of metals within the offgas system. The train was based on the EPA Method 29 Test and is applicable to the determination of metal releases. The train can also be used to determine particulate emissions according to EPA Method 5. For the demonstration, an isokinetic source sampler was used to perform the Method 29 test. Organics were also monitored during offgas sampling.

Glass Sampling
Samples of the glass product were taken during the demonstration and removed from the graphite crucibles poured at the end of the demonstration. These samples were submitted to the SRTC for analyses and characterization. Analyses included total constituent, redox, phase assemblage, and the Product Consistency Test (PCT), ASTM C1285-94[7]. Total constituent analyses of the glass samples consisted of digestion by Na_2O_2 fusion with a HCl uptake, lithium metaborate fusion, and microwave digestion of the glass samples. These solutions were analyzed by Inductively Coupled Plasma – Emission Spectroscopy (ICP-ES) and Atomic Absorption (AA) spectroscopy to determine the major cation concentrations.

The redox state of the glass was determined from the Fe^{2+}/ Fe ratio by the colorimetric method. The Fe^{2+}/ Fe ratio was determined since the redox is a very important factor for glass processing. High ratios, which are possible when high amounts of organics are fed to the melter, are not desirable in joule-heated melters due to the potential to reduce metal compounds or oxides to sulfides or pure metals, respectively. When these form in the melter or from the melter components, the lifetime and efficiency of joule-heated melters can be decreased. The redox ratio can also affect foaming in the melter, glass exit viscosity, wasteform durability, and crystallization in the glass product.

Phase assemblage or devitrification was determined using X-Ray Diffraction (XRD) analysis. The presence of crystals can affect glass

durability and can also lead to processing problems if they form in the melter or drain spout.

The PCT, ASTM C1285-94[7], was performed to determine the durability of the glass in a neutral to alkaline-driven environment. It is the standard leach test for HLW glasses and determines the leach resistance of the glass structure. The PCT is performed on a crushed glass (74 - 149 µm) specimen that is washed to remove the fines. The test is performed at 90°C in ASTM Type I water over a period of seven days. A volume of solution per mass of sample ratio of 10 (ml:g) is used during the standard test protocol. The resulting leachate is filtered and then analyzed to measure the releases of B, Si, Na, and other elements. The Toxicity Characteristic Leaching Procedure (TCLP) was not performed since hazardous metals were not contained in the glass additives and the resins were not considered hazardous wastes.

MELTER OPERATION OBSERVATIONS

The melter was slowly heated up with residual borosilicate glass using the resistance heaters. Once the melter was at temperature (>950°C), joule-heating was established by starting the impeller. The demonstration took five days of eight hour shifts to complete. The melter was maintained in hot-hold during the off-shifts.

Slurry was initially added at a rate of 80 ml/min. This rate was maintained for the first day of feeding. However, as more of the feed built up in the melter, the feed rate had to be decreased because of cold-cap build-up and foaming. This foam layer was easily controlled by adjusting the impeller height, turning off the sidewall resistance heaters, or adjusting spindle speed. Adjusting the vacuum in the melter did not help alleviate foaming, but did result in more organics being ignited on the melt surface. Vacuum was maintained at a half inch water. Decreasing the O_2 sparge rate did help decrease the foaming. Only minimal O_2 flow (~0.6 standard liters/min) was needed during the demonstrations. The optimal feed rate was determined to be 50 ml/min.

No problems with controlling the feed system were encountered. At the beginning of feeding, problems occurred with the consistency of the feed. After stirring for approximately two hours, the feed material gelled. Fluidity was returned to the feed by adding approximately 2500 ml of water with stirring. The other feed batches were adjusted so that gelling became less of a problem. Foaming of the feed material did occur in the feed vessel as soon as the ferric nitrate was added and before the resin was added. Therefore, it was determined that some of the foaming seen in the bench-scale studies was likely the result of the nitrates reacting with the carbonates in the glass additives and not just the carbon in the resin. This has since been verified in other bench-scale tests. This finding also means that less ferric nitrate could be used or higher resin loadings could be obtained if carbonates are not a part of the glass additives. Ferric oxide has been substituted for some of the ferric nitrate when carbonates were not used and this theory was verified.

