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Evaluation and Comparison of SuperLig® 644, Resorcinol-Formaldehyde and CS-100 Ion Exchange Materials for the Removal of Cesium from Simulated Alkaline Supernate

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Summary

Pacific Northwest Laboratory (PNL), in conjunction with 3M and IBC Advanced Technologies, conducted this study for the Efficient Separations and Processing Integrated Program (ESPIP) under the Develop and Test Sorbents task. The purpose of the study is to assess and compare the performance of several ion exchange materials for the removal of cesium from a simulated alkaline Hanford tank waste supernatant liquid.

Pretreatment of nuclear process wastes for the removal of cesium and other radionuclides by adsorbents has been previously proposed as one method of minimizing the amount of high-level radioactive waste (HLW) at Hanford. In this study, PNL evaluated three polymeric materials (SuperLig® 644, R-F, and CS-100) for Cs removal efficiency from a simulated Hanford Neutralized Current Acid Waste (NCAW) supernatant liquid using 200 mL ion exchange columns. The overall objectives of ESPIP are 1) to identify, assess, and compare new technologies capable of separating cesium, strontium, technetium, and other radionuclides from alkaline supernate, 2) to obtain radionuclide batch distribution data for several adsorbent materials in a wide variety of solution compositions, and 3) to obtain ion exchange loading and elution data for newly developed materials, processes, and/or designs, and provide a direct comparison of these results to baseline technologies.

The removal of cesium from simulated NCAW supernatant liquids can be achieved, with varying degrees of success, with either SuperLig® 644, R-F, or CS-100 organic adsorbents. Cesium can be recovered from the exchangers and concentrated into a smaller volume by elution with dilute nitric acid. The following specific conclusions and recommendations resulted from the study:

- The cesium loading (mmole Cs per gram of resin) for each material in the NCAW simulant (Na/Cs = 1.0E+04) was calculated to be 0.20, 0.18, and 0.039 for SuperLig® 644, R-F, and CS-100, respectively.

- The cesium loading (mmole Cs per milliliter of resin) for each material in the NCAW simulant was calculated to be 0.045, 0.070, and 0.011 for SuperLig® 644, R-F, and CS-100, respectively. The total volume (cv = 200 mL) of NCAW simulant required to achieve 0.5 C/C_0 was 93.6, 139, and 22.5 for SuperLig® 644, R-F, and CS-100, respectively.

- Elution of each resin material with 0.5 M HNO_3 required 3.5, 7.0, and 3.2 cv to reach 0.1 C/C_0 for SuperLig® 644, R-F, and CS-100, respectively. This resulted in a volume compression of 27, 20, and 6.9.

- The peak cesium concentration achieved during the elution process was 185, 38.5, and 27.8 C/C_0 for SuperLig® 644, R-F, and CS-100, respectively. These values correspond to a molar cesium concentration of 93, 19, and 14 mmole/L Cs.

- The cesium mass balances based on analysis of the column loading and elution effluent composite solution values were calculated to be 105%, 90%, and 98% for SuperLig® 644, R-F, and CS-100, respectively.

- Before pretreatment, the NCAW simulant feed exhibited a Na/Cs mole ratio of 10,000 and a K/Cs ratio of 240. The elution effluent composite from the fully loaded ion exchange column exhibited a Na/Cs mole ratio of 10.5, 20.6, and 78.1; and a K/Cs ratio of <0.046, 0.136, and 0.160 for SuperLig® 644, R-F, and CS-100, respectively.

Analysis of these single-cycle loading and elution experiments demonstrates that the SuperLig® 644 polymer exhibits the highest cesium loading per gram of adsorbent material in NCAW and the greatest volume compression on acid elution with 0.5 M HNO_3. Because of the relatively high density and poor elution, R-F exhibits the highest cesium loading per unit volume of adsorbent material and a lower volume compression. CS-100, the baseline material for cesium removal at Hanford, was found to be inferior to either SuperLig® 644 or R-F in terms of Cs loading and selectivity over sodium.

Acknowledgments

Pacific Northwest Laboratory (PNL) is collaborating with universities, national laboratories, and industry to develop and test new materials for the pretreatment of nuclear wastes stored at Hanford. The experimental work described in this report would not have been possible without the encouragement and resources provided by Dr. Teresa Fryberger, manager of the U.S. Department of Energy's Efficient Separations and Processing Integrated Program. In addition, the authors would like to acknowledge the contributions to this effort of J. DesChane and P. Tanaka at PNL, Richland, Washington; D. Anderson, D. Boggs, K. Carlson, T. Fredrickson and D. Seeley at 3M, St. Paul, Minnesota; and B. Tarbet and G. Maas at IBC Advanced Technologies, Provo, Utah.

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1.0 Introduction

The contents of Hanford's 177 underground storage tanks (UST) include a mixture of sludge, salt cake, and alkaline supernatant liquid. The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains the bulk of the ^{90}Sr and many of the long-lived or transuranic (TRU) radionuclides. The salt cake, generated by extensive evaporation of aqueous solution, consists primarily of dried sodium salts. The supernatant liquid consists of concentrated aqueous solutions of sodium nitrate/nitrite salts with smaller quantities of hydroxide, aluminum, potassium, carbonate, sulfate, and phosphate. The bulk of the water soluble radionuclides such as ^{137}Cs are contained in the salt cake and supernatant solution fractions.

Although the pretreatment and disposal requirements are still being defined, one of the first steps in most pretreatment scenarios will be a solids/liquid separation of the pumpable waste liquor, followed by ion exchange removal of cesium from the resulting supernatant liquid. Next, a salt cake dissolution and sludge wash step will be initiated followed by another solids/liquid separation. Most of the cesium is expected to be in the aqueous liquids from these processes, and it is these solutions that are the focus of the cesium ion exchange removal process. This process is being designed with the goal of removing enough cesium so that the resulting low-level waste (LLW) will meet the U.S. Nuclear Regulatory Commission's (NRC) 10 CFR 61 Class A limits for ^{137}Cs (1 Ci/m^3).

The technology for Cs decontamination of high-level alkaline wastes and sludge wash waters is being developed at the Westinghouse Hanford Company (WHC),[(a),(b),(c)] Richland, Washington (Bray 1989; Bray et al. 1990; Bray et al. 1993; Kurath et al. 1994); the Westinghouse Savannah River Company (WSRC), Aiken, South Carolina (Bibler et al. 1989; Bray et al. 1990); and at the West Valley Nuclear Services Company, Inc. (WVNS) in West Valley, New York (Bray et al. 1984; Kurath et al. 1989; Bray and Hara 1991). With this technology as a starting point, experimental studies are being conducted by Pacific Northwest Laboratory (PNL)[(d)] to evaluate the performance of newly emerging technologies for the removal of cesium, strontium, and technetium from simulated and actual alkaline wastes at Hanford. Ultimately, each process must be evaluated in terms of removal efficiency, process chemical consumption and recycle, chemical and radiation stability of materials, compatibility with other process streams, secondary waste generation, process and maintenance costs, and final material disposal.

(a) Bray, L.A. , K.J. Carson, R.J. Elovich, and D.E. Kurath. 1992. *Equilibrium Data for Cesium Ion Exchange of Hanford CC and NCAW Tank Waste*. TWRSPP-92-020, Pacific Northwest Laboratory, Richland, Washington.

(b) Bray, L.A., C.D. Carlson, K.J. Carson, J.R. DesChane, R.J. Elovich and D.E. Kurath. 1993a. *Initial Evaluation of Two Organic Resins and their Ion Exchange Column Performance for the Recovery of Cesium from Hanford Alkaline Wastes*. TWRSPP-93-055, Pacific Northwest Laboratory, Richland, Washington.

(c) Bray, L.A. 1989. *Studies of Technology for the In-Tank Removal of Cesium/Strontium from Double Shell Tank Feeds*. Milestone letter report for the Westinghouse Hanford Company.

(d) PNL is operated by Battelle Memorial Institute for the U.S. Department of Energy.

2.0 Objectives

The overall objective of the Efficient Separations and Processing Integrated Program's (ESPIP) Develop and Test Sorbents task is 1) to develop and evaluate newly conceived novel materials for the recovery of cesium, strontium, and technetium from alkaline wastes, 2) to determine the loading and elution efficiency of these processes, 3) to determine the physical life cycle (including radiation and chemical stability) of these materials, and 4) to determine if basic ion exchange data can be applied to a broad range of tank wastes. The goal is to provide the technology to produce a LLW effluent with radioactivity suitable for treatment in the LLW glass vitrification facility. The goal of this subtask is to determine the cesium loading and elution efficiency for the newly synthesized SuperLig® 644 (IBC Advanced Technologies, Provo, UT) sequestering agent in simulated Hanford alkaline waste supernate and compare these results to those obtained for other commercially available materials under similar conditions.

