IMMOBILIZATION OF THE RADIONUCLIDES FROM SPENT ION-EXCHANGE RESINS USING VITRIFICATION

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ABSTRACT

Approximately 60 g of an iron-enriched borosilicate glass was made in the radiochemical labs of the Savannah River Technology Center (SRTC). The glass was made to demonstrate the immobilization of the radioisotopes contained on representative Argentine ion exchange resins (similar to those used at the *Embalse* plant). The product was approximately 90% amorphous and was quite durable as measured by the release rates from the Product Consistency Test (PCT). The release rates were considerably better than those of the U. S. High Level Waste (HLW) benchmark DWPF EA glass. The release rate of the Cs-137 was predictably similar to that of Na and Li. No Co-60 or Sr-90 was measured in the PCT leachate. The mass balances for the inactive additives were quite good. Of the radioisotopes, approximately 71% of Cs-137 was accounted for in the glass product. This was similar to the Na mass balance. Approximately 89% of the Co-60 was accounted for in the glass product.

INTRODUCTION

Under the Science and Technology Implementing Arrangement for Cooperation on Radioactive and Mixed Waste Management (JCCRM), the Department of Energy (DOE) is helping to transfer waste treatment technology to international atomic energy commissions. In 1996, as part of the JCCRM, DOE established a collaborative research agreement with Argentina's *Comisión Nacional de Energía Atómica* (CNEA). A primary mission of the CNEA is to direct waste management activities for Argentina's nuclear industry (1).

The CNEA is investigating treatment and disposal options for organic ion exchange resins. Presently, large amounts of ion exchange resin are stored at two nuclear power plants, the *Atucha* plant and the *Embalse* plant. The *Atucha* plant creates approximately 2.8 m^3 of waste per year, while the *Embalse* plant creates approximately 9.5 m^3 of waste per year. The current inventory (in 2001) of spent resin is approximately 56 m^3 for the *Atucha* plant, while the inventory at *Embalse* is approximately 178 m^3. A treatment and disposal method is needed due to continued generation of the resins and limited storage capacity at both plants. Past work by CNEA has shown that an acceptable resin-loaded grout wasteform can be produced. However, the resin loading in the grout was limited to about 10 to 15 wt-% (1).

Vitrification technology has been developed by the DOE to convert hazardous and/or radioactive wastes to a form suitable for permanent disposal and is already being applied by the DOE and in other countries for the stabilization of high-level radioactive wastes. The Environmental Protection Agency (EPA) has declared vitrification to be the Best Demonstrated Available Technology (BDAT) for high-level radioactive liquid waste. The technology is also being applied to low-level and mixed wastes because of the advantages seen for high-level radioactive wastes.

The DOE has an interest in treatment options for ion exchange resins because they are used in several of the Department's processes to remove both hazardous and radioactive constituents from solutions and/or sludges. Vitrification is an attractive technology because it is capable of consistently producing a durable, leach resistant

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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.

In the late 1980s, SRTC performed vitrification studies with resorcinol-based organic ion exchange resin. These early studies indicated that only low levels of resins could be fed to the small-scale Joule-heated ceramic melter. The resin loading was bound mainly by the REDOX of the glass (as indicated by the Fe^{2+}/Fe_{total}). Melter feeds containing large amounts of organics tend to cause more reduced glasses. In the mid-1990s, SRTC performed vitrification studies with resins similar to those used in Argentina (divinylbenzene, polystyrene). Those tests revealed that ion exchange resins are suitable candidates for treatment by vitrification. Nitrates and iron oxide were used to help increase the loading of resins in the melter feed. Using an iron-enriched borosilicate glass composition, a durable waste form was produced which allow the processing of up to 44 grams of the wet organic ion exchange materials per 100 grams of glass.

While this formulation was shown to produce acceptable glasses in a crucible and in small melter demonstrations, complete off-gas characterization was not performed and melter demonstrations with actual materials were needed to fully access the viability of the process. Another melter demonstration with a similar resin performed after the Argentine representative run provided an additional opportunity to improve melter and glass performance. One improvement involved reducing the amount of nitrates added in the glass formers, which was possible with a change in glass formers from $CaCO_3$ to $Ca(OH)_2$. This resulted in less NO_X being emitted in the off-gas system and also reduced the amount of foaming seen in the feed. The second was related and involved increasing resin feed loadings because more nitrates were available for organic oxidation instead of carbonate neutralization. These options were used to slightly increase the resin feed loading so that approximately 30 grams of the dry *Embalse* resin could be processed per 100 grams of glass produced.

