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Commercial Ion Exchange Resin Vitrification Studies

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Summary

In the nuclear industry, ion exchange resins are used for purification of aqueous streams. The major contaminants of the resins are usually the radioactive materials that are removed from the aqueous streams. The use of the ion exchange resins creates a waste stream that can be very high in both organic and radioactive constituents. Therefore, disposal of the spent resin 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 disposal 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 been only moderately successful from a waste loading and volume reduction standpoint.[1,2] The present study used an iron-enriched borosilicate glass formulation, which was previously shown to be the most successful in vitrifying organic ion exchange resins used by Department of Energy (DOE) nuclear facilities and by nuclear industries in Argentina.[3]

In this study, the iron-enriched borosilicate resulted in high loadings, with associated high volume reductions for six resins representative of those used in the commercial nuclear industry. The waste loadings determined in the bench-scale studies were limited by adverse chemical shifts (redox reduction reactions) resulting in formation of metal sulfides in the glass. Waste loadings varied from 38 to 70 grams of resin per 100 grams of glass produced depending on the particular resin. These waste loadings represented volume reductions of 28% to 68.3% for the six resins. The strong cation sulfonated styrene resins were found to have the most waste loading limitations.

The results from these bench-scale studies will be used to perform a melter demonstration with one of the resins at the Clemson Environmental Technologies Laboratory (CETL). The intent of the demonstration will be to verify the vitrification parameters and determine the radioactive material partitioning using radioactive surrogates.

Introduction and Background

The commercial nuclear industry utilizes ion exchange resins to clarify their process and storage waters. The resins are used to remove unwanted impurities, such as radioactive materials or other contaminants that could potentially harm the equipment or corrode reactor fuel rods. The resins can clarify water which is to be reused at the plant or all solutions in the plant can be passed through the resins; thus, creating larger volumes of waste. Ion exchange resins are used in several processes to remove both hazardous and radioactive constituents from solutions or sludges. In reactor facilities, ion exchange resins are used for purification of water in reactor basins and fuel storage basins.

Over time, these resins have to be re-generated or replaced because they can only remove so much material before they become ineffective. When this happens, the spent resins have to be disposed. In many cases, the spent resins present disposal problems because of the organic matrix and the radioactive and sometimes hazardous contaminants present. Some of the radioactive contaminants that can be present are Cs^{137}, Sr^{90}, Co^{60}, C^{14}, and Tc^{99}. In the United States, resin wastes from Boiling Water Reactors (BWR) are enriched in constituents such as Fe_3O_4, while wastes from Pressurized Water Reactors (PWR) are enriched in borate from moderators and in Li^7 which is used for pH control. Approximately 100,000 lbs of BWR and 30,000 lbs of PWR spent resins are generated a year in the United States per commercial reactor.[4]

An independent study performed by the Electric Power Research Institute (EPRI) determined that a significant return on investment capabilities was possible by applying vitrification technology to the treatment of spent ion exchange resin. Another important determination was that implementation of the technology would give insurance to reactor operators that operations could continue even if regional compacts for low level waste disposal were delayed.[4]

Vitrification of organic ion exchange resins presents a challenge because of the high organic content and the volatile Cs^{137} that is usually present. High organics tend to induce reducing environments in melters, which can result in the reduction of metals in the waste that separate from the bulk glass matrix. Alloying of the reduced metals with the melter electrodes or corrosion of other melter components can also be a problem, which reduces the useful life of the treatment equipment. As for the glass products, the presence of organics can result in reduced glasses, which have been shown to have poorer durability compared to glasses of the same composition that are oxidized or less reduced.[5] Cs^{137} has been shown to be extremely volatile at high temperatures; thus, stabilization of this contaminant in the glass matrix presents a challenge which must be met if the waste is to be successfully stabilized.

At the Savannah River Technology Center (SRTC), vitrification has been shown to be a feasible treatment method for ion exchange resins.[6] The organic compounds which make-up the matrix of the resins can be destroyed either by pyrolysis or combustion at typical vitrification temperatures. Some of the heavier organic compounds are pyrolyzed within the melt. The majority of the combustion usually occurs above the melt in the plenum or in a secondary combustion chamber.