Electrical parameters and temperatures during melting the Argentine resin feed were recorded throughout the demonstration. This data is given as Appendix A. At steady-state, the nominal operating spindle power was 1.6 kW using a frequency of 54 Hz, and the auxiliary power was 2.2 kW with 240 V and 6 A. Melt circuit power varied greatly and was 4.5 - 6.1 kW, 30 - 45 V, and 175 - 275 A. Power readings were off for the melt circuit. Stir-Melter personnel believed that the digital display calibration was wrong. The drain setpoint was set at 1075 or 1090°C when pouring, and the melt temperature was set at 1050°C. The actual temperature readings were a little lower for the pour temperature, but were at target for the melt temperature. Only one set of resistance heaters had to be kept on to maintain the melt; temperature was maintained between 771 to 872°C during pouring.

Continuous pouring from the melter was maintained during the demonstration as soon as enough feed was contained in the melter. The pour rate from the melter was about 0.72 kg (1.58 pounds) of glass per hour. No problems with drain pluggage or glass exit viscosity were seen during the demonstration.

One melter excursion did occur during hot-hold in the demonstration. An O_2 flow meter fell during the night and caused a drastic increase in O_2 flow (~3.6 L/min). Glass boiled over and filled the melter crevices and had to be removed.

After the demonstration was completed, the melter system was visually inspected and examined for wear or corrosion to the melt vessel and the impeller. Minimal wear or corrosion was seen to the melt vessel and impeller due to the vitrification of the Argentine material.

The offgas output from the Stir-Melter was estimated to be less than 100 acfm, which was approximately 1% of the 8,400-acfm capacity of the laboratory exhaust system. At this level of dilution, the offgas had no noticeable effect on the building system.

FEED AND GLASS ANALYTICAL RESULTS

Samples of the feed were taken throughout the demonstration to determine the mixing and settling behavior of the feed. Feed samples #2 and #4 corresponded to Batch 1, while samples #6 and #8 corresponded to Batches 2 and 3, respectively. The physical properties of each feed sample are shown in Table 7. Weight percent solids was determined by drying at 105°C, while calcined solids were determined by drying at 1050°C, which was the melt temperature.

Table 7: Physical Properties of Feed Samples

Sample ID	Wt% Solids	Calcined Solids (Wt%)	Density (g/ml)	pH
#2	21.0	19.39	1.20	1.54
#4	29.0	16.64	1.14	3.94
#6	25.9	13.69	1.09	3.98
#8	23.1	20.16	1.36	1.60

The calculated solids content was approximately 22%, so the samples were pretty close to the target. Samples #4 and #6 were slightly higher than targeted and could possibly indicate some settling of the additive or resin materials or simply heterogeneity in the feed sample. The small difference in the wt% solids versus calcined solids results can be attributed to the degradation of the resin material, which occurs almost completely above 650°C.[5] Density is consistent with values reported by the CNEA in Table 2.

The chemical composition of the material fed to the melter was determined by the Mobile Laboratory of SRTC from four separate samples using ICP-ES. Cs could not be measured using this instrument. Cs was measured by the Analytical Development Section (ADS) using AA spectroscopy; however, only feed sample #6 was analyzed. All feed samples were assumed to contain equal amounts of Cs (i.e., 0.0195 wt%). The normalized oxide concentrations of the feed samples are given in Table 8. Since extra sodium had to be added to decrease viscosity, the target composition given in Table 5 had to be recalculated. However, part of the extra sodium was added directly to the melter and not in the feed for the first two batches so these samples were still roughly equivalent to the original target composition. The original target and final target glass compositions are shown in Table 8. Both target compositions take into account the radionuclide surrogate addition.