3.0 Scope

The work described in this report involves the direct comparison of three cesium adsorbent materials (SuperLig® 644, R-F, and CS-100) based on the results obtained from bench-scale (200 mL) column loading and elution experiments. The materials were loaded with a simulated NCAW supernatant liquid and eluted with 0.5 M HNO_3. The column testing was completed in the New Products Department of the 3M Company in St. Paul, Minnesota. Each material's loading and elution efficiency was determined by periodic sampling of the column effluent followed by alkali metal analysis with inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS).

4.0 Experimental Approach

Previous experimental work completed during Fiscal Year 1994 for cesium recovery included the small-scale determination of Cs batch distribution coefficients (Cs K_d) for the SuperLig® 625 and 644 materials in various simulated alkaline waste compositions and limited chemical and radiation stability tests. In addition, these and other related SuperLig® formulations have been immobilized within polytetrafluoroethylene-based Empore™ and other membranes (3M, St. Paul, Mn) and tested for loading and elution characteristics in flowing systems. In this report, three materials (SuperLig® 644, R-F, and CS-100) were loaded with cesium from a simulated NCAW solution in separate 200-mL ion exchange columns and eluted with dilute (0.5 M) nitric acid. Because of the cost and limited availability of actual radioactive waste, simulated solutions have been used for the current batch and column testing. Contingent upon receipt of actual waste supernate from one or more of the Hanford tanks, these materials will also be tested on actual radioactive supernatant liquid.

4.1 Ion Exchange Material Selection

The SuperLig® 644 polymer resin is the latest version of the covalently bound SuperLig® 625 macrocycle ligand from IBC Advanced Technologies and has been shown to be highly selective for cesium even in the presence of excess sodium or potassium. CS-100 and resorcinol-formalydehyde (R-F) are two organic ion exchange resins that are currently available and under consideration for cesium removal from Hanford tank wastes. CS-100 is a granular (20 to 50 mesh) phenol-formaldehyde condensate polymer ion exchange resin which is commercially available from Rohm & Haas and is considered to be the baseline material for Cs removal at Hanford (Eager et al. 1994).[a] R-F is produced by Boulder Scientific and has been shown to exhibit a much greater selectivity and loading for Cs over sodium or potassium than the CS-100 resin (Kurath et al. 1994). These two ion exchange materials were directly compared to the newly developed SuperLig® 644 material in side-by-side experimentation. Crystalline silicotitanate (CST), another potential cesium adsorbent material, is not currently available in an engineered form and could not be evaluated during this experiment.

4.2 Simulant Solution Selection

The Hanford NCAW simulant described in Table 4.1 was chosen for these experiments because much of the previous column loading tests were completed in a similar manner with this same composition (Bray et al. 1993; Kurath et al. 1994). With the data collected during this experiment, a direct comparison of the new SuperLig® 644 sequestering agent (IBC Advanced Technologies, Provo, Utah) can be made to other commercial ion exchange materials (CS-100 and R-F). Future testing of this material immobilized in Empore™ and other membranes (3M, St. Paul, Minnesota) will provide a

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(a) Gallagher, S.A. 1986. *Report of Current NCAW Ion Exchange Laboratory Data*. Internal Letter #65453-86-088, Rockwell International, Richland, Washington.

Table 4.1. NCAW Simulant Composition

Species	NCAW, M
Na	5.00
K	0.12
Rb	5.00E-05
Cs	5.00E-04
Al	0.43
SO_4	0.15
OH (Total)	3.40
OH (Free)	1.68
CO_3	0.23
NO_2	0.43
NO_3	1.67
F	0.089
PO_4	0.025
Na/Cs Ratio:	1.00E+04
K/Cs Ratio:	2.40E+02

direct comparison of the two individual technologies (membranes and columns). If the initial results from these tests warrant, other simulants with varied solution composition (e.g., with a higher potassium concentration) may be formulated. In addition, if actual waste supernatant solutions become available for testing with these materials and processes, new compositions will be prepared in order to more accurately model those solutions.

4.3 Batch Distribution

The batch distribution coefficient (K_d) is a measure of the overall ability of a solid phase adsorbent material to remove an ion from solution under the particular equilibrium experimental conditions. The batch K_d is not necessarily the affinity of a material for a particular ion but can be used as an indicator of the selectivity, loading, and affinity of a particular ion for an adsorbent material in the presence of a complex matrix of interfering ions. The addition of a small quantity of these materials into a small volume of supernatant solution is an extremely rapid and cost-effective method for comparing a wide variety of adsorbents. With some difficulty and the proper sampling procedure, this method can provide information about exchange kinetics but is normally only useful for measuring equilibrium ion exchange under the particular conditions of the test. Accurate comparison of K_d results requires identical experimental conditions at equilibrium (mass:volume ratio, solution composition, material pretreatment, temperature, duration, etc.) because all of these factors are known to affect K_d.

In most batch K_d tests, a known quantity of adsorbent material is placed in contact with a known volume of solution (e.g., NCAW) containing the particular ions of interest. The material is allowed to contact the solution for a known time at a constant temperature, after which the solid material and liquid supernate are separated. The concentration of the species of interest is determined in the solution and in the solid phase. For most batch contacts approximately 0.1 to 0.5 g of ion exchange material is contacted with 10 to 20 mL of supernatant liquid. For the K_d experiments described in this report, 0.1 g of each material in 15 mL of NCAW was shaken gently for 16 hours in standard 20-mL scintillation vials. In practice, it is easier to measure the concentration of the particular ion of interest in solution instead of in the solid. Therefore, the equation for calculating K_d (mL/g) can be simplified by measuring the concentration of the analyte before and after contact and calculating the quantity of analyte on the adsorbent by difference (Equation 1).

$$K_d = \frac{(C_0 - C_1)}{C_1} * \frac{V}{M * F} \tag{1}$$

C_0 is the initial concentration of the ion of interest in the feed solution before contact, C_1 is the concentration after contact, V is the solution volume, M is the exchanger mass, and F is the mass of dry (85° C for 24 hours) exchanger divided by the mass of "as received" or wet exchanger (F-factor). K_d represents the theoretical volume of solution that can be processed per mass of exchanger under equilibrium conditions. Lambda, the theoretical number of bed volumes of solution that can be processed, is obtained by multiplying K_d by the exchanger bed density, ρ_b (g/mL) as shown in Equation 2.

$$\lambda = K_d * \rho_b \tag{2}$$

The batch K_d experimental equipment included an analytical balance, a constant temperature water bath, an oven for F-factor determinations, a variable speed shaker table, 20-mL scintillation vials, 0.2 μm syringe filters, the appropriate adsorbent material, and simulant solutions.

4.4 Column Loading and Elution

As was discussed in the previous section, the batch K_d is a rapid and cost-effective method of determining a material's ion exchange efficiency under certain equilibrium conditions. However, many materials do not possess large enough K_d's to be used in a batch processing mode, and therefore the behavior of the material in a flowing system must be assessed. In this case, column loading and elution provides information concerning the extent of analyte breakthrough as a function of flow rate, feed composition, temperature, column dimension, and adsorbent material.

The ion exchange column system used in this experiment consists primarily of three ion exchange columns, feed storage bottles, pumps, and effluent weighing bottles. The glass columns each have a maximum capacity of 200 mL of ion exchange material and are 2.54 cm in diameter and 41.9 cm tall (including head space for solution above the resin bed). They are equipped with water jackets, which are connected to a constant temperature water bath. The column equipment was used as a single independent column for each adsorbent material to be tested. The solution to be processed was individually pumped downflow through the separate columns from a single feed reservoir. Each column's effluent was sampled periodically through valves located at the column exits. The effluent from each column was routed to separate weighing/collection bottles where a balance was used to determine the effluent weight. The volume of solution processed in column volumes (cv = 200 mL) was determined by dividing the effluent weight by the specific gravity of the feed.

Initially, the empty 200 mL column assembly was volume calibrated and prefilled with 2 M NaOH. Each material was slowly (ca. 1 hour) weighed by difference into the column in the form that it was received from the manufacturer with no additional processing. The solution flow rate was set at 9 cv/hr (1800 mL/hr), and the pumps were calibrated by flowing 2 M NaOH through the entire system including the ion exchange material. Before initiating cesium loading, the solution flow was interrupted, the solution dead volume above the ion exchange material was minimized, and the column feed solution was changed from 2 M NaOH to NCAW. Zero volume during loading was defined as the point at which the NCAW solution reached the ion exchange material at the column inlet. After loading, the column was flushed with 3 cv of 2 M NaOH followed by 6 cv of water each at 9 cv/hr. The pumps were recalibrated to 1 cv/hr (200 mL/hr) during the water flush; the solution flow was again stopped and elution was accomplished with 0.5 M HNO_3. Zero volume during elution was defined as the point at which the 0.5 M HNO_3 solution reached the ion exchange material at the column inlet.