Vitrification studies with organic ion exchange resins have been performed at the SRTC with both a resorcinol based organic ion exchange resin and divinylbenzene/styrene copolymer resins.[1,2] The resorcinol resin was originally proposed for use in removing the Cs from High Level Waste (HLW) supernate, with the proposed disposal method being vitrification in the Defense Waste Processing Facility (DWPF) with the HLW sludge and glass frit. Resins for removing Cs from DOE HLW are being investigated by several DOE sites. If the use of resins is implemented, the DOE will need a disposal method for several thousand pounds of spent resin. The divinylbenzene/styrene copolymer resins are used by reactor facilities at the Savannah River Site (SRS) to purify fuel rod storage basin water. These resins do not have a defined disposal method.

Using direct vitrification methods, 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. The waste loadings were mainly limited by the redox ($Fe^{2+}/\sum Fe$) of the glass. Lab-scale melter studies performed at the SRTC[1] and at Clemson University[2] with the resorcinol resins verified the findings of the SRTC bench-scale studies. The data provided a strong indication that vitrification of the resorcinol resin in DWPF type feed was plausible, and that melter operating conditions were not greatly affected. As expected, glasses made with the resin were found to have slightly poorer durability because of the higher redox ratio of the glass. However, the durability was still magnitudes better than the Environmental Assessment (EA) glass durability results[7] when subjected to the Product Consistency Test (PCT)[8].

An important finding in the SRTC 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. Therefore, this information was used in studies with Argentine ion exchange materials to successfully stabilize high quantities of styrene resins in an iron-enriched borosilicate glass formulation.[3] Lab-scale melter studies with the styrene resins representative of the Argentine materials were performed in August 1997.

An alternative to direct vitrification of the resins involves the use of a relatively new oxidation process developed by SRTC for oxidizing organic wastes. This process uses 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 can then be stabilized in an iron-phosphate glass matrix or a magnesium-phosphate ceramic. Homogeneous, durable glasses were produced with both clean and spent styrene resins from the SRS Reactor basin. Waste loadings were maximized by using the nitric-phosphoric acid pre-treatment step in conjunction with iron-phosphate glass stabilization. Approximate volume reduction was 50%, with expectations of higher volume reductions when radiation field is not a concern. This process could be directly applied to the commercial nuclear industry resins because of the similarities in the matrices of the resins.

Commercial Nuclear Industry Ion Exchange Resins

Six resins were obtained that are considered representative of the ion exchange resins used by the commercial nuclear industry. These resins were received from the EPRI as part of a Cooperative Research and Development Agreement. The resins were identified as A-550, IRC-50, 21H, 900-OH, 200-H, and 650-C. The resins were characterized for chemical composition and thermal stability by Peeler and Jantzen.[4] All of the resins contained some fraction of Ca and Fe, with Ni, Zr, Cr, and Se being detected in approximately half of the resins.[4] These results will not be discussed in detail in this report. However, a brief description of the structure and properties of the resins follows.

A-550 Resin

The A-550 resin is a strongly basic polystyrene divinylbenzene anion gel. It is manufactured by Ionac. Typical properties of the resin are contained in Table 1.

Table 1 - A-550 Ion Exchange Resin Properties

Ionic Form	Cl
Active Group	Quaternary Amine Type II Alkyl
Matrix	Polystyrene
Structure	Gellular

Differential Thermal Analyses (DTA) and Thermal Gravimetric Analyses (TGA) of these resins indicated that NO and NO2 were the first products to decompose from this resin and continued to be major degradation products at elevated temperatures. This was attributed to the degradation of part of the quaternary ammonium groups. Cl, which is the ionic form of the resin, begins to come off between 200-300°C, with SO_x generated above 350°C. The presence of Cl was verified in digestion and subsequent chemical analyses of the resin, as was the release of the Cl at the temperatures listed above.[4]

IRC-50 Resin

The IRC-50 resin is a weakly acidic methacrylic cation exchange resin. It is manufactured by Rohm and Haas under their Amberlite resin trade name. This resin is normally used for dealkalization or demineral-ization. Its composition is approximately 47 - 53% divinylbenzene/ methacrylic acid copolymer and 47 - 53% water. The physical properties are shown in Table 2.