In the bench-scale studies at SRTC, non-radioactive cesium at levels 1000 times greater than expected were used to determine cesium retention in the glass. This was done since the small amount of cesium that would have been added to the resins would have been difficult to detect during analysis of the final glass. Even at these high levels, the cesium retention in the glass was nearly 100%. For the melter demonstration using representative Argentine ion exchange material, cesium and strontium retention was nearly 100% when the resins were spiked with excess levels (1000x).

In FY97-99, the Savannah River Technology Center (SRTC), under the auspices of the JCCRM, completed bench-scale studies and melter demonstrations with the Argentine organic ion exchange resins. Bench-scale studies were performed using both types of Argentine ion exchange resin. In the bench-scale studies, ~30 wt-% resin loadings were demonstrated, resulting in an ~65 % volume decrease (Note: In this case, the term "resin loading" is defined as the mass of dry resin processed per the mass of glass produced, the organic resin is not actually "loaded" into the glass). This was accomplished using an iron-enriched borosilicate glass and direct vitrification of the resin material. The data from the early studies were used to perform a melter demonstration with one of the Argentine ion exchange resins. In both studies, homogeneous and durable glasses were produced.

Irradiation studies with the Argentine resins were also performed in FY97. These studies showed that no significant degradation of the resins occurred due to radiolysis. The studies also revealed that some potential flammability concerns exist if large amounts of the resins are stored in small, unvented storage containers.

In FY99, studies were conducted using a stirred melter at the Clemson Environmental Technologies Laboratory (CETL) at Clemson University (Anderson, South Carolina). In these studies, representative *Atucha* and *Embalse* resins that had been doped with inactive cesium were vitrified. Off-gas and other operational data were collected. There was considerable entrainment and solids carryover associated with cold cap disruption and incorporation; and glasses produced without melt air sparging tended to be overly reduced (Fe^{2+}/Fe_{total} approximately 0.7).

In FY00, two runs were conducted in the Research Scale Melter (RSM) at the Pacific Northwest National Laboratory in Richland, WA. Off-gas and other operational data were collected in a system much more prototypical of what would be expected to be used in an actual operation. In contrast to the CETL Stir-Melter™ runs, there was

very little solids entrainment or carryover. The product glass tended to be reduced (Fe^{2+}/Fe_{total} approximately 0.9); but, it was quite homogeneous (very low crystal content) and was very durable, as indicated by the PCT leaching protocol.

TEST DETAILS

Experimental Set-up

The experiments were performed in a radiochemical hood in Laboratory B-102 at the Savannah River Technology Center. A detailed diagram of the furnace, as it was configured for this test, is presented in Figure 1.

The furnace was a DelTech™ Model DT-29-TL-610 Top Loading Laboratory Furnace with a programmable setpoint temperature control. The furnace, which is capable of 1200°C, was custom designed by Deltech™ to fit the off-gas system and to fit inside a radiochemical hood. The off-gas system contained a primary chilled-water condenser, a dry ice bath and two activated carbon beds in series. A sampling port was available on the water condenser for collection of condensate accumulated during the evaporation and vitrification steps. As shown in Figure 1, ambient air was pulled into a quartz tube through an inlet carbon filter. The quartz vessel inside of the furnace contained an alumina insert that held the 600 mL Pt/Rh crucible. The incoming air acted to sweep through the quartz tube to carry off-gas from inside the sealed quartz vessel system to the off-gas system (condenser, cold trap, and carbon filters). The central off-gas tube exited the furnace through a 1" diameter opening cut out of the top of the furnace. All loading of equipment and samples into the furnace was performed through a top-located circular furnace door of 6" diameter (not shown in Figure 1).

The two final carbon filters in the off-gas system were connected to a facility-supplied vacuum system. A vacuum of approximately 2-3 inches of water was maintained on the crucible during the evaporation and vitrification steps.