For the SuperLig® 644 material, additional pretreatment steps were required before initiation of the previously described cesium loading procedure. In this case, the material was pre-weighed and pre-swollen in a beaker of 2 M NaOH for approximately 2 hours. The resin was pre-swollen in a specially prepared Rb- and Cs-deficient NCAW simulant for an additional 2 hours before being slurry loaded into the column assembly. Once filled, the column was backflushed upflow with the Rb- and Cs-deficient NCAW at approximately 1 cv/hr (200 mL/hr) before initiation of downflow cesium loading. All other loading and elution procedures were as described for the R-F and CS-100 resins.

Analytical samples (1 to 5 mL) were collected at each column's exit every hour (1800 mL) during loading and every 1/2 hour (100 mL) during elution. Accurate analytical measurement below 1 ppm in a high ionic strength matrix was required in order to accurately determine material distribution coefficients and the extent of column loading and elution. Radioanalytical techniques are preferred, but ICP-MS and ICP-AES was used in this experiment and provided sufficient detection limits to achieve the objectives of the test.

The test equipment required for the column loading and elution experiment included standard laboratory glassware, an analytical balance, a high-capacity balance, a constant temperature water bath, an oven for F-factor determinations, ion exchange columns, pumps, feed and effluent storage containers, and associated tubing, valves, connections, etc.

5.0 Results and Discussion

A new class of sequestering agents (SuperLig®) has been recently developed by IBC Advanced Technologies that can selectively remove various radionuclides (cesium, strontium, etc.) from high ionic-strength alkaline solutions based on molecular recognition technology. Preliminary tests have demonstrated that one of these materials (SuperLig® 644) is capable of removing cesium from simulated Hanford tank waste even in the presence of excess sodium and potassium. To more accurately assess the potential use of this technology for the pretreatment of nuclear process wastes, SuperLig® 644 was tested under identical conditions in a side-by-side experiment with two current baseline materials (R-F and CS-100). The materials were tested for cesium removal efficiency by equilibrium batch contact and bench-scale (200 mL) column ion exchange loading and elution.

5.1 Batch Distribution

The results of the batch distribution contact for SuperLig® 644, R-F, and CS-100 are displayed in Table 5.1. Based on the Cs K_d values alone, the SuperLig® 644 appears to be the superior cesium adsorbent material by about a factor of two (1340 average vs. 620) and thirteen (1340 vs. 99) over the R-F and CS-100 resins, respectively. It is important to note, however, that Cs K_d results have been

Table 5.1. Cesium and Rubidium Batch Distribution Results for Three Ion Exchange Materials

Experimental Parameter	SuperLig® 644	R-F	CS-100
Initial Cs Concentration (M)	5.0E-04	5.0E-04	5.0E-04
Initial Na Concentration (M)	5.0E+00	5.0E+00	5.0E+00
Initial Na/Cs Ratio	1.0E+04	1.0E+04	1.0E+04
First Duplicate Cs K_d (mL/g)	1176	633	99
Second Duplicate Cs K_d (mL/g)	1509	614	99
First Duplicate Cs λ	264	231	28
Second Duplicate Cs λ	339	224	28
First Final Cs Concentration (M)	4.3E-05	1.1E-04	3.4E-04
Second Final Cs Concentration (M)	5.4E-05	1.1E-04	3.4E-04
First Equilibrium Na/Cs Ratio	9.2E+04	4.7E+04	1.5E+04
Second Equilibrium Na/Cs Ratio	1.2E+05	4.7E+04	1.5E+04
First Duplicate Rb K_d (mL/g)	10	4	0
Second Duplicate Rb K_d (mL/g)	14	12	6

shown to vary with solution composition and equilibrium Na/Cs ratio (Kurath et al. 1994). Since each material has a different affinity for cesium under the current conditions and is able to remove differing amounts of cesium, the final equilibrium Cs concentration will be different for each material. Since the NCAW solution contains excess sodium (5 M Na) when compared to the total exchange capacity (3 mmole/g), the equilibrium Na concentration after batch contact is equal to the initial concentration. Consequently, those materials which have a greater affinity for cesium will raise the equilibrium Na/Cs ratio. Accurate comparison of a material's loading during batch contact (i.e., K_d) must occur at the same equilibrium Na/Cs ratio in order to be valid. Kurath and co-workers (1994) reported the cesium lambda values for BSC-187 (an earlier batch of the resorcinol-formalydehyde resin) as a function of equilibrium Na/Cs ratio (page A-9). From those data a Cs K_d of 1190 mL/g at 1.0E+05 Na/Cs can be calculated ($K_d = \lambda/\rho = 550 * 200$ mL/92.2 g) for R-F which is only slightly smaller than the 1340 mL/g reported in Table 5.1 for SuperLig® 644. These data demonstrate that in NCAW the equilibrium Cs loading of SuperLig® 644 per unit mass is slightly greater than that of R-F at the same Na/Cs ratio.

Because SuperLig® 644 is able to decrease the Cs equilibrium concentration (increase the Na/Cs ratio) more than R-F or CS-100 during batch contact suggests that this material is more highly selective for cesium and has a larger equilibrium binding constant with the exchange site(s) or ligand (L) as shown in Equations 3 and 4.

$$Cs^{+}_{(aq)} + L^{-}_{(s)} \rightleftarrows Cs^{+}\text{-}L^{-}_{(s)} \tag{3}$$

$$K = \frac{[Cs^{+}\text{-}L^{-}]_{(s)}}{[Cs^{+}]_{(aq)} * [L^{-}]_{(s)}} \tag{4}$$

These data also suggest that the SuperLig® 644 performance will exceed that of R-F for higher Na/Cs ratio wastes for most batch contact processes and when compared on a mass basis. Unfortunately, these data provide no information concerning cesium loading at other equilibrium Na/Cs ratios (i.e., that of the NCAW feed) or the kinetics of cesium removal. The rubidium K_d results displayed in Table 5.1 are inconclusive due to analytical error and data scatter. The Rb solution concentration decreased less than 10% (3.9 mg/L to 3.6 mg/L) during batch contact and is not thought to be significant.

5.2 Column Loading

The column ion exchange results for resin cesium loading from a simulated NCAW alkaline supernate are displayed in Figure 5.1 for three polymeric materials. In Figure 5.1 and all subsequent calculations, one column volume (cv) is equal to 210 mL, 210 mL, and 220 mL for the SuperLig® 644, R-F, and CS-100 resin materials, respectively. This loading curve clearly shows the inferiority of CS-100 as compared to SuperLig® 644 or R-F. Cesium breakthrough in the column effluent