Table 2 - IRC-50 Ion Exchange Resin Properties

Ionic Form	H
Active Group	Carboxylic Acid
Matrix	Polystyrene
Structure	Beads
Minimum Capacity	4.2 eq/L
pH Range	5 - 7

DTA and TGA indicated that SO was the principal decomposition product starting at around 200�C and continued to decompose to about 400�C. Total decarboxylation of the resin followed by depolymerization was believed to occur after 500�C.4

21H Resin

The 21H resin is a strong two parts cation to one part anion mix with cellulose fiber. The manufacturer was not disclosed, but it is believed that it is similar to Graver Water ECODEX P-202-H, which is a H/OH ionic form of resin mixed with approximately 1/3 cellulose fiber. ECODEX P-202-H is composed of approximately 25 - 40% sulfonated copolymer of styrene and divinylbenzene in the hydrogen form, 25 - 55% trimethylamine functionalized chlormethylated copolymer of styrene and divinylbenze in the OH form, 10 - 50% cellulose fiber, and 50 - 65% water. The physical properties of the ECODEX resin are shown in Table 3.

Table 3 - ECODEX P-202-H Ion Exchange Resin Properties

Ionic Form	H/OH
Matrix	Polystyrene/Cellulose
Structure	Powdered

When subjected to DTA and TGA, the resin appeared to be thermally stable up to 200�C. Initial off-gassing did not occur until 228�C, with major products being carbon or nitrogen compounds and water. The 21H resin did not appear to be sulfonated or chlorinated, so it may be slightly different in chemical matrix than the ECODEX P-202-H. The presence of nitrogen compounds in the 21H resin was verified in digestion and chemical analyses of the resin.4

900-OH Resin

The 900-OH resin is a strong base styrene-divinylbenzene anion resin. It is manufactured by Rohm and Haas under their Ambersep resin trade name and is normally used for condensate applications. Its composition is approximately

35 - 55% quaternary amine divinyl-benzene/styrene copolymer of the OH form and 45 - 65% water. The physical properties are shown in Table 4.

Table 4 - 900-OH ION Exchange Resin Properties

Ionic Form	OH
Active Group	Quaternary Amine Type I Alkyl
Matrix	Polystyrene
Structure	Macroreticular
Minimum Capacity	0.90 eq/L
Decomposition Temp.	140&#65533;F

DTA and TGA indicated that initial off-gassing of the resin occurred at 175&#65533;C, but SOx was not generated until above 425&#65533;C. The decomposition and off-gassing of the SOx resulted in a major weight loss (~70%).4

200-H Resin

The 200-H resin is a strong acid sulfonated styrene/divinylbenzene cation resin. It is manufactured by Rohm and Haas under their Ambersep resin trade name and is normally used for condensate applications. The physical properties are given in Table 5.

Table 5 - 200-H Ion Exchange Resin Properties

Ionic Form	H
Active Group	Sulphonic Acid
Matrix	Polystyrene
Structure	Macroreticular
Minimum Capacity	1.7 eq/L
Decomposition Temp.	300&#65533;F

When subjected to DTA and TGA, the resin was thermally stable up to 200&#65533;C. SO was the primary offgas to first come off and continued to be generated up to 490&#65533;C. Almost full decomposition or total decarboxylation followed by depolymerization occurred by 525&#65533;C. The presence of sulfate was verified during digestion and subsequent chemical analyses of this resin.4

650-C Resin

The 650-C resin is a strong acid sulfonated styrene/divinylbenzene cation resin. It is manufactured by DOW chemical. Its composition is approximately 47 - 53% divinylbenzene/methacrylic acid copolymer and 47 - 53% water. The physical properties are shown in Table 6.

