WSRC-TR-97-0198, Rev. 1

Bench-Scale Studies with Argentine Ion Exchange Material

C. A. Cicero-Herman
Westinghouse Savannah River Company
Aiken, SC 29808

This document was prepared in conjunction with work accomplished under Contract No. DE-AC09-96SR18500 with the U.S. Department of Energy.

Summary

The United States Department of Energy (DOE), as well as international atomic energy commission, facilities use ion exchange materials for purification of aqueous streams in the nuclear industry. Unfortunately, the use of the ion exchange materials creates a waste stream that can be very high in both organic and radioactive constituents. Therefore, disposal of the spent resins 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. Vitrification of this waste stream presents a reasonable disposable alternative because of its inherent destruction capabilities, the volume reductions obtainable, and the durable product that it produces.

Past attempts to vitrify ion exchange materials have met with limited success from a waste loading and volume reduction standpoint. This study used borosilicate glass formulations, which were previously shown to be successful in vitrifying organic ion exchange resins, to evaluate the viability of vitrifying the Argentine ion exchange materials.

Higher waste loadings, with associated higher volume reductions, were found in these studies using the Argentine ion exchange materials and the predetermined borosilicate glass formulations. Based strictly on the results of the bench-scale studies, the waste loading for the Embalse resin seemed to be limited by adverse chemical shifts (redox reduction reactions), while loadings for the Atucha resin were limited by the salt content of the resin. The waste loadings were 42 grams of resin per 100 grams of glass produced or 29.6 wt% waste for the Atucha resin, and 44 grams of resin per 100 grams of glass produced or 30.6 wt% waste for the Embalse resin. These waste loadings represented a 65% volume reduction for the Atucha mix and a 76% volume reduction for the Embalse mix.

Increased volume reductions may be possible by using the Savannah River Technology Center (SRTC) developed nitric-phosphoric acid oxidation process to pre-treat the ion exchange resin. Past studies with this pre-treatment process and similar ion exchange resins demonstrated 50% volume reductions when this process was coupled with vitrification of the resulting oxidation solution. In the pre-treatment studies, practical limitations were shown to result from the resins' content of non-radioactive inorganic species and from the radiation field generated from the radioactive content of the resin. Therefore, higher volume reductions are possible when low levels of contaminants are present or when the contaminants do not affect the treatment process.

Keywords: organics, low level wastes, glass, vitrification, resin

Introduction and Background

The DOE is responsible 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 and learn from their experiences with waste treatment.

As part of the JCCRM, the 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. The CNEA acts as a hub for the nuclear enterprises in Argentina by

- advising the President of Argentina on nuclear waste management,
- facilitating technology transfer and other marketing efforts by the Argentine nuclear industry, and
- "gluing" the private and public nuclear sector together - this includes nuclear power generation, waste management, isotope and heavy water production, and nuclear medicine.

In a joint meeting in November 1996, several areas for collaborative research were identified. Immobilization of ion exchange materials was identified as one area of technical collaboration. This area was selected because of the CNEA's need to immobilize spent ion exchange resins currently stored at the countries' nuclear power plants.[1]

The CNEA currently has a contract with the Atucha and Embalse nuclear power plants in Argentine to immobilize spent ion exchange resins. Approximately 42 m^3 are stored at Atucha, and 130 m^3 are stored at Embalse. Atucha 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. The resins were originally stored in two 15 m^3 capacity tanks at Atucha (TC 51 and 52), 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 other tank is currently empty. The Embalse resins are stored in a large tank. Both resins have been in storage for about 10 years.[1]

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%. As a result, the CNEA is interested in pursuing vitrification treatment of this waste stream.[1]

The DOE has also been interested in pursuing vitrification of this waste stream because ion exchange resins are used in several processes to remove both hazardous and radioactive constituents from solutions or sludges. Another large user of ion exchange resins is nuclear reactor facilities. In reactor facilities, ion exchange resins are used for purification of water in reactor basins and fuel storage basins. Thus, by finding a feasible treatment solution for the ion exchange resins, the needs of several entities in the nuclear industry can be satisfied.

At SRTC and other DOE sites, vitrification has been shown to be a feasible treatment method for ion exchange resins because the organic compounds which make-up the matrix of the resins can be destroyed either by pyrolysis or combustion at typical vitrification temperatures with some of the heavier organic compounds being pyrolyzed within the melt.[2] The majority of the combustion usually occurs above the melt in the plenum or in a secondary combustion chamber.

Previous vitrification studies with organic ion exchange resins have been performed at the SRTC.[3,4] These studies were performed 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 divinylbenzene/styrene copolymer resins, which are used by the reactor facilities to purify their basin water. 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 Amberlite resins did not have a defined disposal method.

Using direct vitrification methods without pre-treatment, early studies at SRTC indicated that the maximum amount of resorcinol resin that could be incorporated in the glass matrix was 5 grams of resin/100 grams of glass produced, while the maximum amount of Amberlite resin that could be incorporated in the glass matrix was 20 grams of resin/100 grams of glass produced. These loading were mainly bound by the redox (The $Fe^{2+}/\Sigma Fe$) 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.