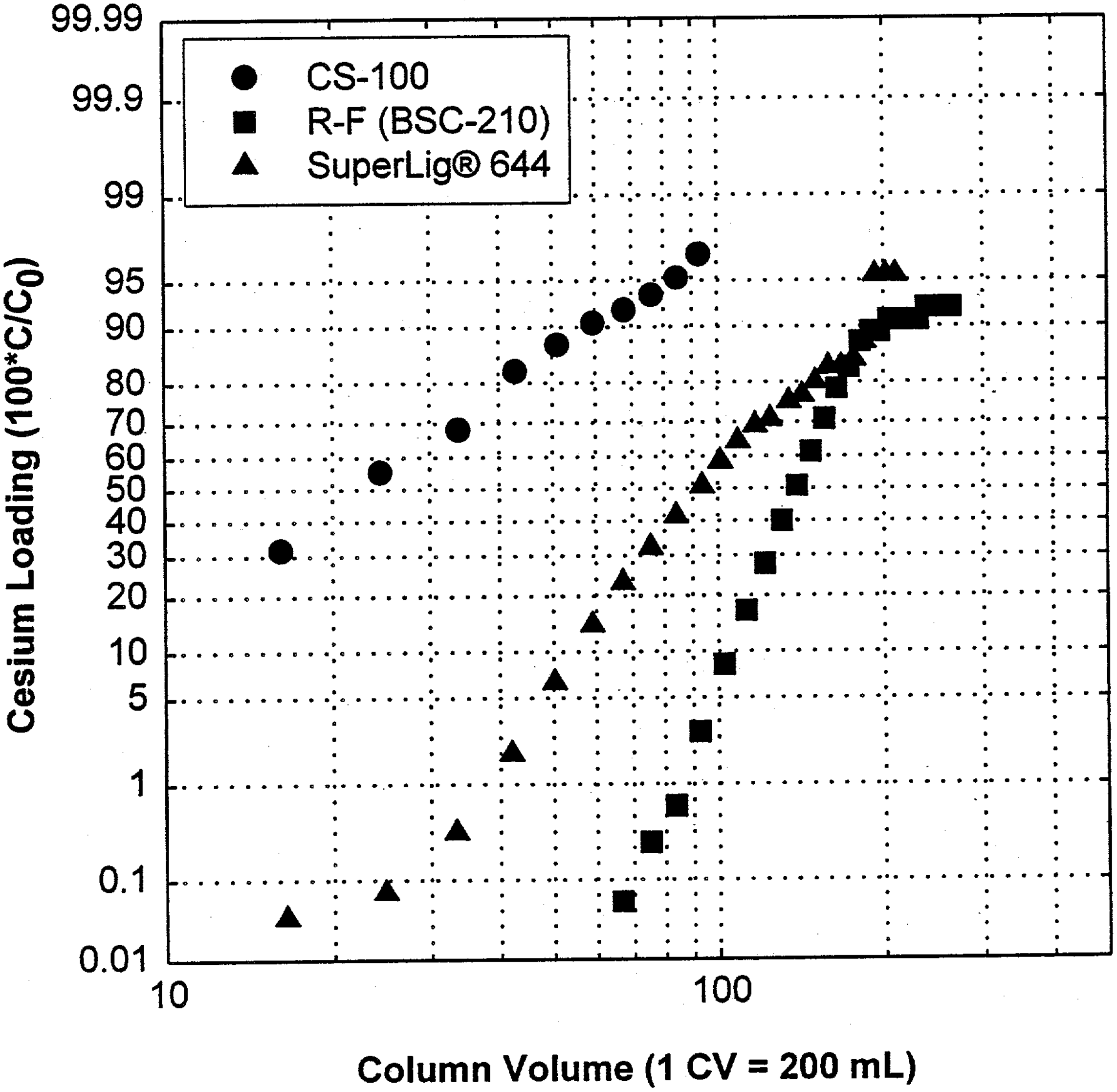

Figure 5.1. Comparison of SuperLig® 644, R-F, and CS-100 Resins During Cesium Ion Exchange Column Loading with NCAW at 9 cv/hr (cv = 200 mL) and 25°C

(5.7E-02 C/C_0) was observed for the first sample (8.2 cv or 1800 mL), and only 22.5 cv (4940 mL) was required to achieve 0.5 C/C_0. A Cs resin loading of 1.36 mg/mL (0.011 mmole/mL) or 4.74 mg/g (0.039 mmole/g) can be calculated assuming complete loading at the volume required to reach 0.5 C/C_0. The R-F resin demonstrated a much higher Cs loading of 9.4 mg/mL (0.070 mmole/mL) or 25.6 mg/g (0.18 mmole/g), which was calculated from the 139 cv (29,600 mL) required to reach 0.5 C/C_0. Cesium was not detected (<0.02 mg/L) in the column effluent until 66.6 cv (14,200 mL) had been processed. The slope of the loading curve illustrates the effect of resin particle size on the diffusion rate in the particle and the overall kinetics of the exchange process. The smaller R-F particles (45 to 70 mesh) reach equilibrium more quickly than the larger CS-100 or SuperLig® 644 particles (20 to 50 mesh), which results in a steeper slope and delayed initial breakthrough.

The loading curve for the SuperLig® 644 material demonstrates intermediate performance between the R-F and CS-100 resins. Detectable cesium breakthrough was observed at 25 cv (4960 mL), and 0.5 C/C_0 was reached at 93.6 cv (18,700 mL). From these data the calculated Cs loading is 5.9 mg/mL (0.045 mmole/mL) and 26.5 mg/g (0.20 mmole/g) based on resin volume and mass, respectively. The apparent low loading (as displayed in Figure 5.1) is due to the lower density of SuperLig® 644 (0.22 g/mL) as compared to R-F (0.37 g/mL). On a dry mass basis, only 47.12 g of SuperLig® 644 (compared to 76.78 g of R-F) would fit into the same 210 mL column volume.

The decreased slope (i.e., slower exchange kinetics) of the SuperLig® 644 loading curve in Figure 5.1 is partially due to the larger particle size (20 to 50 mesh) as compared to R-F (45 to 70 mesh). This result has been previously reported for two different sizes (BSC-210 and BSC-187) of the R-F resin (Kurath et al. 1994, p. 5.52). It is likely that batches of SuperLig® 644 specifically prepared to the smaller particle size will exhibit enhanced kinetic exchange and a steeper slope of the loading curve. However, it should be noted that the overall material capacity may increase or decrease due to changes in the surface area/volume ratio or the exchange site density and is not necessarily related to particle size.

5.3 Resin Density Considerations

Of primary concern is an accurate comparison and reporting of resin performance without bias. Difficulties arise when comparing various adsorbent materials because of differences in resin density, particle size, solution composition, flow rate, temperature, etc. Since the amount of cesium removed from solution must be attached to a specific "site" on the ion exchange resin, the overall material capacity is related to the mass of exchanger and the number of sites per unit mass. For example, the mass of SuperLig® 644 and R-F used in this 200-mL column test was 47.12 g and 91.20 g (47.12 g and 76.78 g on a dry weight basis), respectively. The cesium loading on the SuperLig® 644 is nearly 40% less than the R-F loading, based on column density alone. If a dry weight equivalent mass (76.78 g) of SuperLig® 644 had been loaded into the same 200 mL column, the loading (volume to reach 0.5 C/C_0) would have increased to 150 cv. IBC Advanced Technologies is currently investigating methods to increase the material density and reduce swelling in alkaline solution. At this time it is unknown if the different pretreatment method for SuperLig® 644 had an adverse effect on the resin column packing density.

The resin particle size is also an important parameter and has been shown to affect the kinetics of exchange and hence the slope of loading profile. Most commercial ion exchange resins are prepared between 20 and 45 mesh in order to minimize pressure drop across the column. Smaller particles (R-F) will yield a steeper loading breakthrough curve due to enhanced exchange kinetics at the expense of an increased back pressure.

5.4 Column Elution

The previously loaded cesium ion exchange materials (Section 5.2) were eluted with 0.5 M HNO_3 at 1 cv/hr (200 mL/hr), and the results are displayed in Figures 5.2 through 5.8. The column effluent was analyzed for Na, K, Cs, and Rb. Zero volume is defined as the point at which the 0.5 M HNO_3 initially contacts ion exchange material at the column inlet. Each resin required approximately 1.2 cv of nitric acid to neutralize and displace the column void volume. Beginning at this point, the eluate cesium concentration increased by 2 to 3 orders of magnitude and then decayed exponentially to below the detection limit (0.02 mg/L). The peak Cs concentration (mmole/L) was 90 (185 C/C_0), 19 (38.5 C/C_0), and 13 (27.8 C/C_0) for SuperLig® 644, R-F, and CS-100, respectively. These peaks occurred at volumes of 1.7, 4.6, and 2.1 cv and correspond to Cs concentrations (g/L) of 12, 2.5, and 1.8 for SuperLig® 644, R-F, and CS-100, respectively. Assuming 30% of the total cesium in a typical Hanford HLW is ^{137}Cs, these concentrations correspond to 320, 67, and 38 Ci/L ^{137}Cs.

Nearly complete elution was achieved by the time the column effluent reached 0.1 C/C_0 (5.0E-05 mole/L Cs) after passage of 3.5, 7.0, and 3.2 cv of 0.5 M HNO_3 for SuperLig® 644, R-F, and CS-100, respectively. Elution to this point resulted in a volume compression of 27, 20, and 6.9. The entire elution effluent volume (18.3 cv, 17.6 cv, and 8.6 cv for SuperLig® 644, R-F, and CS-100, respectively) was composite and analyzed for total Na, K, Rb, and Cs. The resulting Na/Cs ratio was 10.5, 20.6, and 78.2 and the K/Cs ratio was <0.046, 0.14, and 0.16 for SuperLig® 644, R-F, and CS-100, respectively. Based on these results, if sodium concentration is the limiting factor which defines the amount of HLW glass produced, then a process which uses the SuperLig® 644 material will reduce the HLW volume by nearly 10^3 when compared to the original untreated NCAW. By the same token volume reductions of 485 and 128 can be calculated for R-F and CS-100, respectively.

Based on composite analysis of the column loading and elution effluent, the cesium mass balance was calculated to be 105%, 90%, and 98% for SuperLig® 644, R-F, and CS-100, respectively. Analytical error is likely responsible for most of the apparent inaccuracy. However, an earlier batch of the R-F resin was previously shown to elute with some difficulty (Kurath et al. 1994), and this may explain the low elution efficiency. It is clear from Figures 5.2 and 5.3 that the R-F resin exhibits extensive tailing when compared to either SuperLig® 644 or CS-100. The reason for this tailing is likely due to the fact that the Cs K_d for R-F is greater than one even in 0.5 M HNO_3. Using Molecular Recognition Technology, SuperLig® 644's cesium affinity has been specifically designed to be extremely pH sensitive. As a consequence, this material has virtually no Cs affinity at neutral or acidic pH and can be eluted more easily than R-F. A summary of the important material properties and column loading and elution results are displayed in Table 5.2.