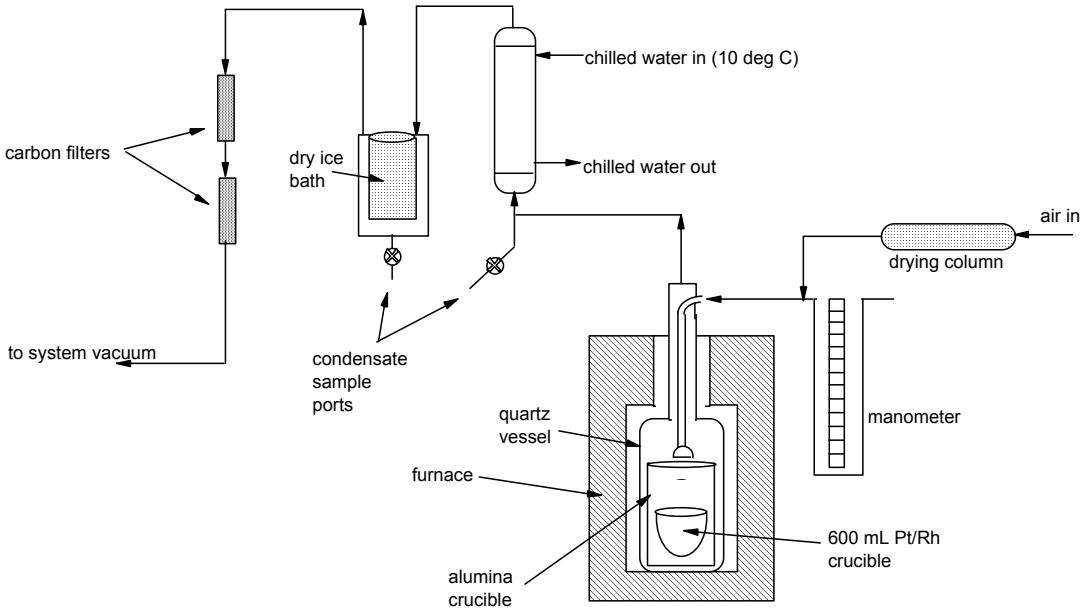

Fig. 1. Experimental Set-up

Waste Description

Ion exchange materials are widely used in the nuclear industries (including at the facilities of the DOE) for purification of various aqueous streams. Unfortunately, their use 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 hazards of the ion exchange resins are their organic composition and the contaminants that are present on the resins after purification processes. The principal contaminants are usually the radioactive species that are removed.

For this study, resins similar to those used at CNEA's *Embalse* plant were used. The resins were doped with representative amounts of ^{137}Cs, ^{90}Sr, and ^{60}Co. The *Embalse* plant currently uses or has historically used four different types of Amberlite™ (Rohm & Haas) 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 Li^+/OH^- based. The four resins have been used in various combinations at the plant depending on the particular application.

The properties of the Amberlite™ resins are shown in Table I; the radionuclide loading is given in Table II.

Table I. Properties of the CNEA *Embalse* Ion Exchange Resins

Property	**IRN-77**	**IRN-78**
Ionic Form	H^+	OH^-
Functional Group	Sulfonic Acid	Quaternary Ammonium
Matrix	Cross Linked Polystyrene	Cross Linked Polystyrene
Structure	Gellular	Gellular
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

Table II. CNEA Estimated Radionuclide Levels of *Embalse* Ion Exchange Resins*

Radionuclide	**Quantity* (mmol/mL)**
^{137}Cs	1.1×10^{-6}
^{60}Co	2.0×10^{-8}
^{90}Sr	1.0×10^{-9}

* mmol/mL of wet resin

Glass Formulation

The target glass composition for these tests was an iron-enriched borosilicate and was consistent with that used in previous testing. The target glass composition is shown in Table III.

