**Initial Evaluation of Two Organic Resins
and Their Ion Exchange Column
Performance for the Recovery of Cesium
from Hanford Alkaline Wastes**

**L. A. Bray
K. J. Carson
R. J. Elovich**

**C. D. Carlson
J. R. DesChane
D. E. Kurath**

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**Prepared for
the U.S. Department of Energy
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**Pacific Northwest National Laboratory
Richland, Washington 99352**

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SUMMARY

At the request of Westinghouse Hanford Co. (WHC), the Pacific Northwest Laboratory (PNL) has studied several ion exchange materials for the recovery of cesium from Hanford waste tanks. The WHC program was divided into two main tasks, 1) to obtain equilibrium data for cesium ion exchange (initiated in FY92), and 2) to evaluate ion exchange column performance. The subject of this letter report is the initial evaluation of the ion exchange performance for CS-100 (an organic resin produced by Rohm and Haas) and BIB-DJ (a new resorcinol-formaldehyde organic resin, first prepared by Dr. Jane Bibler [Westinghouse Savannah River Co. (WSRC)] and produced by Boulder Scientific Co.

The following conclusions were developed after completion of the initial ion exchange column study:

- Recovery of cesium from Hanford highly alkaline wastes can be achieved by using an organic ion exchange resin (CS-100 or BIB-DJ). The cesium can be recovered from the exchangers using acid elution.
- CS-100 resin extracts cesium and can be acid stripped to decontamination levels suitable for resin reuse. Acid stripping results for BIB-DJ do not show that the resin is reusable. Additional stripping test conditions will be evaluated.
- Batch cesium distribution data (Bray et al, 1992) for both CS-100 and BIB-DJ accurately projected the ion exchange capacity of the exchangers.
- The capacity of the CS-100 resin using 5M Na⁺ NCAW feed with a cesium concentration of 5E-4M Cs⁺ was 30 cv or 2 g of Cs/L of exchanger. The capacity of BIB-DJ was 190 cv or 12.6 g of Cs/L of exchanger, providing a cesium capacity factor of 6.3 greater than for CS-100.
- Multiple column tests (three in series) provide valuable flow rate data, indicating that the data provided by the laboratory 200 mL ion exchange columns (2.54 cm dia.) can be used to directly scale-up to large-scale processing columns.

- The BIB-DJ organic resin is outstanding in its loading kinetics as compared to the CS-100. The volume of feed through the column at which the initial detectable cesium breakthrough ($C/Co = 0.0001$) was noted varied for the CS-100 resin from ~2.5 to 7 cv as the flow rate was varied from 9 to 3 cv/hr. Under similar conditions for the BIB-DJ resin, the detectable cesium breakthrough varied from 100 cv to 160 cv.
- Formic ($HCOOH$) and nitric (HNO_3) acids were used to elute the cesium from the loaded ion exchange columns. Both 0.1M HNO_3 and 1M $HCOOH$ were effective in the removal of cesium from the CS-100 resin. The volume of acid consumed doubled when the flow rate was increased from 1 cv/hr to 6 cv/hr. No effect on reducing the eluant volume was noted when the temperature was increased from 25°C to 40°C. Formic acid was more effective in the removal of cesium from BIB-DJ resin. Using 25 cv of acid, ~40% of the cesium was recovered using 0.1M HNO_3 and ~97% using 1M $HCOOH$.

ACKNOWLEDGMENTS

Pacific Northwest Laboratory (PNL) is collaborating with universities, national laboratories, and industry to develop ion exchange materials for the pretreatment of nuclear wastes stored at Hanford. The authors would like to acknowledge the contributions to this effort of Mr. Ronald M. Orme, Westinghouse Hanford Company; Dr. Jane Bibler, Westinghouse Savannah River Laboratory; and Mr. John Burningham, Boulder Scientific Co.