Lab-scale melter studies performed at the SRTC[3] and at Clemson University[4] with the resorcinol resins verified the findings of the bench-scale studies. The data provided a strong indication that vitrification of the resorcinol resin in DWPF type feed was plausible. Melter operating conditions were not greatly affected in either study. Glasses made with the resin were found to have slightly poorer durability, which was expected because of the higher redox ratio of the glass. However, the durability was still magnitudes better than the Environmental Assessment (EA) glass durability results[5] for HLW. Lab-scale melter studies were not performed with the Amberlite resins due to a lack of funding.

Due to the relatively low weight percentage of resin that was incorporated in studies where direct vitrification of the resin waste was attempted, resin pre-treatment studies were also performed with the Amberlite resins. A relatively new oxidation process developed by SRTC for oxidizing organic wastes was used. This process used a nitric-phosphoric acid solution to completely destroy the organic content of the resin leaving a waste residue in the solution after about 30 minutes of processing. This residue was stabilized in an iron-phosphate glass due to the high concentration of phosphoric acid in the waste solution.

The glass easily melted at 1150�C in four hours and produced homogeneous durable glass with both clean and spent ion exchange resin from the Savannah River Site (SRS) Reactor basin. This process has been submitted in a patent application by Westinghouse Savannah River Company (WSRC).

Waste loading of resin glasses was maximized by using the nitric-phosphoric acid pre-treatment step in conjunction with iron-phosphate glass stabilization. The volume reduction was two fold, with expectations of higher volume reductions when radiation field is not a concern. This process could be directly applied to the Argentine resin materials because of the similarities in the types of resin. In fact, one of the Amberlite resins used in the SRS reactor basin (IRN-78) is also used by the Argentines. The pre-treatment method was not tested with the Argentine resins, but the results should be directly applicable.

Argentine Ion Exchange Materials

Atucha Resin

At the Atucha plant, the ion exchange resins that have been used are Lewatit S100 and M500. The S100 is the cation form, whereas the M500 is the anion form. The resins are combined in quantities of 60% M500 and 40%

S100. Typical properties of the resins are contained in Table 1. The total amount of spent Atucha resin generated annually is 2.83 m^3.[1]

From analyses and characterization performed by the CNEA, it appears that 30% of the volume of stored material is freestanding water. The resin bed is composed of 40.3 wt% dried resin and 59.7 wt% total water, with 53.2 wt% as embedded water and 6.5 wt% as interstitial water. An estimate of the associated radioactivity of the waste was also made. It is believed that the total ß/g activity is 1.5 TBq/m3. The activity is believed to be 68.6% from Cs-137, 25.3% from Co-60, 4.6% from Cs-134, and 1.5% from others.[1]

TABLE 1 - ATUCHA ION EXCHANGE MATERIAL PROPERTIES[1]

Property	S100	M500
Ionic Form	Na+	Cl-
Functional Group	Sulphonic Acid	Quaternary Amine
Matrix	Cross Linked Polystyrene	Cross Linked Polystyrene
Structure	Gellular	Gellular
Bead Size	0.4 - 1.25 mm	0.4 - 1.25 mm
Effective Size	0.55 mm	0.55 mm
Bulk Weight	850 g/L	710 g/L
Density	1.29 g/ml	1.09 g/ml
Water Retention	45-48 wt%	45-49 wt%
Volume Change	+10%	+22%
Stability Temp. Range	-10 to +120°C	+1 to +40°C

Embalse Resin

The Embalse plant has used four different types of Amberlite ion exchange resins over the years. 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 2. As mentioned earlier, the resins used at the Embalse plant are used in purification of several kinds of process water; therefore, different resins are used in different purification processes. The total amount of resin generated annually is approximately 9.5 m^3.[1]

TABLE 2 - EMBALSE ION EXCHANGE MATERIAL 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
Effective Size	0.45 to 0.60 mm	0.38 to 0.45 mm
Density	1.26 g/ml	1.11 g/ml
Max. Moisture Content	55%	45-49 wt%
Volume Change	+10%	60%
Stability Temp. Range	-10 to +120°C	+1 to +40°C

The CNEA has not been able to characterize the Embalse resins to the extent that they were able to characterize the Atucha resins. They did some experiments to simulate the current condition of the resins in storage. From these experiments, the parameters given in Table 3 were defined.

TABLE 3 - EMBALSE HYPOTHESIZED PROPERTIES[1]

Parameter	Condition	IRN 77	IRN 78	1:1 Mix
Total Water	Slurry	76.0%	82.4%	79.9%
Total Water	Dewatered	66.7%	76.6%	71.3%
Total Water	Damp	55.2%	63.3%	56.6%
Total Water	As Received	53.4%	59.8%	57.9%
Density (g/ml)	Slurry	1.06	1.01	1.04
Density (g/ml)	Dewatered	1.05	1.10	1.13
Density (g/ml)	Damp	1.30	1.19	1.28
Density (g/ml)	As Received	1.26	1.11	1.21

Experimental

Surrogate Resins

For these studies, resins representative of those used by the Atucha and Embalse plants in Argentina were obtained. The exact resins were not obtained due to the time constraints imposed by the agreements with the Argentines and because of the small amounts of resins required for the studies. The representative resins used in the studies are given in Table 4.