Table 6 - 650-C Ion Exchange Resin Properties

Ionic Form	H
Active Group	Sulphonic Acid
Matrix	Polystyrene
Structure	Macroreticular

When tested with DTA and TGA, Cl came off below 100°C, but no significant off-gassing occurred again until above 300°C. At higher temperatures, the offgas was dominated by sulfur, carbon, and nitrogen compounds, with most of the Cl gone by 475°C. The presence of sulfate and chloride, along with nitrate and nitrite, was verified by digestion and subsequent chemical analyses.4

Experimental

The amount of the resin material that will remain at typical vitrification temperatures is an important parameter to know so the proper amount of glass additives can be used. Some wastes that are vitrified will contribute a large portion of the glass structure components, whereas some wastes, like the resins, are thermally decomposed and only contribute a small portion. For wastes like the resins, a glass formulation can be determined that will only be slightly affected by the presence of the waste. When DTA and TGA were performed on the resins, measurements of the weight loss behavior with temperature were also made.4 This data was used to estimate material loss for the six resins when vitrified at typical glass melting temperatures.

Typically, vitrifiable wastes are dried around 100°C to determine the water loss or dried solids content, subsequent drying around 600°C and 1150°C are also performed to determine the loss of other species and the cation content. The solids remaining at 1150°C should remain in the glass structure when the waste is treated. Based on the DTA and TGA results, estimates of the loss at 100 and 600°C were made and are given in Table 7. The resins were also pre-weighed and dried overnight at 1150°C to determine the loss at 1150°C. This data is also given in Table 7. A N/A indicates that no appreciable weight loss occurred.

Table 7 - Loss on Heating

Resin	Estimate at 100°C	Estimate at 600°C	Measured at 1150°C
A-550	N/A	80%	99.99%
IRC-50	2-5%	100%	99.83%
21H	N/A	100%	99.98%
900-OH	N/A	99%	100%
200-H	N/A	95%	99.97%
650-C	36%	80%	100%

A large mass loss was not seen for most of the resins at 100°C. The IRC-50 and 650-C were the only two resins that showed an appreciable mass loss. Both of these are methacrylic resins, which may not be as stable as the other types of resins used in these studies. The estimated loss at 600°C for most of the resins was very high. In fact, four of the resins were almost completely gone, indicating that complete decomposition had occurred. According to Korkisch, this loss is attributed to desulfonation of the resins that begins at 100°C and continues as the temperatures increases. Korkisch also found that at temperatures greater than 150°C, a reaction between the

sulfuric acid formed and the oxidizable resin components begins.8 This reaction probably enhanced the further decomposition of these resins. For all of the resins, the structure was completely broken down and almost no remnants of the resins remained after the 1150°C heat treatment. Theoretically, this indicates that high waste loadings with these materials should be achievable in a glass matrix and that the resin components should not greatly affect the glass composition. Therefore, waste loadings would only be limited by processing constraints or from limits on the resin contaminants (e.g. Cs solubility or radiation field).

In order to determine the volume reduction potential from using vitrification treatment, the density of the resins was needed. The bulk density of each resin was measured and the values are reported in Table 8. All resins had bulk densities of less than one and were approximately the same.

Table 8 - Bulk Density of Resins

Resin Type	Density (g/mL)
A-550	0.6365
IRC-50	0.6235
21H	0.6410
900-OH	0.6305
200-H	0.7230
650-C	0.7790

Glass Studies

At the SRTC, the standard method for determining the feasibility of vitrification treatment for a particular waste stream is to perform bench-scale (crucible-scale) vitrification studies on surrogate wastes. These studies are used to determine optimum vitrification processing parameters (e.g. melt temperature and residence times) 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 commercial nuclear industry ion exchange resins were very similar to the ion exchange resins used in previous research with resin vitrification, attempts were made to vitrify these resins using the iron-enriched borosilicate glass compositions used to vitrify previous resins. These compositions were selected because the iron component provides an accurate indicator of the redox of the glass, and 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.

The glass composition selected was 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. In this study, 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. This glass easily melted at 1150°C, which is beneficial in trying to avoid volatilizing the Cs that is normally contained on the spent resins.

Previous testing with this base compositions and organic ion exchange resins had indicated that a resin loading of approximately 42 grams of resin/100 grams of glass produced was optimal for styrene resins. Therefore, this loading was used as the starting point. To calculate the necessary amount of glass additives needed for the 42 grams of resin, information from the DTA and TGA studies was used to estimate the amount of resin solids that would remain in the glass structure. The amount varied slightly from resin to resin.