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1.0 INTRODUCTION

The contents of Hanford's 177 underground storage tanks include a mixture of sludge, salt cake and alkaline supernatant liquids. The insoluble sludge fraction of the waste consists of metal oxides and hydroxides and contains the bulk of many radionuclides. The salt cake, generated by extensive evaporation of aqueous solutions, consists primarily of dried sodium salts. The supernates consist of concentrated aqueous solutions of sodium and potassium nitrate salts. The bulk of the water soluble radionuclides such as ^{137}Cs are contained in the water soluble salt cake and supernatant solutions.

Although the pretreatment and disposal requirements are still being defined, one of the first steps in most pretreatment scenarios will be a salt cake dissolution and sludge wash step followed by a solids/liquid separation. Most of the cesium is expected to be in the aqueous liquids 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 NRC 10CFR61 class A limits for ^{137}Cs (1 Ci/m^3). The separated cesium may be concentrated and vitrified for disposal in the high-level waste repository. The decontaminated aqueous liquid will be solidified as a LLW grout for near-surface disposal.

The technology for Cs decontamination of high-level alkaline wastes and sludge wash waters is being developed at the Westinghouse Hanford Company (WHC), Richland, Washington (Bray et al. 1989b; Bray et al. 1990a; Bray et al. 1991a; Bray et al, 1992); the Westinghouse Savannah River Company (WSRC), Aiken, South Carolina (Bibler et al, 1989c; Bray et al, 1990b); and at the West Valley Nuclear Services Company, Inc. (WVNS) in West Valley, New York (Bray et al, 1984; Kurath et al, 1989d; Bray et al, 1991b). Using this technology as a starting point, experimental studies are being conducted by Pacific Northwest Laboratory (PNL)¹ to evaluate the performance of ion exchange processes and newly emerging technologies using simulated and actual Hanford wastes.

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

2.0 OBJECTIVES

The overall objective of the WHC program is, 1) to evaluate ion exchange materials for the recovery of cesium from alkaline wastes, 2) to determine their loading and elution capacities, 3) to determine the physical life cycle (including radiation and chemical stability) for selected ion exchangers, 4) to determine if basic ion exchange data can be applied to a broad range of tank wastes, and 5) to provide credible laboratory data for engineering-scale evaluation and ion exchange media selection. The goal will be to provide the technology to produce a Class A waste. The results presented in this document provide initial test cesium loading and elution results for ion exchange column operations for two selected ion exchange resins under a limited range of conditions. Data in this report can be found in PNL laboratory record books BNW 54705 and BNW 55026.

3.0 EXPERIMENTAL

Experimental work completed in FY 1992 for cesium recovery included the determination of cesium batch distribution coefficients for three exchangers and two waste forms (Bray et al. 1992). FY 1993 experimental work included selected additional batch data and the initiation of ion exchange column studies. Ion exchange processes being investigated can be applied over a wide range of alkaline tank wastes. Complexant Concentrate (CC) and Neutralized Current Acid (NCAW) wastes were selected for the initial FY 1992 investigation. CC wastes represent a high sodium waste containing organic complexants. NCAW represents a high sodium waste containing a low organic content. The FY 1992 study showed that there was no difference between waste forms in the recovery of cesium from high sodium wastes. Because of the limited availability of actual waste, simulated NCAW solutions are being used to perform parametric studies. Actual wastes have only been used to obtain reference points and to verify that cesium ion exchange for simulated and actual wastes are equivalent. In 1989, radioactive waste from Tank 101AW was used to complete a batch contact with the Savannah River developed formaldehyde-resorcinol (BIB-DJ) resin (Bray 1989b). Additional radioactive tank wastes may be used after engineering-scale evaluation and ion exchange media selection has been completed.

3.1 ION EXCHANGE SELECTION

Two organic ion exchange resins were selected for the ion exchange column investigation; a granular phenol-formaldehyde condensate polymer ion exchange resin (CS-100) with carboxylic acid functional groups prepared by the Rohm and Haas Co., and a resorcinol-formaldehyde ion exchange resin (BIB-DJ). The BIB-DJ resin was first prepared by Dr Jane Bibler and Dr. Dick Wallace at the Westinghouse Savannah River Laboratory. The BIB-DJ resin is currently being manufactured by the Boulder Scientific Co, Mead, CO. Coordination continues between PNL, WHC and Dr. Jane Bibler of WSRC to test and verify the BIB-DJ resin (Bibler 1989c).