TABLE 4 - SURROGATE RESINS USED

Actual Resin	Surrogate Resin
Lewatit S100	Lewatit SP120
Lewatit M500	Amberlite 900 OH
Amberlite IRN 77	Amberlite IR 120
Amberlite IRN 78	Amberlite IRN 78
Amberlite IRN 150	Amberlite IRN 150
Amberlite IRN 154	Amberlite IRN 150

The substitutions for the resins were based on information available on equivalent resin types, given in Reference 6. The surrogate resins were of the same resin form (divinylbenzene/styrene copolymer) and active group. Amberlite IRN 150 was used for IRN 154 since it was available and the only difference was the LiOH ionic form.

Based on the data provided by the CNEA, the approximate quantity of each resin type in storage was determined. This information was used with the surrogates given in Table 4 to make two 200 gram batches of each resin mixture. The batches of resins were labeled the Atucha mix and the Embalse mix. The calculated percentages are shown in Table 5.

TABLE 5 - RESIN MIXTURES

Resin Mix	Actual Resin	Surrogate Resin	Amount
Atucha	M500	900 OH	60%
Atucha	S100	SP120	40%
Embalse	IRN 154	IRN 150	31.8%
Embalse	IRN 150	IRN 150	49.4%
Embalse	IRN 77	IRN 77	4.7%
Embalse	IRN 78	IRN 78	14.1%

The resin mixtures batched for this study were dried at 105, 650, and 1150�C to determine the water content and the non-oxide content. This information is helpful when determining the glass batch formulations. The material losses at the different temperatures are shown in Table 6. Data presented is from the average of two samples.

TABLE 6 - LOSS ON HEATING

Resin Mix	Loss at 105°C	Loss at 650°C	Loss at 1150°C
Atucha	63.41%	94.73%	95.25%
Embalse	44.46%	99.95%	N/A

After the 105�C drying, it appeared that most of the water had been removed from the resin mixtures, and the resins still resembled their initial state. The calculated water loss for the Atucha mix is consistent with the water content given on the Material Safety Data Sheet (MSDS) for the Amberlite resin, 45 - 65%. The results found for the Embalse mix were slightly lower than the water content data presented in the MSDSs for the Amberlite resins, 45 - 65%, and the total water loss numbers given by the CNEA, see Table 3. A small amount of this loss at 105�C can also be attributed to sulfur loss, since some of the resins contain sulphonic acid groups. Korkisch has demonstrated that desulfonation of sulfonated cation exchange resins and styrene-divinylbenzene resins is initiated at 100�C.[7]

When heated to 650�C, most of the mass of the Atucha resin had been lost, but the material remaining in the crucible still resembled the original resin. For the Embalse mix, all of the resin was pyrolyzed at 650�C. No remnants of the resin remained in the crucible, only a color stain remained. Loss at 1150�C was not performed on the Embalse mix, since it was all gone by 650�C. For the Atucha mix, most of the resin structure was broken down after the 1150�C drying and only a salt coating remained on the crucible. This coating had a blue tint. The fact that the Embalse mix was totally pyrolyzed by 650�C and that the Atucha mix was totally pyrolyzed by 1150�C theoretically indicates that high waste loadings with these materials should be achievable in a glass matrix.

Further testing was performed with the resin mixtures to find the proper amounts of water to mix with the resin to obtain slurries with similar properties to the slurries currently being stored in the Argentine tanks. For the Atucha resin mix, the tests consisted of duplicating the free standing water concentrations. Based on the data available from CNEA, the tank consists of 30% by volume freestanding water. However, this number does not take into account the amount of water that is adsorbed on the resin. Lab studies were performed to determine the amount of water necessary to obtain this freestanding volume. It was determined that for 5 ml of resin, 4 ml of water was necessary to obtain 30% by volume free standing water. This is equivalent to twice the volume necessary if none of the water were to be adsorbed. During these experiments, the density of the Atucha resin mix was determined to be approximately 0.610 g/ml, while the slurry density was approximately 0.978 g/ml. The volume of water necessary to obtain this freestanding ratio is important for determining waste volume reductions.