The resins were mixed with the necessary glass additives, slowly heated (~10°C/min) to melt temperature (1150°C), melted for four hours, removed from the furnace, and then were allowed to cool to room temperature in the crucibles. In all tests, covered high purity alumina crucibles were used to melt the glasses. After cooling to room

temperature, the glasses produced were examined for completeness of reaction, visual homogeneity, and presence of metal sulfides.

Successive testing with the resins involved slowly increasing or decreasing the amount of resin until problems with processing, salt layer formation, visual homogeneity, or metal sulfide formation were not a concern.

The resin loadings tested and a description of the final products produced are given in Table 9. For the glass ID, only the number associated with each resin type was used, while the number following the hyphen represents the grams of resin added/100 grams of glass produced. The "R" in the glass ID indicates that the batch materials had to be reacted before melting to allow complete oxidation of the resin to occur. The waste loading for each glass is also given in Table 9.

Most of the resins produced black-brown or black homogeneous glasses. However, in a few instances, small pellets were found in the glass matrix that easily separated from the glass matrix and disintegrated when crushed. These pellets were examined using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDS). They were determined to be iron sulfide pellets, which have been shown to form when glasses become too reduced. Therefore, glasses which produced these pellets were not considered acceptable, and either the waste loading was lowered or the reaction time for the Fe(NO3)3 and the resin was increased. The strong cation sulfonated styrene resins seemed to have the most problems with metal sulfides forming and incorporating high waste loadings. No problems with salt formation on the glass surface were seen for any of the resins.

Table 9 - Resin Loadings Tested

Glass ID	Waste Loading	Description
550-42	29.6%	Dark brown glass
550-46	31.5%	Black glass
550-50	33.3%	Black-brown glass
550-54	35.1%	Black-brown glass
50-42	29.6%	Dark brown glass
50-46	31.5%	Black glass
50-50	33.3%	Black-brown glass
50-54	35.1%	Black-brown glass
21-42	29.6%	Dark brown glass
21-46	31.5%	Black glass
21-50	33.3%	Black-brown glass
21-54	35.1%	Black-brown glass
21-58	36.7%	Black-brown glass
21-62	38.3%	Black-brown glass
21-66	39.8%	Black glass
900-42	29.6%	Dark brown glass
900-46	31.5%	Black glass

900-50	33.3%	Black-brown glass
900-54	35.1%	Black-brown glass
900-58	36.7%	Black-brown glass with someshiny particles on the surface
900-62	38.3%	Black-brown glass, some unreactedmaterial on one side of crucible line
900-66	39.8%	Black-brown glass
900-70	41.2%	Black glass
900-74	42.5%	Rough black glass on surface, black glass underneath, metallic on sides
200-34	25.4%	Black glass
200-38	27.5%	Black glass
200-38-R	27.5%	Reacted ~16 hrs, black-brown glass
200-40	28.6%	Unreacted surface with black glass small underneath, pellet in glass
200-42	29.6%	Black glass under matted surface, small metal pellet in glass
650-32	24.2%	Unreacted at surface with orange and bluestreaks, black glass underneath
650-34	25.4%	Brown glass with orange streaks at surface,metals in glass
650-38	27.5%	Black glass, small metal pellet
650-38-R	27.5%	Reacted ~16 hrs, unreacted surface, black glass underneath
650-38-RR	27.5%	Reacted ~16 hrs and melted 6 hrs, black glass
650-42	29.6%	Dark brown glass with small metal pellet in glass

After visual examination, several of the resin glasses were analyzed to determine the glass redox ratio. This is the most important property for these glasses because of the high organic content of the wastes. Since it is likely that the resins would be treated in a joule-heated vitrification unit, acceptable redox ratio was considered to be between 0.10 and 0.33 for Fe2+/·Fe, which is consistent with the operational limits established for the DWPF melter10. If the redox ratio was found to be acceptable, the glass was further characterized for chemical composition, crystalline content, and durability.

The optimum compositions based on this characterization were then used to melt doped resin glasses. Dopants used were based on the radioactive contaminants typically found in the commercial nuclear industry. Analyses of spent commercial industry resins have shown that the principal radioactive isotopes of concern are Mn54, Co60, Cs134, and Cs137.11 The reported contaminant concentrations and the amounts actually used to dope the resins are shown in Table 10. Higher levels of dopants had to be used because of the small amounts of resins that were used in the tests. The actual amounts of the isotopes only equated to very small gram quantities of the elements, which would have been difficult to detect in the glasses when they were analyzed.