Figures 5.4 through 5.6 display the Na, K, Cs, and Rb concentration (mmole/L) in the column effluent as a function of volume passed through the column for the SuperLig® 644, R-F, and CS-100 exchangers, respectively. All data below the detection limit were excluded. The data indicate that all of the adsorbent materials, even the highly-selective SuperLig® 644, have an affinity for all the alkali metals tested. Note the much higher K concentration for R-F (20 mmole/L) as compared to either SuperLig® 644 or CS-100 (1 mmole/L). Direct comparison of the figures demonstrates the relatively

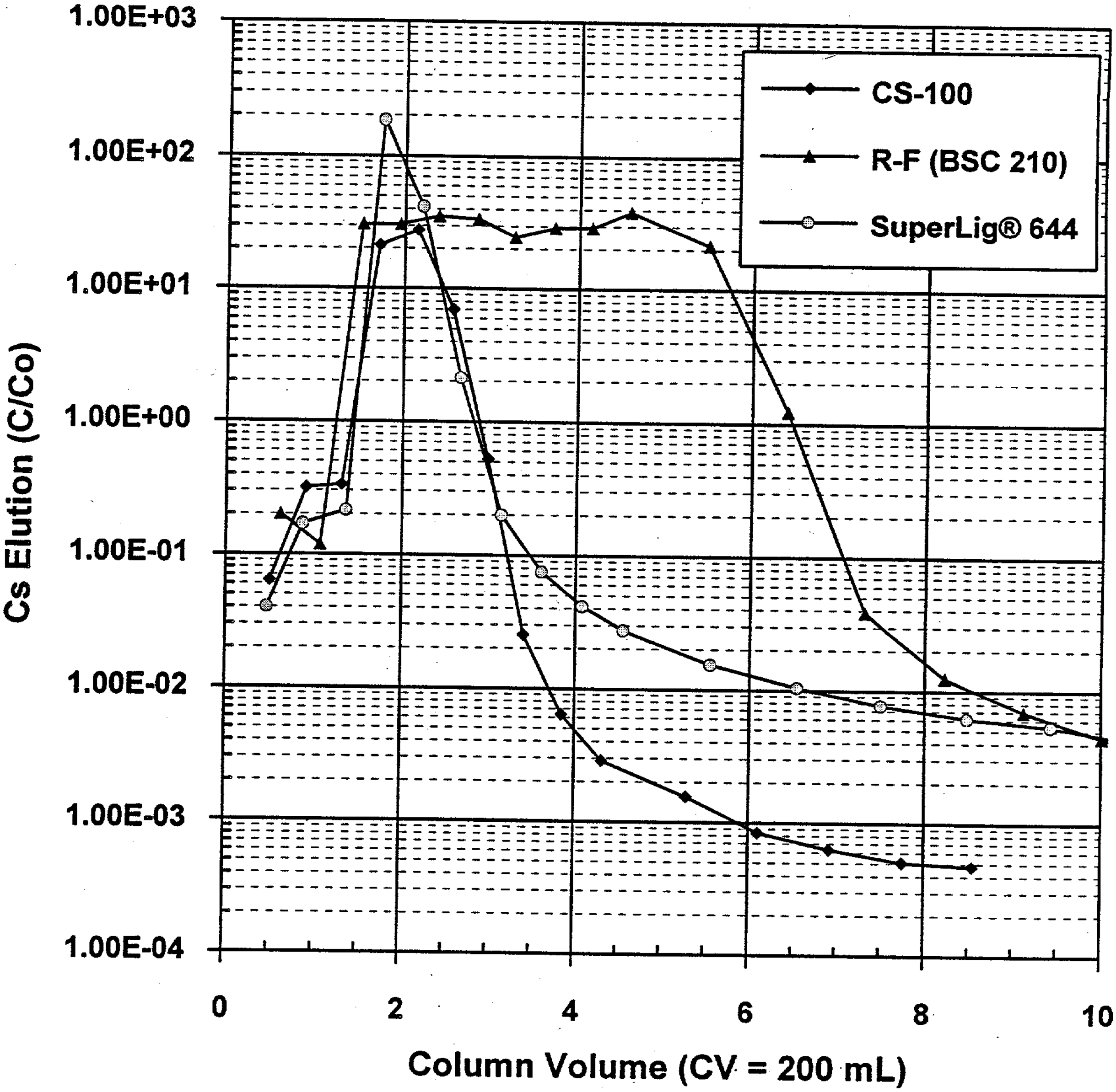

Figure 5.2. Comparison of SuperLig® 644, R-F, and CS-100 Resins During Cesium Ion Exchange Column Elution with 0.5 M HNO_3 at 1 cv/hr (cv = 200 mL) and 25°C

poor elution characteristics and K selectivity of R-F as compared to SuperLig® 644 and CS-100, the poor Na selectivity and Cs loading of the CS-100, and the high Cs selectivity and loading of SuperLig® 644. The double peak in the Na concentration for the SuperLig® 644 and CS-100 resins indicates that additional separation of Na from Cs may be possible with a selective elution technique. The first Na peak occurs before the first column volume (void volume) of 0.5 M HNO_3 had passed through the system.

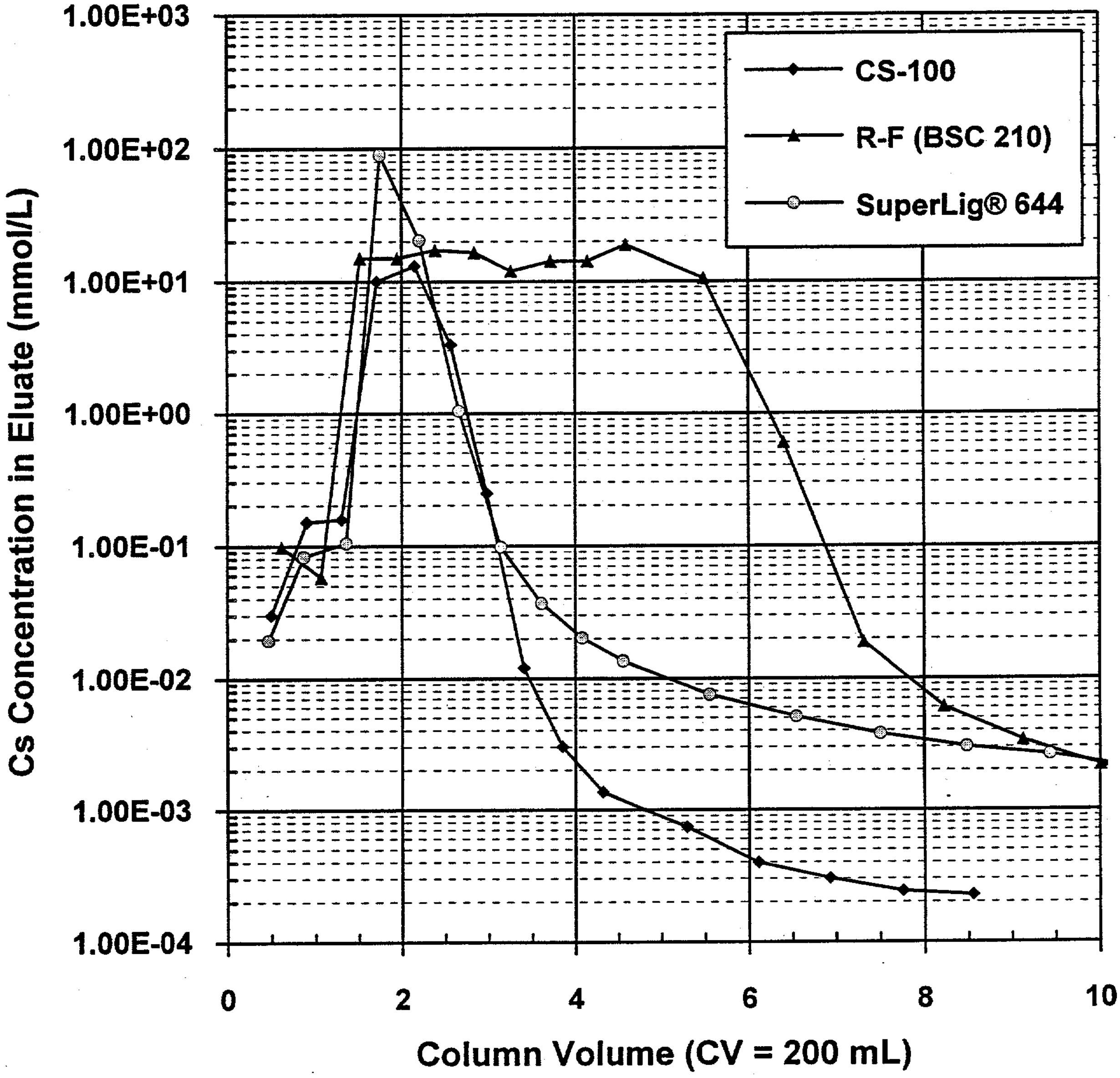

Figure 5.3. Comparison of SuperLig® 644, R-F, and CS-100 Resins During Cesium Ion Exchange Column Elution with 0.5 M HNO_3 at 1 cv/hr (cv = 200 mL) and 25°C