The data from CNEA for the Embalse resin did not give a freestanding volume of water. Instead, different densities and total water percentages were given for the different states of the resin. In order to determine the proper amount of water to be added to this mix to make the slurry, the data from Table 3 was used as a baseline. Based on this data, ratios of added water to resin were calculated and tested in the lab. To verify the total water content, the sample was dried overnight at 105�C. For the resin mixture used in this testing, the proper ratio was determined to be approximately 4 ml of resin to 5.4 ml of water. This resin solution had an approximate 81% total water content, which was consistent with the 79.9% total water for the slurry reported in Table 3. The density of the as batched resin was approximately 0.589 g/ml, while the slurry had a density of approximately 1.00 g/ml. The density of the resin was much lower than the as received density reported in Table 3 by the CNEA, while the slurry density was very close to the slurry density reported by the CNEA, 1.06 g/ml.

Glass Studies

A standard practice at the SRTC is to use bench-scale (crucible-scale) vitrification studies on surrogate wastes to determine optimum vitrification processing parameters and the necessary glass additives. These results can then be used to study bench-scale treatment of the actual wastes or to perform pilot-scale studies with either surrogate or actual wastes.

Since the Argentine ion exchange materials were very similar to the Amberlite resins used in previous research with resin vitrification, attempts were made to vitrify the Argentine materials using iron-enriched borosilicate glass compositions that were used to vitrify the previous Amberlite resins. Originally, these compositions were selected because the iron component provides an accurate indicator of the redox of the glass. Ferric oxide also can serve as a redox buffer by being reduced prior to other glass forming elements and, thus, provides oxygen for oxidation reactions.

Two glass compositions were selected from the previous Amberlite resin studies based on final product durability, homogeneity, and redox state. These compositions are shown in Table 7. The base compositions were fabricated from reagent grade chemicals with $Fe(NO_3)_3$ used as the glass additive for the Fe_2O_3 component to help oxidize the organics. Initial melts were performed using the selected compositions without the resins added to ensure that the base composition met processing requirements and so a control glass would be available for determining the effects of the organic components on the glass properties.

TABLE 7 - BASE COMPOSITIONS TESTED

Batch ID	B_2O_3 Wt%	CaO Wt%	Fe_2O_3 Wt%	Na_2O Wt%	SiO_2 Wt%
5	10.5	9.4	5.3	20.7	54.1
11	9.1	14.8	22.2	8.1	45.8

The base glasses were melted in covered high purity (99.8%) alumina crucibles at 1150�C for four hours. Lower melting temperatures were desired because of the volatility of Cs, which is the main contaminant on the resins. After four hours at melt temperature, the crucibles were removed from the furnace and allowed to cool to room temperature. Once at room temperature, the glasses were removed from the crucibles for characterization.

The two base glass compositions, #5 and #11, did not appear to be visually different. Both produced a dark brown, visually homogeneous glass.

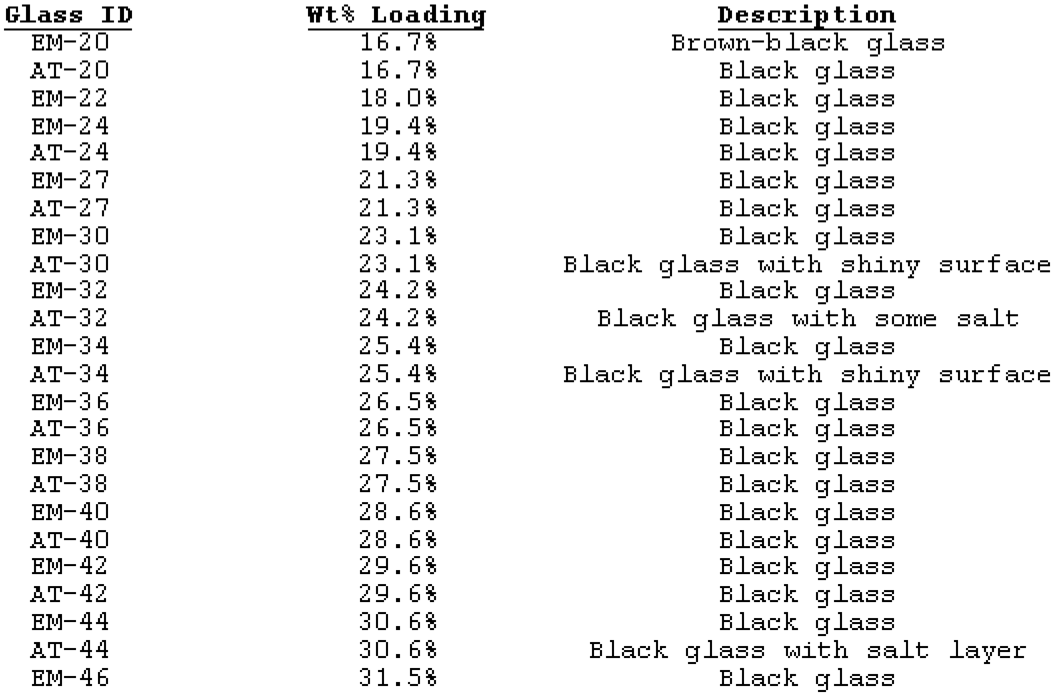
Previous testing with base compositions #5 and #11 had indicated that a resin loading of around 20 grams of resin/100 grams of glass produced was optimal. This was used as the starting point with the Argentine resin materials. Base compositions #5 and #11 were tested with each resin mixture using this waste loading and covered high purity alumina crucibles. The glasses were once again melted at 1150�C for four hours.