Table III. Target Glass Composition

Oxide	**Wt-%**
B_2O_3	8.75
CaO	14.23
Fe_2O_3	21.35
Na_2O	11.63
SiO_2	44.04

Testing Strategy and Objectives

The objectives of these demonstrations were outlined in the Test Plan (2). The test plan provided some additional guidelines for planning and performing the test. Specifically, the objectives of this tests were to obtain data on wasteform durability (as measured using the Product Consistency Test, PCT), crystal formation in the glass, and radionuclide retention and partitioning. Some additional objectives were specified (offgas characterization and organic destruction efficiency). However, due to the limited space available in the radiochemical hood, a gas chromatograph or other gas analysis instrumentation, could not be installed. But, considerable (and more representative data) was collected during the CETL and PNNL/RSM tests.

EXPERIMENTAL AND RESULTS

Resin and Slurry Make-up

The IRN-154 is no longer commercially available. So, using a procedure prescribed by personnel at CNEA, IRN-154 was made by converting a 1:1 mixture of IRN-77 and IRN-78 to the lithium form using 60 g of LiOH per 1 kg of cationic resin.

The resins were then loaded with reference amounts of the radionuclides. The resins were put in a beaker containing 500 mL of DI water. The beaker was then placed on a magnetic stirplate in a radiochemical hood. The contents of glass ampules were then added to the resin slurry. The mixture was then stirred for several hours before being allowed to sit, unstirred, overnight. The slurry was then stirred for about 7 hours, filtered, and bottled for use in the radioactive test. The amounts of the radionuclides are given in Table IV.

Table IV. Radionuclide Loading in the Resins

Isotope	sol'n added	sol'n density	isotope conc'n	isotope added	isotope conc'n	activity added
	(g)	(g/mL)	(μg/mL)	(μg)	(μCi/g)	(μCi)
Cs-137	4.945	0.9996	10	49.47	130.3	644.33
Co-60	4.903	0.9996	10	49.05	14.05	68.89
Sr-90	4.841	0.9996	10	48.43	0.2025	0.98

On 5/7/01 the radionuclide-loaded resins, glassforming additives (given in Table V), and 100-mL of DI Water were added to the 600-mL Pt/Rh crucible and mixed thoroughly with a laboratory spatula. The crucible was then put into the furnace and held at room temperature overnight.

Table V. Batch Recipe for Slurry Make-up (g)

Source Chemical	Amount (g)
Iron nitrate ($Fe(NO_3)_3$-$9H_2O$)	34.390
Iron oxide (Fe_2O_3)	6.792
Borax ($Na_2B_4O_7$-$10H_2O$)	11.652
Calcium hydroxide ($Ca(OH)_2$)	11.982
Silica (SiO_2)	28.056
Sodium nitrate ($NaNO_3$)	13.633

Experimental

On 5/8/01 at 7:00am, the temperature of the furnace was slowly increased to remove the water from the slurry contained in the crucible and collect it in the trap below the condenser. The temperature was increased to an indicated temperature of 140 °C (from previous experience with this furnace we know that the actual temperature

was approximately 100 °C. Condensate was collected during this period. At 3:40pm the furnace was shut off overnight and allowed to cool to room temperature.

On 5/9/01 at 9:00am, the crucible was removed from the furnace and the contents were mixed with a laboratory spatula to ensure homogeneity. The crucible was put back into the furnace and the heat-up sequence was initiated. The heat-up rate was 50 °C/hour for the segment from 140 °C to 500 °C. Then, from 500 °C to 1150 °C, the heat-up rate was programmed at 150 °C/hour. At about 1:00pm, 300 °C, "smokey" gas was noticed in the off-gas line. There was then a sudden burst of offgas, organic matter, *etc*. This is likely due to a rapid decomposition of the organic resin (and possible reaction with the oxidizing nitrates). The furnace continued to heat-up to 1150 °C. After the crucible has been held at 1150 °C for four hours, it was cooled inside of the furnace according to the cooling schedule shown in Table VI. This cooling schedule is that typically used by SRTC to simulate a Defense Waste Processing Facility (DWPF) canister centerline cooling (CCC) curve for HLW glass. The heat-up and cool-down curve is shown in Figure 2. The crucible was removed from the furnace on 5/11/01.