Table 8: Melter Feed Analyses (Wt%)

Oxide	Sample #2	Sample #4	Sample #6	Sample #8	Original Target	Final Target
B_2O_3	6.37	6.94	6.98	7.00	9.09	8.74
CaO	15.044	15.790	15.501	14.608	14.785	14.217
Co_2O_3	0.021	0.033	0.029	0.020	0.030	0.030
Cs_2O	0.034	0.041	0.039	0.026	0.040	0.040
Fe_2O_3	22.52	20.76	21.23	21.38	22.18	21.326
Na_2O	9.141	9.455	9.829	11.283	8.092	11.623
SiO_2	46.8	46.9	46.4	45.7	45.8	44.0
SrO	0.031	0.042	0.045	0.035	0.030	0.030

The melter feed composition was very similar from sample to sample, especially for samples #2, #4, and #6. The increase in sodium to the last batch of feed is evidenced by the increase of Na_2O in the Sample #8 results. Compared to the target compositions, all feed samples were lower in B_2O_3 than targeted. CaO, Fe_2O_3, and SiO_2 were close to the target both before and after the sodium addition. Na_2O was a little higher than expected for the first three samples and lower than targeted for the last sample.

The chemical composition of two glass samples taken at the end of the demonstration were determined using the wet chemistry methods listed earlier. Cs was only determined for the first glass sample, and it was assumed that it was also present in the second glass sample at this amount. The normalized oxide compositions for each sample and the targeted composition are given in Table 9.

Table 9: Product Glass Analyses (Wt%)

Oxide	Sample #1	Sample #2	Final Target
B_2O_3	8.34	8.19	8.74
CaO	11.363	11.589	14.217
Co_2O_3	0.012	0.010	0.030
Cr_2O_3	0.488	0.471	N/A
Cs_2O	0.0529	0.0528	0.040
Fe_2O_3	15.69	16.59	21.326
Na_2O	15.372	14.925	11.623
NiO	0.519	0.520	N/A
SiO_2	48.1	47.6	44.0
SrO	0.049	0.047	0.030

The glasses analyzed were very similar in composition. However, as compared to the target, CaO and Fe_2O_3 were low and Na_2O was high. This deviation may have resulted from incomplete mixing when the Na_2O was added directly to the melter. If the contents of the melt were not completely homogenized, portions of the glass could contain excess levels of Na_2O. Cr_2O_3 and NiO are present in the glass from the corrosion of melter materials of construction. Given that a total of 17.67 Kg of glass were produced, these numbers indicate that a total of 58.98 g or Cr and 72.20 g of Ni were corroded from the melter tank walls and impeller.

The normalized glass oxide composition was compared to the Sample #8 feed oxide composition. Theoretically, the feed and glass compositions should be roughly the same with minor differences due to volatility during vitrification. CaO, Co_2O_3, and Fe_2O_3 were lower than the concentrations found in the feed, while Cs_2O and Na_2O were higher than what was found in the feed. CaO and Fe_2O_3 are not very volatile, which may indicate that the feed samples were not representative of the batches of feed (i.e., samples were not homogeneous).

The Fe^{2+}/ Fe ratios for a sub-sample of the glasses analyzed for chemical composition were measured in duplicate by the Mobile Laboratory. All glasses had Fe^{2+}/ Fe ratios of 0.010, which indicates that the glass was very oxidized. The measured ratios were lower than limits established at SRTC for joule-heated melters.[8] For joule-heated melters, very oxidizing conditions can result in foaming in the melter. Foaming was seen during the early part of the demonstration.
Visual examination of the resulting glass indicated that the glass appeared amorphous. The glass was dark brown with no visible signs of crystallinity. XRD analysis on two different glass samples confirmed that the glasses were amorphous. The PCT was performed on two samples of glass from the end of the demonstration to determine the durability. The standard PCT[7] procedure was performed and the triplicate results were averaged. These results were normalized for the glass elemental content

and compared. They were also compared to the DWPF Environmental Assessment
(EA) glass results[9]. The DWPF EA glass was selected for comparison because it
is a known standard for high-level waste glass performance and no standards
have been set for other waste glasses in the United States. The normalized
PCT results and the EA glass values are contained in Table 10.