After the four glasses had cooled to room temperature, glasses made with base composition #5 appeared to have a small white salt layer on the surface. This salt layer had been seen in previous studies with Amberlite resins, but it appeared to be a greater quantity with the Argentine resin materials. Glasses made with base composition #11 did not have the salt layer and visually appeared to be homogeneous glasses. Thus, it was decided that further testing would only involve base composition #11.

Successive testing involved slowly increasing the amount of resin until problems with processing, salt layer formation, or visual homogeneity became a concern. These glasses were melted in the same way that the base glasses were melted. All were melted at 1150�C for four hours, removed from the furnace, and allowed to cool. Once the glasses were cool, they were broken out of the crucibles for characterization. Each glass was examined for physical appearance. The physical appearance did not seem to vary from sample to sample, with the exception of salt layer formation. The resin loadings tested and a description of the final products produced are given in Table 8. In the glass ID, the AT or EM stands for the type of resin used, either Atucha (AT) or Embalse (EM), while the number represents the grams of resin added per 100 grams of glass produced.

For the Atucha resin mix, the highest loading that appeared feasible based strictly on visual observations was 42 grams of resin/100 grams of glass produced. The glass melted with 44 grams of the Atucha mix had a small white salt layer form on the surface, and so it appeared that the salt solubility of the glass had been exceeded from the anion components present in the resin. The Embalse resin mix glasses were stopped at 46 grams of resin/100 grams of resin produced. This glass still appeared to be visually homogeneous and looked good, but it was felt that the other properties of the glass had to be evaluated before going further with increased loadings.

TABLE 8 - RESIN LOADINGS TESTED



Glass ID	Wt% Loading	Description
EM-20	16.7%	Brown-black glass
AT-20	16.7%	Black glass
EM-22	18.0%	Black glass
EM-24	19.4%	Black glass
AT-24	19.4%	Black glass
EM-27	21.3%	Black glass
AT-27	21.3%	Black glass
EM-30	23.1%	Black glass
AT-30	23.1%	Black glass with shiny surface
EM-32	24.2%	Black glass
AT-32	24.2%	Black glass with some salt
EM-34	25.4%	Black glass
AT-34	25.4%	Black glass with shiny surface
EM-36	26.5%	Black glass
AT-36	26.5%	Black glass
EM-38	27.5%	Black glass
AT-38	27.5%	Black glass
EM-40	28.6%	Black glass
AT-40	28.6%	Black glass
EM-42	29.6%	Black glass
AT-42	29.6%	Black glass
EM-44	30.6%	Black glass
AT-44	30.6%	Black glass with salt layer
EM-46	31.5%	Black glass

Characterization of each glass sample was not performed due to the similarities in glass composition from resin to resin. Also, the waste loadings of the glasses were not changing drastically from sample to sample because of the small amount of resin solids that actually remained in the glass structure. Glass characterization that was performed included chemical composition, durability, the redox ratio, and morphology.

Since previous lab-scale melter testing[3] had shown that the Stir-Melter® stirred melter was suitable for processing resorcinol resins, batches with the Atucha resin were melted at 1050�C and 1100�C and a batch with the Embalse resin was melted at 1050�C to determine if homogeneous glass could be produced at lower temperatures. The Stir-Melter® is limited to operating temperatures of 1050�C because of the Inconel components.

Crucible studies were also performed to simulate slow cooling of the glass after exiting a melter. The DWPF HLW glass canister cooling schedule was used for these glasses. The DWPF HLW glass is melted at 1150�C and poured into a 10 ft. tall canister with a diameter of 2 ft. This cooling schedule presents a worst case scenario for cooling of the resin glasses. The cooling schedule was applied to the AT-42 and the EM-46 glass since these represented the perceived upper limits of resin loading. Samples of the glass were analyzed by X-ray Diffraction (XRD) to determine the amount of crystals that formed, since the formation of excess crystals can impact the final product durability.

The last variable to be tested in the crucible studies was the impact of the contaminant on the process. The primary contaminant on the resins should be Cs since it is the primary element that is removed during nuclear facility water purification, and it was the primary radioactive contaminant based on the analyses performed with the Atucha resin. Cs has been shown to be very volatile during vitrification treatment. Therefore, a sample of the Atucha resin was doped with non-radioactive Cs at levels 1000 times greater than expected, so the glass retention could be determined. The greater level had to be used because the expected Cs concentration on the resin would have been too low to detect in the final glass. This resin was used with the glass formulation for AT-40 and was melted at 1150�C to determine the Cs retention.