Figures 5.7 and 5.8 display the Na/Cs and K/Cs ratio of the effluent as a function of total volume (cv) passed through the column, respectively. The Na/Cs and K/Cs ratios of the initial feed before Cs removal were 1.0E+04 and 2.4E+02, respectively. For CS-100 and SuperLig® 644 the minimum Na/Cs ratio approaches unity during the peak cesium elution much earlier than for the R-F resin. In the case of K/Cs ratio, a similar trend is observed; however, the SuperLig® 644 demonstrates a much smaller ratio than CS-100. R-F appears to have less selectivity for Cs over K and exhibits broader

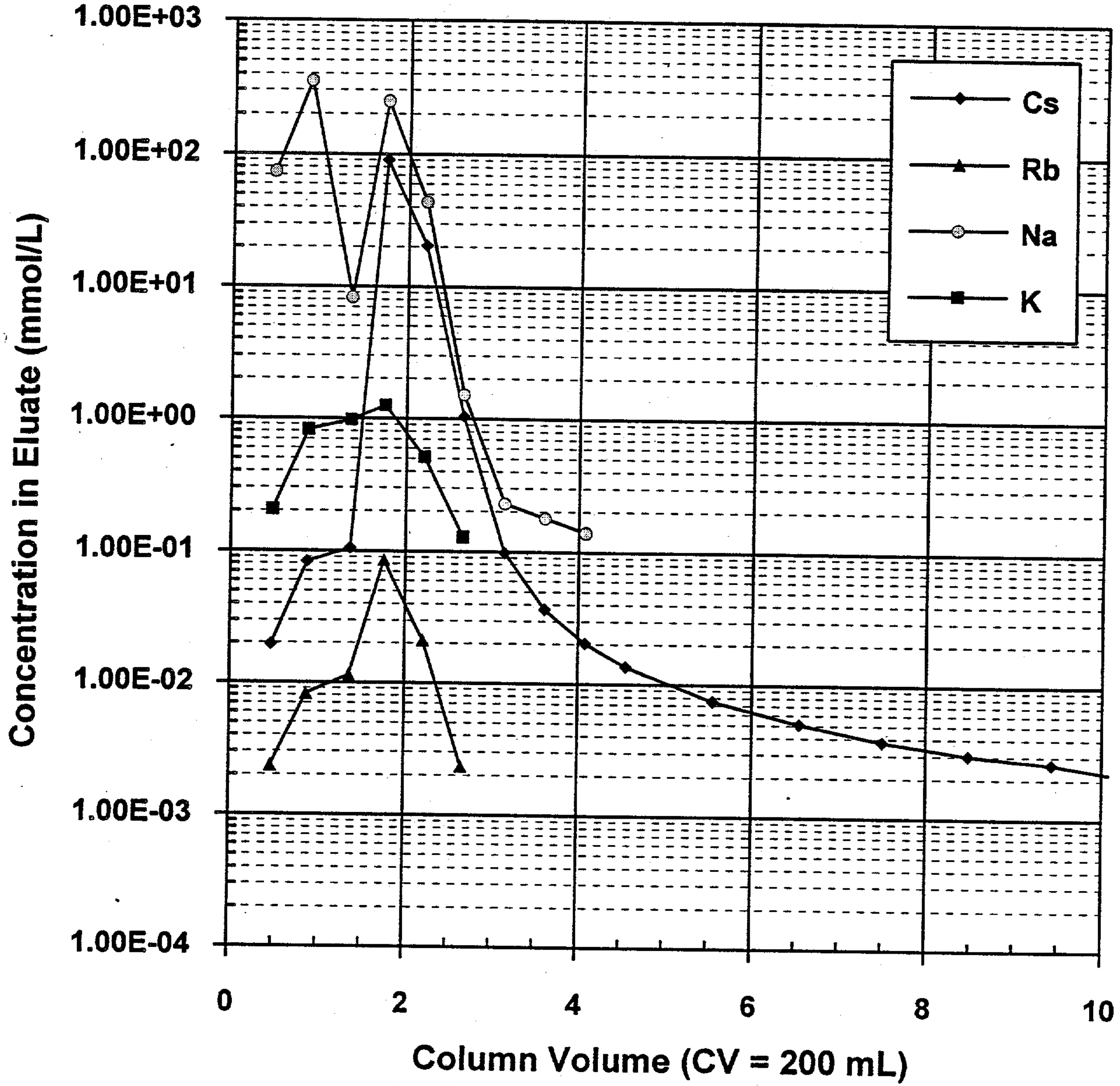

Figure 5.4. Alkali Metal Ion Concentration Profiles During Elution of SuperLig® 644 with 0.5 M HNO_3 at 1 cv/hr (cv = 200 mL) and 25°C

elution than either SuperLig® 644 or CS-100. The Na/Cs ratio of the column effluent composited over the entire elution volume was 10.5, 20.6, and 78.2 for SuperLig® 644 (18 cv), R-F (18 cv), and CS-100 (9 cv), respectively. The K/Cs ratio was calculated to be <0.046, 0.14, and 0.16, respectively.

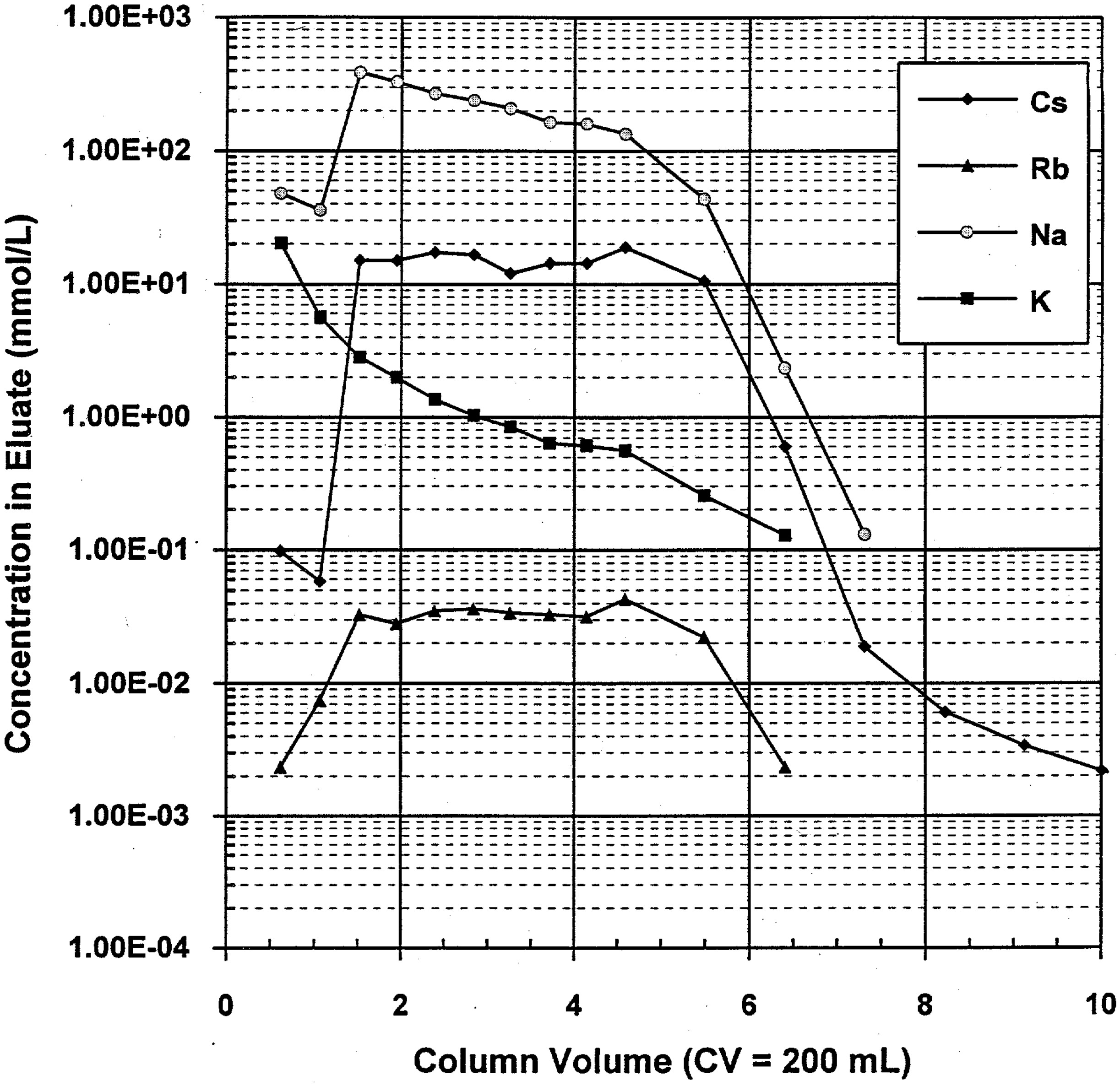

Figure 5.5. Alkali Metal Ion Concentration Profiles During Elution of R-F with 0.5 $\underline{M}$ HNO_3 at 1 cv/hr (cv = 200 mL) and 25°C