3.2 VARIABLES TO BE CONSIDERED TO OBTAIN COLUMN OPERATION DATA

The effect on cesium loading and breakthrough was measured during column operation by selecting time-dependent variables (superficial velocity, bed volumes per hour, or flow rate). Other effects such as temperature or feed variables (Na to K mole ratio and OH^-) may be the subject of future column tests.

3.3 EQUIPMENT DESCRIPTION

The equipment consists of a constant temperature water bath, an analytical balance, temperature controlled ion exchange columns, and gamma counting equipment.

3.3.1 Ion Exchange System

The ion exchange column system consists primarily of six 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. They 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 connected to a water bath so that a constant temperature may be maintained. The columns may be run as independent columns or can be connected in series. The solution to the columns is normally fed downflow through pumps from feed tanks. Column elution can be initiated upflow. The feed pump located just upstream of the first column is used to control the flow rate. A valve is located at the bottom of each column from which each column's effluent may be sampled as a function of time. The effluent from the final column is routed to the weighing bottle. The column volumes (cv's) of the effluent processed are determined by the effluent weight divided by the specific gravity of the feed. A $24,600 \pm 0.1$ -g balance is used to determine the weight of the effluent.

The operation of the ion exchange system for removing cesium, containing ^{137}Cs tracer, from simulated NCAW alkaline salt solution was varied as each test procedure was developed. The influent and effluent counting rates were measured to determine optimum performance of the ion exchange columns as a function of time and feed flow.

3.3.2 Single Column Configuration

Single column configuration operation consists of individual ion exchange columns operated independently. The columns were operated 24 hours/d until the objective of the test was met.

3.3.3 Multi-Column Configuration

Multi-column operations can be performed by connecting two to six columns in series. The columns were operated 24 hours/d until the objective of the test was met. Samples were taken as a function of time at the bottom of each column. Care was taken to limit the amount of effluent in the head space on the top of each column so that the liquid mixing area did not perturb the overall results.

3.4 PREPARATION OF SYNTHETIC WASTES

Complexant concentrate (CC) and neutralized current acid waste (NCAW) were selected for the initial investigation (Bray et al, 1992). Organic CC waste represent a high sodium waste containing organic complexants. NCAW represents a high sodium waste with a low organic content. The results of that study show that the organic content of the waste had no effect on the basic cesium ion exchange data and that basic ion exchange data can be applied to a broad range of tank waste types. For this study, simulated solutions were prepared to represent NCAW. The ion concentration of NCAW is shown in Table 3.1.

TABLE 3.1. Neutralized Current Acid Waste - Synthetic Test Solution

<u>Species</u>	<u>NCAW,M</u>
Na	5.0
K	0.12
Rb	5.0E-5
Cs	5.0E-4
Al	0.43
SO ₄	0.15
OH(free)	3.4 (1.3)
CO ₃	0.23
F	0.089
NO ₂	0.43
NO ₃	1.69

3.5 ION EXCHANGE COLUMN TEST INSTRUCTIONS

The conditions selected for the initial exchange column loading tests were, to determine the effect of the time-dependent variables (superficial velocity or bed volumes per hour) for cesium loading, to keep the temperature (25°C) and feed variables (Na⁺ concentration, Na/Cs mole ratio) constant during the test series; to use an ion exchange column consisting of one to three 200 mL segments; to obtain samples between each segment; and to continue operation until the final column had a Cs C/Co value of 1 (C = concentration in the effluent, and C₀ = concentration in the influent).