Table VI. Cooling Schedule Used to Simulate DWPF Canister Centerline Cooling*

Ramp Number	**Ramp Rate**	**Target Temperature**	**Dwell Time at Target Temperature**	**Total Time Including Ramp and Dwell**
	(C/min)	**(C)**	**(hours)**	**(hours)**
#1	8	926	0.1	0.57
#2	1	779	2.8	5.25
#3	1	715	3.4	4.47
#4	1	598	4.2	6.15
#5	1	490	4.3	6.1
#6	1	382	7.4	9.2
#7	100%	70	Finish	5.2
				Total Time ~ 37 hours

* Note: Ramp Number #1 initiates after glass melt has been held at 1150°C for typically four hours.

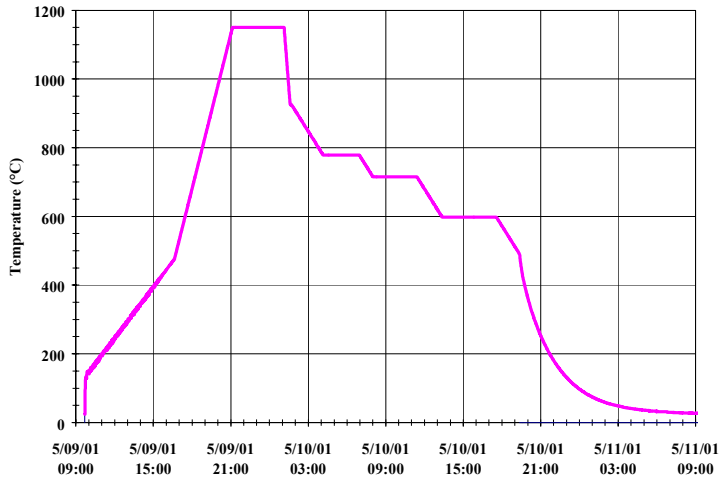

Fig. 2. Heat-up and Cool-down Curves for This Experiment

Glass Product Composition

The glass product glass was analyzed by the Analytical Development Section (ADS) of SRTC. The glass was dissolved using two techniques: a high temperature sodium peroxide fusion with HCl uptake, and a microwave digestion. These are standard analytical techniques that are used in the SRS DWPF laboratory for analysis of HLW glass. The glass was dissolved in duplicate for both techniques and analyzed via Inductively Coupled Plasma – Atomic Emission Spectroscopy (ICP-AES). A standard glass was dissolved and analyzed along with the Argentine resin glass. The complete results are given in the Appendix. Table VII gives the average composition. The results from the Na_2O_2/HCl dissolution were used for all elements except Na, the results from the microwave digestion were used for the Na. The ADS labs are not equipped to measure the ratio of Fe^{2+}/Fe_{total} for radioactive glass. A surrogate glass was submitted to the SRTC/ITS Mobile Lab for this analysis. The surrogate glass had gone through the same melting procedure as the radioactive glass. The Fe^{2+}/Fe_{total} of the radioactive glass was assumed to be the same as that of the surrogate. X-Ray Diffraction (XRD) analysis showed that the glass contained an estimated 10% crystallization. The crystals were identified as $NaFe^{+3}(SiO_3)_2$ and Li_6FeO_4.

Table VII. Measured and Targeted Glass Composition

	Elem	**Oxide**	**Target**
Component	**wt-%**	**wt-%**	**wt-%**
Al_2O_3	0.171	0.323	-
B_2O_3	2.184	7.033	8.750
CaO	9.164	12.830	14.230
Cr_2O_3	0.144	0.210	-
Fe_2O_3	15.626	17.004	21.350
FeO	15.626	4.806	-
Li_2O	0.212	0.457	-
MnO_2	0.027	0.043	-
Na_2O	5.976	8.067	11.630
NiO	0.096	0.122	-
SiO_2	21.773	46.594	44.040
Total-% Oxides		97.49	100.00
$Fe^{2+/}Fe(tot)$		0.239	-

Glass Product Durability (PCT)

The Product Consistency Test (PCT) is the standard durability analysis for High Level Waste Glass in the United States. The PCT was performed in triplicate on the glass produced during this test. The standard PCT procedure (3) was performed and the triplicate results were averaged. These results were normalized for the glass elemental contents and compared. They were also compared to the DWPF Environmental Assessment (EA) glass results. The DWPF EA glass is the benchmark for HLW glass in the United States (4). The normalized release rates from the PCT are given in Table VIII. The results from the SRTC resin glass (rad), the PNNL/RSM resin glass (non-rad) and the benchmark EA glass are shown.