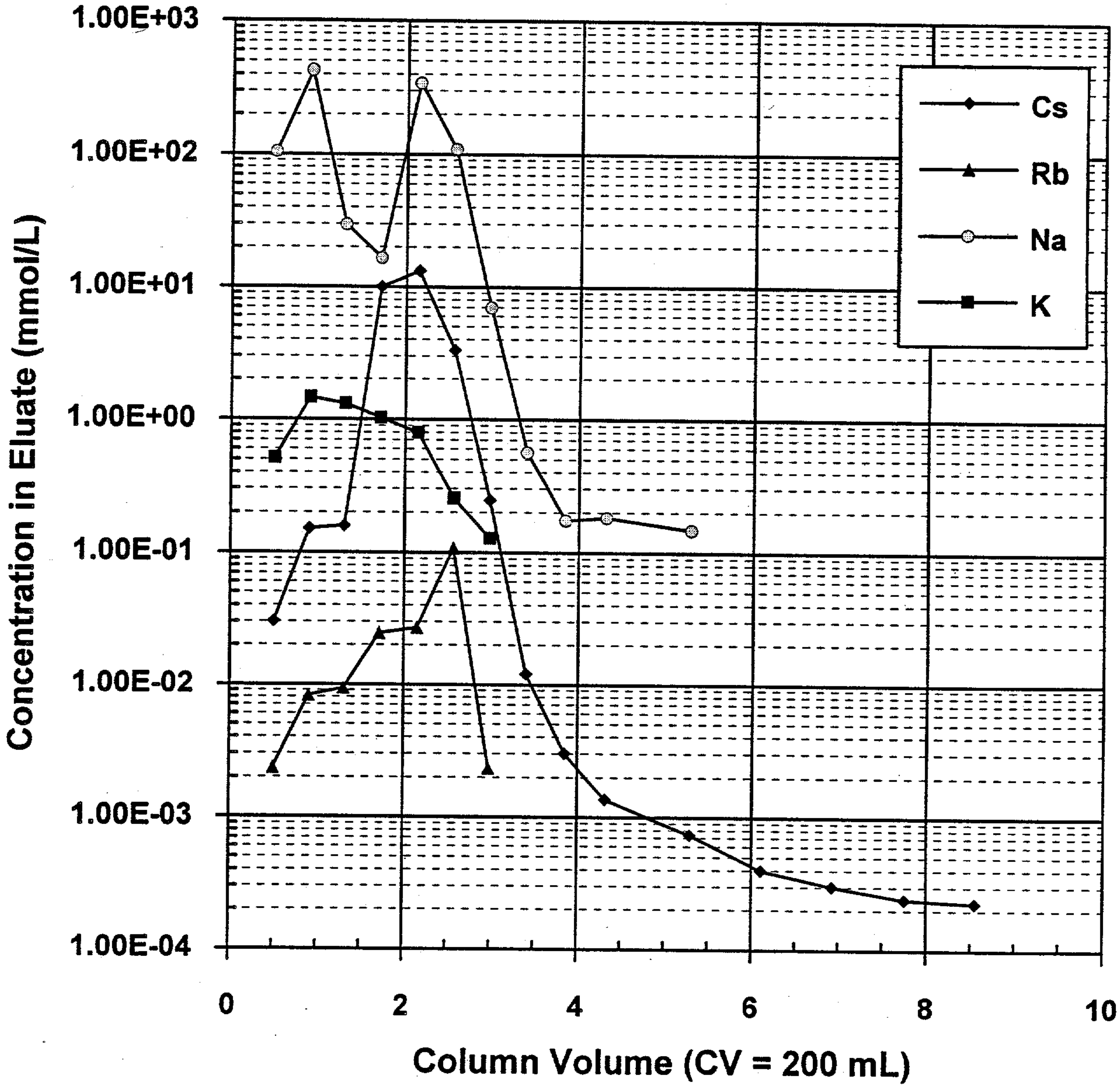

Figure 5.6. Alkali Metal Ion Concentration Profiles During Elution of CS-100 with 0.5 M HNO_3 at 1 cv/hr (cv = 200 mL) and 25°C

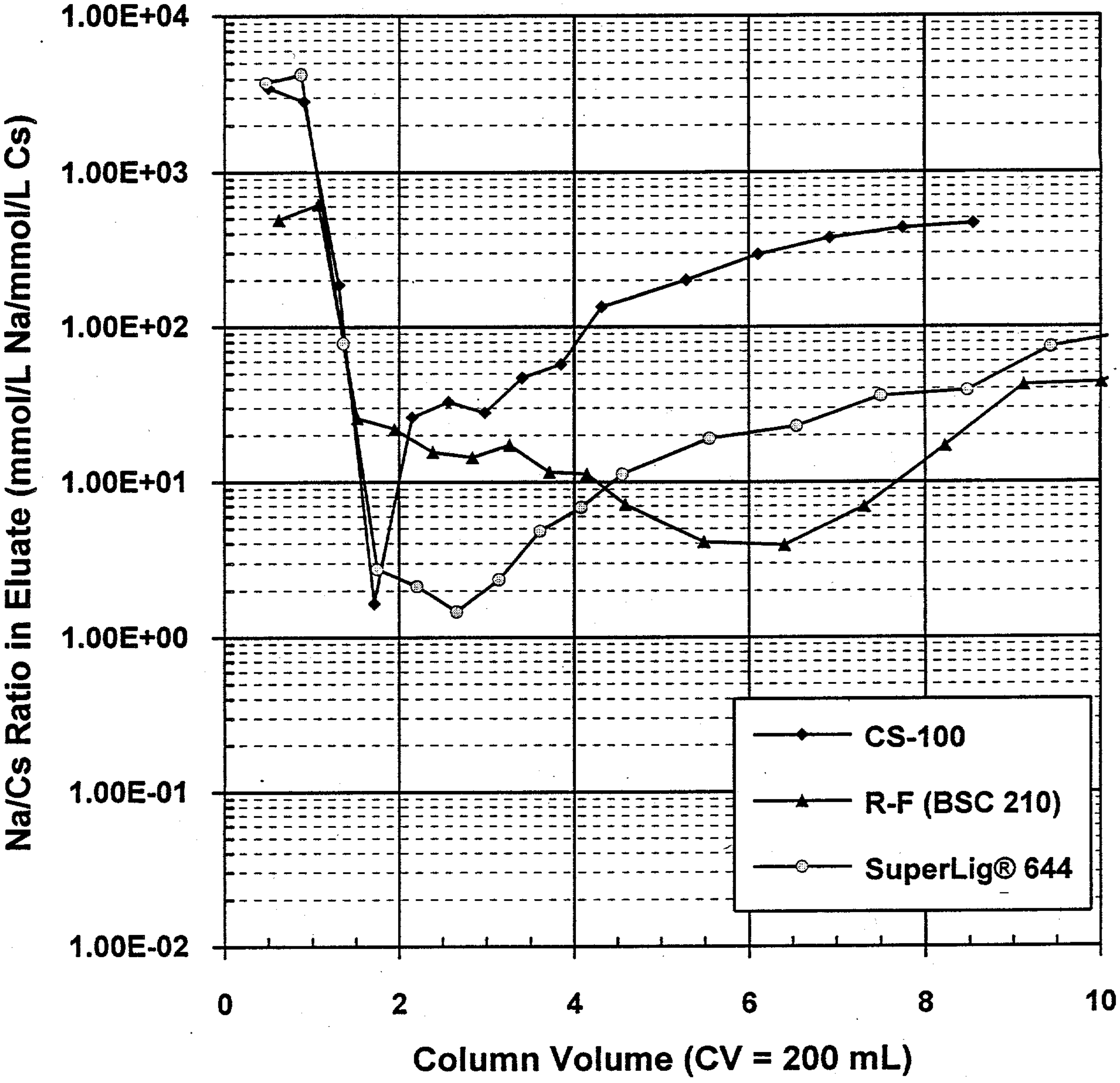

Figure 5.7. Comparison of Na/Cs Mole Ratio Concentration Profiles for SuperLig® 644, R-F, and CS-100 Resins During Ion Exchange Column Elution with 0.5 M HNO_3 at 1 cv/hr (cv = 200 mL) and 25°C