Table 10 - Radioactive Contaminant Concentrations (mCi/g)

Isotope	Actual Amount11	Dopant Amount
Mn54	5.4 x 10-4	5.4 x 104
Co60	5.8 x 10-4	5.8 x 108

Cs134	6.2 x 10-4	6.2 x 105
Cs137	7.9 x 10-4	7.9 x 102

Non-radioactive compounds were used as the dopants: CsNO3 for Cs134 and Cs137; Co(NO3)2*6H2O for Co60; and MnO for Mn64. These compounds were dissolved in 10 mL of water and mixed with an amount of resin equal to the optimum waste loading for each resin glass. For example, approximately 50 grams of the 21H resin glass was made from 31 g of resin mixed with 10 mL of water containing the radioactive contaminant simulants. The resins were then mixed with the glass additives and melted at 1150°C for 4 hours. Once again, the glasses were allowed to cool to room temperature and were then visually examined. The glasses were analyzed for Co, Cs, and Mn content so the radioactive retention could be determined. The retention numbers are important for determining the amount of radioactive isotopes that will volatilize and have to be captured by the offgas system.

The only information found on other contaminants indicated that iron and sodium may also be present on spent resins. However, since both of these are components of the glass matrix used in these studies, their presence should not affect the glass forming ability of this waste stream using this glass composition. Thus, no additional amounts of these materials were added to the resins to determine the incorporation ability.

Results

The Fe2+/·Fe ratio was determined by the SRTC Mobile Laboratory for several of the glasses using the colorimetric method. As mentioned earlier, 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 or interact with melter components, such as electrodes. Theoretically, the measured ratio should be higher for glasses with higher resin loading because of the higher organic content. The Fe2+/·Fe ratios determined for several of the resin glasses are given in Table 11. The base glass (without resin added) redox ratio was previously determined to be 0.054.

Table 11 - Measured Redox Ratios

Glass ID	Fe2+/·Fe Ratio	Glass ID	Fe2+/·Fe Ratio
550-42	0.054	900-42	0.055
550-50	0.259	900-54	0.039
550-54	0.715	900-66	0.074
50-42	0.047	900-70	0.124
50-50	0.119	200-34	0.502
50-54	0.540	200-38	0.532
21-42	0.040	200-38-R	0.269
21-54	0.033	650-42	0.673
21-62	0.054	650-38	0.519
21-66	0.398	650-38-RR	0.330

For the 21H and 900-OH 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, so very large quantities of the resins could be incorporated in the glass structure. The redox ratios of the 200-H and 650-C resin

glasses, on the other hand, were very dependent on the amount of resin present in the glass. A large affect on the redox ratio is shown, even at the low amounts, compared to the base glass redox ratio of 0.054. The glass redox ratio strongly affected the ability of the glass to incorporate the resin and make homogeneous glass. The benefits of longer resin and Fe(NO3)3 reaction times are seen with the redox ratios of the 200-H and 650-C resin glasses. Glasses with the same resin loadings and longer reaction times had substantially lower measured redox ratios. For the A-550 and IRC-50 resin glasses, the redox ratio gradually increased and became a limiting factor at the 54 gram loadings.

Based strictly on the redox ratio results, the optimum waste loadings for the resins would be 50 grams of resin/100 grams of glass for the A-550 and IRC-50 resins, 62 grams of resin/100 grams of glass for the 21H resin, 70 grams of resin/100 grams of glass for the 900-OH resin, and 38 grams of resin/100 grams of glass for the 200-H and 650-C resins.

The optimum waste loading glasses were analyzed for chemical composition by the Analytical Development Section of the SRTC. The analyses were performed after Na2O2-HCl dissolution and Microwave digestion using Inductively Coupled Plasma-Emission Spectroscopy (ICPES). The glass compositions should be fairly consistent because the resin solids contribute only a minor amount of material to the glass composition. Results are presented in Table 12 for the major glass oxides. The base glass iron-enriched borosilicate composition produced in earlier studies with Argentine ion exchange materials is also shown in the table so the effects of the resin addition could be better quantified.