Table VIII. Normalized Release Rates (g/L) from the Product Consistency Test (PCT)

Glass Sample	**r(B)**	**r(Si)**	**r(Na)**	**r(Li)**	**r(Cs)**	**pH**
PNNL/RSM Resin Glass (non rad)	0.12	0.07	0.29	0.27	-	10.8
SRTC Resin Glass (rad)	2.07	0.44	1.39	1.35	1.60	9.3
EA Glass	9.42	2.68	7.40	5.79	-	11.5

As can be seen from the results given in Table VIII, the normalized releases for B, Si, Na, and Li for both the SRTC (rad) and the PNNL (non-rad) glasses were considerably less than the EA glass. The normalized release rate for the Cs-137 was also measured for the SRTC resin glass. As expected, it is similar to that of the Na and Li. No Co-60 or Sr-90 was measured in the PCT leachate.

Though the SRTC resin glass is quite durable as compared to the benchmark EA, it is not as durable as the PNNL/RSM resin glass. The PNNL/RSM glass was more homogeneous and was produced with a more representative process (more like what would actually be used to immobilize the radionuclides on ion exchange resins).

Mass Balance

A total of 60.26 g of glass was made during this test. A mass balance was performed to determine how much of the added components were maintained in the glass. The results are given in Table IX. Of the non-radioactive components, several balanced quite well. The Fe, Si, B, and Li all were accounted for to 99 – 102%. Approximately 85% of the Ca and 71% of the Na were accounted for in the final glass product. The Na and Ca could have been preferentially entrained with the offgas (especially during the sudden burst early in the heating cycle).

Of the radioisotopes, 71% of the Cs-137 and 89% of the Co-60 were accounted for in the glass. The Cs-137 retention was quite similar to that of the Na. No reliable measurements were obtained for the Sr-90 which was present in very small quantities.

Table IX. Component Mass Balance for FY01 Test

	Loaded on Resin	**Added with Batch Chemicals**	**In Glass Product**	**In Glass and Condensate**	**% Accounted for**
Component	**(g)**	**(g)**	**(g)**	**(g)**	**(%)**
Fe	0.000	9.505	9.416	9.416	99.07
B	0.000	1.321	1.316	1.317	99.70
Ca	0.000	6.482	5.522	5.522	85.20
Si	0.000	13.116	13.120	13.121	100.04
Na	0.000	5.093	3.601	3.605	70.78
Li	0.156	0.000	0.128	0.160	102.35
Isotope	**(μCi))**	**(μCi)**	**(μCi)**	**(μCi)**	**(%)**
Cs-137	6.44E+02	0.000	4.58E+02	4.59E+02	71.31
Co-60	6.89E+01	0.000	6.16E+01	6.16E+01	89.44
Sr-90	7.99E-01	0.000	BDL	BDL	NA

CONCLUSIONS

Approximately 60.26 g of an iron-enriched borosilicate glass was made in the radiochemical labs of the Savannah River Technology Center. The glass was made to immobilize the radioisotopes contained on representative Argentine ion exchange resins (similar to those used at the *Embalse* plant). The glass contained approximately 10% crystallinity. There was a burst of offgas and organic material early in the heating cycle. This was likely due to decomposition of the organic resin and possible reaction with the oxidizing nitrates. The glass product was durable as measured by the release rates from the Product Consistency Test (PCT). The release rates were considerably better than those of the US HLW benchmark EA glass. The release rate of the Cs-137 was predictably similar to that of Na and Li. No Co-60 or Sr-90 was measured in the PCT leachate. The mass balances for the inactive additives were quite good. Of the radioisotopes, approximately 71% of Cs-137 was accounted for in the glass product. This was similar to the Na mass balance. Approximately 89% of the Co-60 was accounted for in the glass product.

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- Ned Bibler and Debbie Marsh did the Product Consistency Test (PCT).
- The Analytical Development Section of the SRTC provided the glass and condensate analyses, PCT leachate analyses, and XRD and SEM analytical characterizations.

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