Results

Since all of the glasses made for this study were based on the same base composition with the only difference being the type and amount of resin added, only representative glasses were submitted for chemical composition analyses. The glasses should have fairly consistent compositions because the resin solids contribute only a minor amount of material to the glass composition. The representative glasses were examined for chemical composition after Na_2O_2-HCl dissolution and Microwave digestion using Inductively Coupled Plasma-Emission Spectroscopy (ICPES). The base glass #11 composition was also analyzed so the effects of the resin addition could be better quantified. Results are presented in Table 9 for the major glass oxides.

TABLE 9 - GLASS CHEMICAL COMPOSITIONS RESULTS (Wt%)

Oxide	#11	AT-27	AT-34	AT-42	EM-30	EM-38	EM-46
Al_2O_3	1.848	1.984	2.158	4.249	2.318	3.225	6.110
B_2O_3	9.174	8.426	8.848	13.810	8.593	8.842	14.431
CaO	14.565	13.463	14.036	11.986	13.529	13.769	12.372
Cr_2O_3	0.144	0.114	0.117	0.130	0.109	0.116	0.115
Fe_2O_3	20.308	18.422	18.772	17.184	19.157	19.054	16.675
Na_2O	8.096	7.745	7.925	9.430	7.986	7.460	9.237
SiO_2	44.162	41.821	42.834	36.463	42.363	42.426	38.283

All of the glasses were very similar in composition for the major oxides. Glasses AT-42 and EM-46 differed the most from the rest of the compositions. All of the glasses contained some amount of Al_2O_3 contamination from the Al_2O_3 crucibles used in melting. The higher resin loading glasses contained the most Al_2O_3 contamination, which is probably the reason for the composition difference for the rest of the oxides. Higher concentrations of one species would dilute the other major species in the glass. When compared to the base glass #11 composition, most of the compositions were similar with the biggest difference being slightly higher concentrations of Al_2O_3 for the resin containing glasses and slightly lower concentrations of the other major oxides. Overall, the type of resin did not seem to greatly impact the glass composition. A melt with the Embalse resin was performed in a platinum crucible to ensure that the Al_2O_3 was not important for glass formation. The melt in platinum looked the same as the melts in Al_2O_3 crucibles and appeared homogeneous.

To determine the final product durability, the Product Consistency Test (PCT), ASTM C1285-94,[8] was performed on several glass samples and the base glass composition. The PCT is a crushed glass leach test that measures the releases of B, Si, Na, and other elements in 90�C ASTM Type I water over a period of seven days.[8] Glass samples were run in triplicate for the PCT and the results were averaged. The PCT results in ppm are given in Table 10. The measured leachate pH is also listed in Table 10, since this provides a secondary indication of durability.

TABLE 10 - PCT RESULTS (ppm)

Glass ID	B	Si	Na	pH
#11	4.54	14.94	15.91	9.66
AT-27	4.79	12.07	16.13	9.36
AT-30	4.58	11.26	15.08	9.40
AT-34	4.43	11.77	15.67	9.42
AT-38	4.47	12.82	16.38	9.91
AT-42	7.94	9.81	21.45	9.29
EM-27	4.07	11.77	14.25	9.40
EM-30	4.37	11.08	17.65	9.45
EM-34	4.59	12.40	17.99	9.50
EM-38	4.74	15.24	25.57	9.71
EM-42	4.98	13.55	30.24	9.80
EM-46	10.43	13.96	54.97	9.96

The PCT results were fairly consistent between the different glasses. Once again, the only results that were slightly different were the ones for the highest resin loading glasses, AT-42 and EM-46. Most of the glasses had similar releases to the base glass composition, indicating little effect from the resin on the glass durability performance. The pH results also indicate that the glasses had similar durabilities.

Since only representative glasses were examined for chemical composition, the PCT results for those glasses not analyzed were normalized using the resin loading as the basis. For example, AT-30 was not analyzed for chemical composition, but EM-30 was so this composition was used to normalize the results. The normalized results are presented in Table 11. Since no acceptance criteria have been established for waste glasses other than HLW glasses, the durabilities of the glasses produced were compared against the HLW criteria which states that the glass produced must be more durable than the EA glass.[5] The EA glass values are shown in Table 11 for comparison.

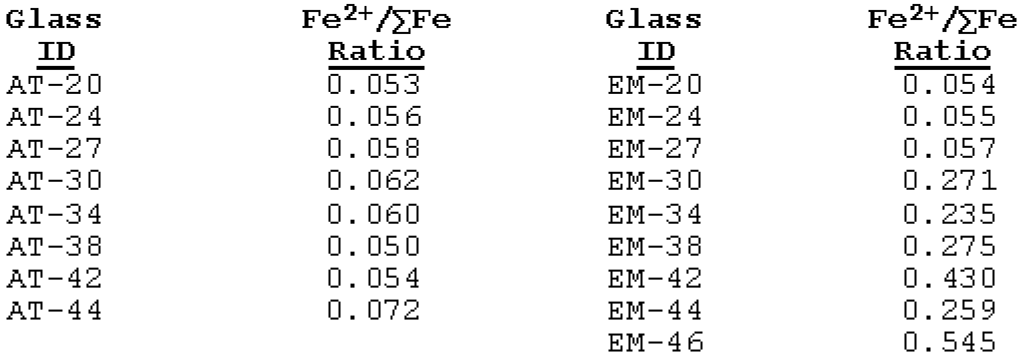
TABLE 11 - NORMALIZED PCT RESULTS (g/L)