Table 12 - Glass Chemical Compositions Results (Wt%)

Glass ID	Al2O3	B2O3	CaO	Fe2O3	Na2O	SiO2
Base	1.848	9.174	14.565	20.308	8.096	44.162
50-50	4.182	14.676	11.471	17.162	9.660	38.188
550-50	5.105	14.459	11.268	15.772	10.707	36.823
21-62	3.078	15.734	11.863	17.734	10.302	39.865
900-70	4.856	15.508	11.081	17.541	9.953	39.683
200-38-R	6.289	13.971	9.904	16.928	8.931	38.018
650-38-RR	8.305	14.558	9.931	15.936	9.668	37.315

The resin glasses were very similar in composition, but were slightly different from the base glass composition. All of the glasses contained some amount of Al2O3 contamination from the Al2O3 crucibles used in melting. Higher Al2O3 contamination seemed to be present in the glasses that were reacted longer before melting. Melts with the iron-enriched borosilicate composition and resin in platinum crucibles have verified that the Al2O3 was not important for glass formation. However, melter materials of construction will have to be selected with the realization that some Al2O3 may be removed and incorporated into the glass matrix. Higher Al2O3 contamination was also seen for the resin containing glasses, which contributes to the slight difference in composition from the base glass, since higher concentrations of one species would dilute the other major species in the glass. It also appears that the resin glasses were slightly higher in B2O3 and Na2O than the base glass composition, which may indicate that the borax additive amount may have been higher than necessary, since borax contributes both of these oxides to the melt. This is possible because waters of hydration are associated with the borax and the base glass was melted at a different time than these glasses were so different forms of borax may have been used. For the batch calculations, ten waters of hydration were assumed, so if a different form of borax was used, then higher amounts of B2O3 and Na2O in the glass would be possible. Overall, the type of resin did not seem to greatly impact the glass composition.

All glasses appeared to be visually homogeneous upon cooling. In order to ensure that no crystalline phases were present, X-Ray Diffraction (XRD) analyses were performed on the optimum waste loading glasses. All glasses were found to be amorphous.

To determine the final product durability, the PCT, ASTM C1285-948, was performed on the optimum waste loading glasses. 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.7 Glass samples were run in triplicate for the PCT and the results were averaged and normalized. The normalized PCT results are given in Table 13. The measured leachate pH is also listed, since this provides a secondary indication of durability. The PCT for the base glass composition is given for comparison. 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 glass6. The accepted values are given in Table 13.

Table 13 - Normalized PCT Results (g/L)

Glass ID	B	Si	Na	pH
Base	0.16	0.07	0.27	9.66
550-50	0.22	0.07	0.50	10.16
50-50	0.19	0.07	0.41	10.05
21-62	0.17	0.07	0.31	9.87
900-70	0.19	0.06	0.48	10.11
200-38-R	0.25	0.07	0.99	10.59
650-38-RR	0.23	0.08	0.90	10.64
EA7	16.695	3.922	13.346	11.85

The PCT results were fairly consistent between the different glasses, with the glasses requiring longer reaction times having slightly higher PCT releases. Most of the glasses had similar releases to the base glass composition for B and Si, with Na releases that were slightly higher. These results indicate that the presence of the resin had little affect on the glass durability performance. The pH results also indicate that the glasses had similar durabilities, with the longer reaction time glasses once again having the slightly poorer durabilities. No apparent trend was observed between the amount of resin in the glass and the PCT release; however a slight increase in B and Na release was seen for the glasses with the higher redox ratios. All glasses had excellent 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.

Based on all of the analytical results, the glasses that were selected as having the optimal waste loading were homogeneous and very durable glasses. The iron enriched borosilicate glass formulation seemed well suited for incorporating these wastes when ferric nitrate is used as the source of iron in the glass formulation. Therefore, these loadings and the given glass formulation should produce acceptable waste forms when used in a melter demonstration.

In order to determine the potential volume reduction of using vitrification treatment on these resins, volume reduction calculations were performed for each resin type given the optimum waste loadings. To do this, the bulk densities given in Table 8 and a measured glass density of 2.854 g/mL were used. The calculated volume reductions are shown in Table 14. The waste loadings represent the grams of resin per grams of glass.