Table 10: Normalized PCT Results (g/L)

Sample	B	Si	Na	pH
1	0.547	0.221	0.724	10.82
2	0.328	0.155	0.429	10.44
EA[9]	16.69	3.92	13.35	11.91

As can be seen from the results given in Table 10, the normalized releases for
B, Si, and Na for the two glasses were substantially less than the EA glass.
The results for the two glasses were slightly different, which is likely the
result of the slight difference in composition found for the two glasses.
Although not listed in the table, the surrogate radionuclide were not detected
in the leachates at any appreciable amounts.

At the request of the CNEA, the glasses used in the PCT were analyzed for
chemical composition after the durability test. This was to determine how the
chemical composition of the glass was affected by the durability testing. The
glass composition of the two glasses, both before and after testing, are given
in Table 11.

Table 11: Glass Analyses after Durability Testing (Wt%)

Oxide	Before PCT Sample #1	After PCT Sample #1	Before PCT Sample #2	After PCT Sample #2
B_2O_3	8.34	7.66	8.19	7.72
CaO	11.363	11.1	11.589	10.8
Co_2O_3	0.012	0.026	0.010	0.022
Fe_2O_3	15.69	16.8	16.59	17.4
Na_2O	15.372	15.1	14.925	13.9
SiO_2	48.1	48.2	47.6	48.7
SrO	0.049	0.072	0.047	0.070

From this data, it appeared that B, Ca, and Na were the principal components
released from the glass during the PCT. This is as expected, since these
oxides can negatively affect glass durability and would be the most leachable
oxides in the glass. The increase in Co_2O_3 and SrO content would indicate
that these elements did not easily leach from the glass. Given these
compositions, the PCT results were re-normalized and the results are presented
in Table 12.

Compared to the results given in Table 10, the normalized releases were very
close for all elements and both glasses. Once again, they were still
significantly less than the normalized results for the DWPF EA glass and would
be considered acceptable.

Table 12: Re-Normalized PCT Results (g/L)

Sample	B	Si	Na	pH
1	0.558	0.207	0.692	10.82
2	0.326	0.142	0.434	10.44
EA[9]	16.69	3.92	13.35	11.91

Viscosity of the glasses was measured as a function of temperature by CETL. The glass viscosity was measured during heat-up and cool down to ensure that no affects related to heating were seen. Results are given in Table 13.

Table 13: Measured Viscosity of Product Glass

Temperature	Viscosity
1209°C	35.5 P
1150°C	50.0 P
1097°C	96.5 P
1070°C	131.5 P
1045°C	177.5 P
992°C	351.5 P
913°C	1200.0 P

The measured viscosities indicate that the glass would be considered acceptable for processing in typical DOE joule-heated melters that are maintained above ~1100°C. For the Stir-Melter, the glass viscosity was near the upper limit of viscosity for the melter.

Total feed to the melter was 69.9 kg (154 lbs). Of this total amount, the resin slurry or Argentine waste was 12.2 kg (26.8 lbs) with an approximate density of 1.04 g/ml. The total mass of glass produced was 13.1 kg (28.82 lbs). Its density was determined to be 2.738 g/ml by the buoyancy method. Therefore, the volume reduction of using vitrification treatment was 59.5%.

Offgas Analyses

The samples from the Multiple Metals Sampling Train were analyzed by the Mobile Laboratory according to EPA methods. Glass formers and other waste components are not usually included in Multipe Metals analyses because of the interference that occurs from the quartz filters, the digestion procedure, and the borosilicate glassware used in the testing. However, these values were not needed for process validation or control and were only needed to provide an estimate of the materials emitted in the offgas, so this sampling was believed to be sufficient. The front half of the impactor used in the sampling was analyzed separately from the back half. The front half is the filter and the probe and nozzle wash, and represents the particulate matter captured during the test. The back half is the solution in the impingers and represents the collected species that were in a volatilized state. Concentrations at actual sampling conditions of the elements in particulate and volatile form are given in Table 14. The feed rate during sampling was 50 mL/min.