3.5.1 Candidate Ion Exchanger Preparation

Two materials were tested using variable column configurations, CS-100 and BIB-DJ. The original NaOH pretreatment of each exchanger is described below. Because the sodium treated BIB-DJ resin appeared to degrade during storage, the majority of the BIB-DJ column tests were then completed by using "as received" resin obtained from the center of the 55 gallon receiving drum.

The CS-100 and the initial BIB-DJ ion exchange resins were pretreated with sodium hydroxide, water washed, and dried. Approximately 10 liters of the "as received" organic ion exchange resin were treated in a large ion exchange column with 3-column volumes (cv) of 2M NaOH, washed with 6 cv of distilled water, placed in a vacuum filter funnel, washed with H₂O, and damp dried in the filter for a predetermined time. The resin was then placed in screw-cap glass storage jars for use.

The amount of material to be placed in each column (200 mL) was added by weight as determined by the following method. First, the specific gravity of the caustic treated CS-100 or BIB-DJ was determined (grams of the dry exchanger in a known volume of wet exchanger). This was accomplished by weighing the prewashed CS-100 or BIB-DJ exchanger into a 200 mL volumetric cylinder containing water to a final tap volume of 200 mL. This specific gravity (g/mL) was then used to determine the weight of 200 mL of resin used in the columns.

To load the resin into each column, the column was filled with 2M NaOH and the ion exchange resin added based on weight. Each column was back flushed with 2M NaOH to remove resin fines before being connected in series.

The temperature of the water jacketed columns was controlled at $25 \pm 2^\circ\text{C}$. The ion exchange and pump system was flushed and tested using at least 3-cv of 2M NaOH solution at a flow rate requested for the specific test.

To initiate the ion exchange column test, the solution head on the top of each column was reduced to the minimum. The columns were then connected as instructed and the excess 2M NaOH above each exchange bed removed through the bottom sampling valve. NCAW feed was then started through the first column and the liquid heads above each column reestablished and held at ~1-inch.

When the last column was loaded to >90% Cs breakthrough [^{137}Cs effluent count rate (C) $\div$ ^{137}Cs feed count rate (Co) = 1], the test was terminated. The system was then flushed downflow with 3 cv of 2M sodium hydroxide solution and then with 6 cv of water at (2 cv/h). All columns were then placed in an interstitial water condition. Sodium hydroxide (2M) wash was used to remove residual feed containing sodium aluminate from the system prior to water washing, to prevent aluminum precipitation due to a lowering of the pH. The loaded and washed columns were then detached and individually eluted using formic acid or nitric acid (Section 4.3).

3.6 BATCH DISTRIBUTION

A batch distribution coefficient is a measure of the overall ability of the solid phase to remove an ion from solution (Bray 1989a). Batch distribution data are reported as radionuclide distribution coefficients (K_d) and/or λ . Under certain conditions, λ is approximated by the bed volumes processed at 0.5 C/Co breakthrough. K_d , in units of mL/g (volume of solution per mass of dry exchanger), represents a theoretical volume of solution that can be processed per mass of exchanger. To convert to λ , the K_d value is multiplied by the bed density of the exchanger (ρ_b) to obtain a value equivalent to the volume of the solution processed per volume of exchanger. The equation for the determination of K_d is:

$$K_d = C_s \div C_l, \text{ mL/g,}$$

where C_s = the concentration of the radionuclide exchanged on the solid phase (Ci or g of radionuclide/g of anhydrous material), and

C_l = the concentration of the radionuclide remaining in the liquid phase after batch contact (Ci or g of radionuclide/mL).

The equation for the determination of λ is:

$$\lambda = K_d \times \rho_b, \text{ dimensionless,}$$

where λ represents the number of ion exchange bed volumes of feed that can be loaded on an exchanger (column volumes or cv). The value for λ is artificial because it is difficult, in practice, to achieve 100% loading of a column.