Table 14 - Calculated Volume Reductions

Resin	Waste Loading	Volume Reduction
A-550	50 g/100 g	55.9%
IRC-50	50 g/100 g	55.9%
21-H	62 g/100 g	63.5%
900-OH	70 g/100 g	68.3%
200-H	38 g/100 g	34.0%
650-C	38 g/100 g	28.0%

The EPRI did not provide any information on the water associated with these resins when they are in use or storage. When the resins are disposed of, they usually have an associated volume of water that also has to be disposed. Volume reductions for resins that have associated water will be higher because of this extra water that is evaporated during the vitrification process. Past studies with resins used in similar applications have shown as much as two times the volume of water being associated with a given volume of resin when it is ready for disposal. In many cases, the resins also have a large volume of water that is adsorbed in the resin matrix. This water would increase the volume reductions in Table 14. The magnitude of the increase could be two times if water volumes found in the past for other resins were the same as those used with these resins.

In order to determine how effective the process would be in immobilizing the radioactive contaminants, doped resins were vitrified. The dopant amounts were listed above in Table 10, with the dopants representing levels six to twelve orders of magnitude higher than what has actually been found in industrial resins. All glasses appeared to be visually homogeneous with no apparent effect on melt behavior or glass formation. The calculated radioactive element retentions are shown in Table 15.

Table 15 - Calculated Retentions for Glasses

Glass ID	Cs	Mn	Co
550-50	73.1%	89.1%	83.3%
50-50	73.5%	81.1%	76.9%
21-62	76.9%	83.5%	81.1%
900-70	100%	84.8%	84.2%
200-38	70.3%	83.3%	86.4%
650-38	72.2%	87.1%	79.0%

Calculated retentions were fairly consistent from glass to glass with the exception of the Cs retention for glass 900-70, which was made from the 900-OH resin. The calculated retentions were lower than anticipated, but were consistent with other vitrification processes. One possible explanation for the low retention values may be the uncertainty about the amount of glass produced. In order to calculate the radioactive material retained in the glass, the total amount of glass produced is used in conjunction with the weight percent of the element found in the glass. During these experiments, the actual weight of glass produced was not measured, but was calculated based on the oxide content of the feed. If the oxide estimate is biased low, then the calculated retentions would also be biased low. Another factor which may have decreased the calculated retentions was the fact that the radioactive surrogates were not processed through a resin column as would be done in practice. Surrogate compounds were dissolved in

water and then mixed with the resin, so it is highly likely that the materials were not adsorbed as well as they would be in a resin column and the amount of radioactive material absorbed on the resin was actually lower than targeted. During the studies, it appeared that most of the Mn did not absorb on the resin. With the radioactive materials strongly bonded to the resin, the potential for higher retentions exists.

Even though most of the calculated retentions were less than 90%, vitrification is still a viable treatment option when an offgas system is utilized that can capture these materials. Given that the dopant amounts were orders of magnitudes higher than what has actually been found in industry resins, the amount of material that would be released to the offgas system is very small.

Conclusions

Based on the studies performed with the six resins representative of commercial industry resins, 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. When using this formulation, ferric nitrate should be used as the source of Fe_2O_3 to help with the organic destruction.

For the resins, different optimum waste loadings were determined. The optimum waste loading was strongly dependent on the type of resin being vitrified. The waste loadings ranged from 38 to 70 grams of resin/100 grams of glass produced. The associated volume reductions were 28.0-68.3%. These waste loadings and associated volume reductions are higher than what has been seen in previous studies with resin treatment when the iron-enriched borosilicate glass formulation was not used, but are similar to volume reductions seen when this formulation was used. In fact, some of the resin loadings were even higher than what was previously seen. The resins that were the most difficult to vitrify were the strong cation sulfonated styrene resins.

Calculated radioactive material retention varied from 70.3-100% for Cs, 81.1-89.1% for Mn, and 76.9-86.4% for Co. Although some of the radioactive surrogates were not retained in the glass matrix, the vitrification process seems to still be a viable treatment option when coupled with an offgas system capable of capturing radioactive species.

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