TABLE 14 - OFFGAS EMISSIONS

Element	Ca	Cr	Fe	Na	Ni
Sample #1 Total Particulate (µg)	15690	831	36530	27280	78.2
Sample #1 Total Volatile (µg)	45.6	0	26.5	124	4.1
Sample #1 Concentration (µg/m^3)	5387	282	12561	9392	23
Sample #2 Total Particulate (µg)	15820	4610	37420	21100	25.8
Sample #1 Total Volatile (µg)	66.3	5.3	21.9	117	3.2
Sample #1 Concentration (µg/m^3)	5350	1558	12654	7145	5

Based on the elements analyzed, Fe was the biggest particulate contributor and Na was the largest volatile contributor. The radioactive surrogate (i.e., Co, Cs, and Sr) concentrations were not measured due to an error with the lab analyzing the results. Based on the metals concentrations given in Table 14 and the average stack gas flow in the offgas system, the total metal amount emitted to the offgas system was conservatively calculated for the entire demonstration. Conservative calculations indicate that ~10% of the Ca, ~17% of the Fe, and ~20% of the Na fed to the melter was emitted. These are conservative calculations because they assume that the emissions were constant throughout the run (i.e., during feeding, hot-hold, etc.). However, the high Ca and Fe emissions are consistent with the low retention numbers found for these metals in the glass. The Na is inconsistent with the glass data, which is likely the result of incomplete mixing of the excess Na that was added to the melter to help with the glass viscosity.

The condensate from the first step of the gas conditioning train was taken as a representative sample of the condensible organics given off by the melter. Organic compounds emitted were not positively identified or quantified, but were believed to be high molecular weight cyclic and heterocylclic nitrates and cynates and organosilicates. The nitrates and cynates were expected with amine resins, whereas the silicates were not. Changes to the offgas and melter system design would be necessary to help break-down these organic compounds into harmless species. In the identified form, the compounds would form tars in the offgas system and may be carcinogenic.

CONCLUSIONS

The vitrification demonstration in the Stir-Melter system located at the Clemson Environmental Technologies Laboratory has shown that vitrification of Argentine ion exchange material is viable using an iron-enriched borosilicate glass composition. A total of 69.9 kg (154 lbs) of wet feed were processed during the demonstration with a total glass production of 13.1 kg (28.82 lbs). The total resin slurry processed was 12.2 kg (26.8 lbs), which represented ~30.6 wt% waste loading. This resulted in a 59.5% volume reduction. The feed composition consisted of 44 g of resin per every 100 grams of glass oxide formers. The target glass composition determined to be most suitable for the Stir-Melter was 44.0 wt% SiO_2, 8.7 wt% B_2O_3, 14.2 wt% CaO, 21.3 wt% Fe_2O_3, and 11.6 wt% Na_2O. Processing of this feed did not result in any significant problems during the

demonstration. The resulting glass product was homogeneous and durable.
Radioactive surrogate retention was ~100% for Cs and Sr, while it was only
~43% for Co.

Iron had the highest concentration of the particulate offgas contaminants
analyzed, while sodium had the highest volatile concentration. High molecular
weight cyclic and heterocyclic nitrates and cynates and organosilicates were
tentatively identified in the offgas system. These compounds present problems
to typical offgas systems and may be considered carcinogenic.

FUTURE WORK

Results of this demonstration have shown that organic resins can be
successfully vitrified in a joule-heated melter without harmful effects to the
melter system. However, an integrated demonstration with complete offgas
characterization is needed to determine the overall viability of the
vitrification process. An important consideration will be the complete
breakdown of the organic constituents.

ACKNOWLEDGMENTS

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