Glass ID	B	Si	Na	pH
#11	0.159	0.072	0.265	9.66
AT-27	0.183	0.062	0.281	9.36
AT-30	0.172	0.057	0.255	9.40
AT-34	0.161	0.059	0.267	9.42
AT-38	0.163	0.065	0.296	9.91
AT-42	0.185	0.058	0.307	9.29
EM-27	0.156	0.060	0.248	9.40
EM-30	0.164	0.056	0.298	9.45
EM-34	0.167	0.062	0.306	9.50
EM-38	0.173	0.077	0.480	9.71
EM-42	0.116	0.079	0.432	9.80
EM-46	0.233	0.078	0.802	9.96
EA[4]	16.695	3.922	13.346	11.85

No apparent trend was observed between the amount of resin in the glass and the PCT release. However, it appeared that as the resin loading increased, the normalized Na release also increased. All glasses had good durability compared to the EA glass based both on the normalized releases and on the measured pH. The normalized releases for all glasses were orders of magnitudes less than the EA glass. It did not appear that the resin in the glass greatly affected the glass durability since the results for the resin glasses were not substantially different than the results for the base glass #11.

The $Fe^{2+}/\Sigma Fe$ ratio was determined using the colorimetric method since the redox is a very important factor for glass processing. High ratios are not desirable in glass melters due to the potential to reduce elemental or metal oxides in the wastes to pure metals or sulfides, which can settle to the bottom of the melter. In addition, reducing conditions can increase the potential for alloying of materials with the melter electrodes and for corrosion of melter components, which can decrease the efficiency and lifetime of joule-heated melters. The redox ratio of the glass can also affect the glass properties, with high ratios or reduced glasses being less durable. Theoretically, the ratio should be higher for the glasses with higher resin loading because of the higher organic content. The The $Fe^{2+}/\Sigma Fe$ ratios determined for the resin glasses are given in Table 12. The base glass #11 ratio was determined to be 0.054.

TABLE 12 - $Fe^{2+}/\sum Fe$ RATIO



Glass ID	$Fe^{2+}/\sum Fe$ Ratio	Glass ID	$Fe^{2+}/\sum Fe$ Ratio
AT-20	0.053	EM-20	0.054
AT-24	0.056	EM-24	0.055
AT-27	0.058	EM-27	0.057
AT-30	0.062	EM-30	0.271
AT-34	0.060	EM-34	0.235
AT-38	0.050	EM-38	0.275
AT-42	0.054	EM-42	0.430
AT-44	0.072	EM-44	0.259
		EM-46	0.545

For the Atucha resin glasses, the measured redox ratio was not strongly affected by the amount of resin present in the glass. Only a slight increase in the ratio occurred as the amount of resin increased. The Embalse resin glasses, on the other hand, were more dependent on the amount of resin present in the glass. A sharp change in the measured redox ratio is seen from the 27 gram of resin glass to the 30 gram of resin glass. However, although the redox ratio is increasing, most of the glasses would still be acceptable for processing in a joule-heated melter. Glasses EM-42 and EM-46 are the only glasses with a higher redox ratio then the limits established for joule-heated melters, which is 0.33. This change in redox state may be partially attributable for the decreased durability shown by these higher resin loading glasses.

All glasses appeared to be visually homogeneous. However, in order to ensure that no crystalline phases were present, XRD analyses were performed on representative glass samples. Samples tested included AT-27, AT-38, AT-42, EM-20, EM-34, EM-42, and EM-46. All samples were found to be amorphous.

It was determined that 1150�C was the most suitable temperature for making homogeneous Atucha resin glass, whereas 1050�C was acceptable for making homogeneous Embalse resin glasses. The Atucha melts performed at lower temperatures did not produce as good of glass as the melt at 1150�C, with the lower temperature melts also producing a large amount of salt on the glass surface.

The samples that were cooled using the DWPF canister cooling program (AT-42 and EM-46) were examined using XRD to determine the effect of slow cooling on crystal formation. Both glasses appeared to have small amounts of crystalline formation near the crucible glass interface, but did not visually appear to have a large amount of crystalline formation in the bulk matrices of the glasses. For AT-42, XRD indicated that the crystals near the wall consisted mostly of Fe_2O_3 and nepheline ($NaAlSiO_4$), but the bulk glass matrix appeared amorphous. For EM-46, the same crystals were found near the crucible walls, but the bulk matrix contained approximately 0.3 wt% augite, $Ca(Mg,Fe^{+3},Al)(Si,Al)_2O_6$, in the bulk matrix. These results seemed to indicate that slow cooling, as experienced when the glass leaves the melter and enters its storage container, will not have a great effect on the final product durability for glasses of this formulation with the two resin mixtures.