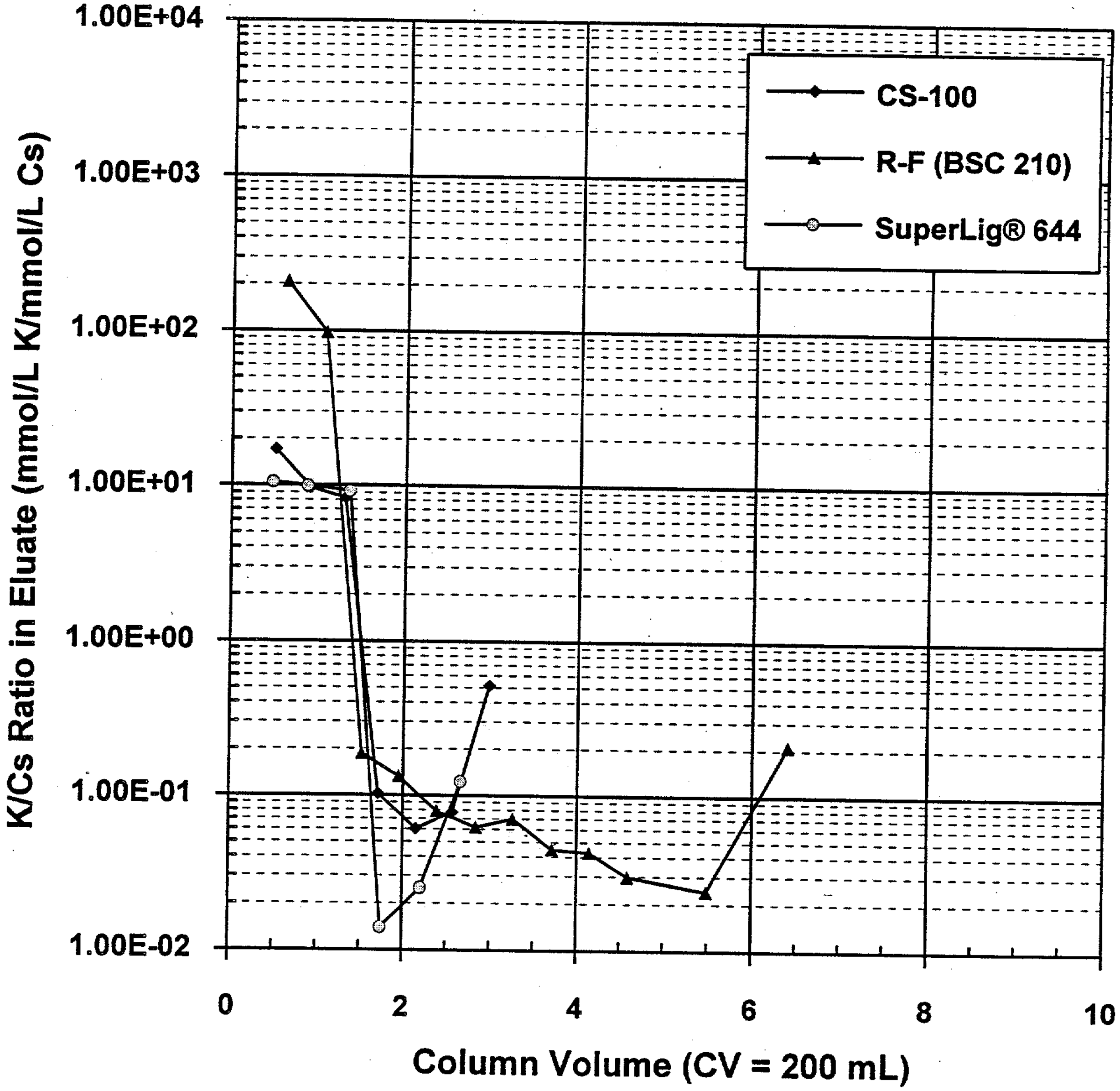

Figure 5.8. Comparison of K/Cs Mole Ratio Concentration Profiles for SuperLig® 644, R-F, and CS-100 Resins During Ion Exchange Column Elution with 0.5 M HNO_3 at 1 cv/hr (cv = 200 mL) and 25°C

Table 5.2. Summary of Ion Exchange Material Properties and Results

Material Properties and Results	CS-100	R-F	SuperLig® 644
Resin F-Factor (Mass Dry/Mass Wet)	0.6353	0.8419	1.000
Resin Mass in Column "As Received" (g)	98.31 g	91.20 g	47.12 g
Resin Mass in Column "Dry Basis" (g)	62.46 g	76.78 g	47.12 g
Initial Column Volume (mL)	220 mL	210 mL	210 mL
Resin Particle Size (mesh)	20-45 mesh	45-70 mesh	20-45 mesh
Average Resin Particle Size (mesh)	35 mesh	60 mesh	35 mesh
Resin Density in NCAW "Dry Basis" (g/mL)	0.28 g/mL	0.37 g/mL	0.22 g/mL
Cs Loading (mmole Cs/g dry resin)	0.039	0.18	0.20
Cs Loading (mmole Cs/mL resin)	0.011	0.070	0.045
Loading Volume (cv) to 0.5 C/C_0 (λ)	22.5	139	93.6
Elution Volume to 0.1 C/C_0 (cv)	3.2	7.0	3.5
Peak Cs Concentration (C/C_0)	27.8	38.5	185
Volume Compression at 0.1 C/C_0	6.9	20	27
Cs Mass Balance	98%	90%	105%
Na/Cs in Elution Composite	78.2	20.6	10.5
K/Cs in Elution Composite	0.16	0.14	<0.046

6.0 Conclusions and Recommendations

The pretreatment of simulated NCAW supernate by removal and concentration of cesium into a smaller volume of nitric acid was demonstrated for three organic ion exchange materials (SuperLig® 644, R-F, and CS-100) in side-by-side 200-mL bench-scale column experiments. The results indicate for the first time the use of the newly synthesized SuperLig® 644 sequestering agent for removal and preconcentration of cesium from alkaline wastes at Hanford. This new material exhibits a higher Cs loading per unit resin mass (0.20, 0.18, 0.025 mmole/g) and requires less volume (3.2, 7.0, 3.5 cv) of 0.5 M HNO_3 during elution to reach 0.1 C/C_0 which results in a higher volume compression (27, 20, 6.9) than either R-F or CS-100, respectively. Additional testing of the SuperLig® 644 distribution coefficient as a function of solution composition, capacity/selectivity during multiple load/elute cycles and radiation and chemical stability is required in order to accurately access this new material's applicability to pretreatment of nuclear process wastes at Hanford.

7.0 References

Bibler, J.P., R.M. Wallace, and L.A. Bray. 1989. "Testing A New Cesium-Specific Ion Exchange Resin For Decontamination of Alkaline-High Activity Waste." In *Proceedings of the Symposium on Waste Management '90*, February 25 - March 1, 1990. Tucson, Arizona.

Bray, L.A. 1989. *Determination of Batch Sorption Ratios for Ion Exchange Materials Using Radionuclide Tracer Techniques*. WTC-006-21-1, PNL Test Procedure, Pacific Northwest Laboratory, Richland, Washington.

Bray, L.A., K.J. Carson, and R.J. Elovich. 1990. *Cesium Recovery Using Savannah River Laboratory Resorcinol-Formaldehyde Ion Exchange Resin.* PNL-7273, Pacific Northwest Laboratory, Richland, Washington.

Bray, L.A., K.J. Carson, and R.J. Elovich. 1993. *Initial Evaluation of Sandia National Laboratory Prepared Crystalline Silico-Titanates for the Recovery of Cesium.* PNL-8847, Pacific Northwest Laboratory, Richland, Washington.

Bray, L.A. and F.T. Hara. 1991. "Use of Titanium-Treated Zeolite for Plutonium, Strontium, and Cesium Removal from West Valley Alkaline Wastes and Sludge Wash Waters." In *First Hanford Separations Science Workshop*. PNL-SA-19697S, pp. II.87-II.91. Pacific Northwest Laboratory, Richland, Washington.

Bray, L.A., L.K. Holton, T.R. Meyers, G.M. Richardson, and B.M. Wise. 1984. *Experimental Data Developed to Support the Selection of a Treatment Process for West Valley Alkaline Supernatant.* PNL-4969, Pacific Northwest Laboratory, Richland, Washington.

Eager, K.M., D.L. Penwell, and B.J. Knutson. 1994. *Preliminary Flowsheet: Ion Exchange Process for Separation of Cesium from Hanford Tank Waste Using Duolite CS-100 Resin.* WHC-SD-WM-TI-667 Rev. 0, Westinghouse Hanford Company, Richland, Washington.

Kurath, D.E., L.A. Bray, K.P. Brooks, G.N. Brown, S.A. Bryan, C.D. Carlson, K.J. Carson, J.R. DesChane, R.J. Elovich and A.Y. Kim. 1994. *Experimental Data and Analysis to Support the Design of an Ion Exchange Process for the Treatment of Hanford Tank Waste Supernatant Liquids.* PNL-10187, Pacific Northwest Laboratory, Richland, Washington.

Kurath, D.E., L.A. Bray, W.A. Ross, and D.K. Ploetz. 1989. "Correlation of Laboratory Testing and Actual Operations for the West Valley Supernatant Treatment System." Presented at the Fourth International Symposium on Ceramics in Nuclear Waste Management, American Ceramic Society Annual Meeting, April 23-27, 1989. PNL-SA-16871, Pacific Northwest Laboratory, Richland, Washington.

10 CFR 61. 1994. U.S. Nuclear Regulatory Commission, "Disposal of Low-Level Radioactive Wastes." U.S. Code of Federal Regulations.

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