To determine the amount of Cs retained in the glass from the incorporation of the Cs doped resin, the Atucha glass was analyzed using a Microwave digestion and Atomic Absorption spectroscopy. The amount loaded was 23.9 mg while the amount detected in the glass was 41 mg. This represents a 171% retention and indicates that almost all of the Cs contained in the resin was retained by the glass during processing, with minimal carry-over to the offgas. The discrepancy in the numbers can be attributed to the difficulties in measuring very low elemental concentrations. No effects on the glass product or processing were seen from the incorporation of the Cs.

Based on all of the analytical results and the observed behavior during processing, the optimal waste loadings appear to be 42 grams of Atucha resin and 44 grams of Embalse resin per 100 grams of glass produced. The lower Embalse resin mix loading was selected because of the higher than desired redox ratio seen for the EM-46 glass. Although the EM-44 glass was not subjected to the PCT, its durability should be more than acceptable since the EM-42 and EM-46 glasses had acceptable durabilities. The iron enriched borosilicate glass formulation seems well suited for incorporating these wastes when ferric nitrate is used as the source of iron in the glass formulation. Based on the data available for water content in the slurry, the measured glass density of 2.854 g/ml, and waste loadings of 42 grams for Atucha and 44 grams for Embalse, volume reductions were calculated. The volume reduction for the Atucha resin was 2.82 fold or 65%, while the volume reduction for the Embalse resin was 4.15 fold or 76%.

Conclusions

Based on all of the analytical results, it appears that using a base glass composition consisting of 9.1 wt% B_2O_3, 14.8 wt% CaO, 22.2 wt% Fe_2O_3, 8.1 wt% Na_2O, and 45.8 wt% SiO_2 will produce very durable and homogeneous glasses with the Argentine resin materials. When using this formulation, ferric nitrate should be used as the source of Fe_2O_3 to help with the organic destruction. For the Atucha resin mix, the optimum waste loading was determined to be 42 grams of resin/100 grams of glass produced or 29.6 wt% resin, while, for the Embalse resin mix, the optimum resin loading was determined to be 44 grams of resin/100 grams of glass produced or 30.6 wt% resin. These represent about a 65% and 76% volume reduction, respectively. The waste loading and associated volume reduction are higher than what has been seen in previous studies with resin treatment using direct vitrification.

Increased volume reductions may be possible by using the WSRC patent pending nitric-phosphoric acid oxidation process as a pre-treatment step, with stabilization of the solution in an iron-phosphate glass matrix. This two-step treatment process was demonstrated on similar spent ion exchange resins and a two-fold volume reduction was demonstrated, but higher volume reductions are expected when the resin contaminants do not affect the processing characteristics.

Acknowledgments

Funding for this research and development work was provided by the Department of Energy - Office of Technology Development under the auspices of the Tanks Focus Area and Technical Task Plan SR1-6-WT-31.

The efforts of all personnel involved with this project are greatly appreciated. These include but are not limited to the following:

- Phyllis Workman for batching and melting the glasses
- Phyllis Workman and Debbie Marsh for performing the PCTs

References

1. M. J. Plodinec, **"Foreign Travel Report Technology Exchange Between CNEA (Argentina) and USDOE November 18-22, 1996"**, WSRC-RP-97-1, January 2, 1997.
2. United States Patent No. 6,329,563, "Vitrification of Ion Exchange Resins", C. A. Cicero-Herman and R.J. Workman, Dec. 11, 2001.
3. N. E. Bibler, J. P. Bibler, M. K. Andrews, and C. M. Jantzen, **"Initial Demonstration of the Vitrification of High-Level Nuclear Waste Sludge Containing an Organic Cs-Loaded Ion Exchange Resin"**, Presented at the Materials Research Society Meeting 1992, WSRC-MS-91-465.
4. T. N. Sargent, **"Vitrification of Cesium-Contaminated Organic Ion Exchange Resin"**, Graduate Thesis for Clemson University - Environmental Systems Engineering, August 1994.
5. C.M. Jantzen, N.E. Bibler, D.C. Beam, C.L. Crawford, M.A. Pickett, **"Characterization of the Defense Waste Processing Facility (DWPF) Environmental Assessment (EA) Glass Standard Reference Material",** WSRC-TR-92-346, Rev. 1, June 1, 1993.
6. L.C. Thomas and G.J. Chamberlin, *Colorimetric Chemical Analytical Methods*, 9th Ed., The Tintometer Ltd., England.
7. J. Korkisch, *Handbook of Ion Exchange Resins: Their Application to Inorganic Analytical Chemistry*, Volume 1, CRC Press (1989).

8. ASTM C1285-94, "Standard Test Methods for Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)", 1994.
9. United States Patent Number 5,960,368, Sept. 28, 1999, �Method for Acid Oxidation of Radioactive, Hazardous, and Mixed Organic Waste Materials�.