4.0 RESULTS AND DISCUSSION

4.1 BATCH EQUILIBRIUM STUDIES

During FY92 and FY93, cesium batch distribution coefficient results were completed for four cesium ion exchangers, CS-100, BIB-DJ, IONSIV IE-96 produced by the UOP Co., and the Sandia National Laboratory crystalline silico-titanates (Bray et al, 1992; Bray et al, 1993). The results for the organic resins CS-100 and BIB-DJ were determined as a function of the equilibrium sodium to cesium mole ratio, Figures 4.1 and 4.2. If we apply these data to ion exchange column experiments, using a NCAW feed with a Na/Cs mole ratio of 10^4 , we can draw a plane through the data to determine λ as a function of the sodium concentration, Figure 4.3. This provides an equivalent estimate of the cesium loading capacity for these exchangers. Thus prior to testing CS-100 and BIB-DJ resins in an ion exchange column system, a cesium loading for $5M Na^+$ NCAW was projected to be 30 cv and 180 cv, respectively (at Cs C/Co of 0.5).

4.2 ION EXCHANGE COLUMN LOADING STUDIES

Cesium loading experiments were performed using the CS-100 and BIB-DJ resins. The tests were designed to determine the effect of flow rate on the cesium loading characteristics of the resin being tested. Tests that have been completed are shown in Table 4.1.

TABLE 4.1 Cesium Loading Experiments

<u>(mL/hr)</u>		<u># of Columns</u> <u>Test #</u>	<u>Flow Rate</u> <u>Resin Used</u>	<u>in Series</u>
1	CS-100	1 (A)	1,200	
2	BIB-DJ	1 (B)	1,200	
3	CS-100	3 (C,D,E)	1,200	
5	CS-100	3 (I,J,K)	600	
7	CS-100	3 (O,P,Q)	1,800	
8	BIB-DJ(as rec)	3 (R,S,T)	1,800

FIGURE 4.1. Batch Distribution Studies - CS-100 and NCAW

39212057.1

FIGURE 4.2. Batch Distribution Studies - BIB-DJ and NCAW

38212057.5

FIGURE 4.3. Comparison Between IE-96, CS-100, BIB-DJ and TAM-70 at an Equilibrium Na/Cs Mole Ratio of 10^4

4.2.1 CS-100 Loading Studies

The initial cesium loading test with NaOH pretreated CS-100 resin was completed using a single column (Test-1, Column A) at 6 cv/hr, Figure 4.4. The initial detectable cesium breakthrough ($C/Co = 0.0001$) occurred at 5 cv. The Cs 0.5 C/Co value was 30 cv and agrees well with that predicted from the batch distribution data, Figure 4.3. The next three tests (Test-5, -3, and -7) involved the use of three columns in series, Figures 4.5, 4.6, and 4.7. The flow rate through the first column in each series was 3, 6, and 9 cv/hr, respectively. The column volumes at which the initial detectable cesium breakthrough ($C/Co = 0.0001$) was detected decreased with increasing flow rate; 10 cv to 3.5 cv. In each case, the column volumes of feed passed through the system at Cs $C/Co = 0.5$ was 30, 60 and 90 for the three columns in series.

Columns in series (C, D, E) can be viewed as three single columns, i.e., C (200 mL), CD (400 mL) and CDE (600 mL). A flow rate of 1,800 mL/h through this series can be used to obtain data at three residence times, i.e., 9 cv/h, 4.5 cv/h and 3 cv/h. Selected results for the four CS-100 ion exchange tests were combined to obtain a better picture of cesium loading as a function of the residence time, Figure 4.8. The column volumes at which the initial detectable cesium breakthrough ($C/Co = 0.0001$) was noted varied from ~2.5, 3.5, 7 to ~19 cv as the flow rate varied from 9, 6, 3 to 1 cv/hr, respectively. However, all of the breakthrough curves merged at ~0.5 C/Co or ~30 cv.

Because there is great interest in the above information for engineering scale-up, selected data was replotted as a function of feed velocity. Assuming a laboratory column with a 5.07 cm² area and a flow rate of 3 cv/h, the superficial velocity through the column varied from 1.97 to 5.92 cm/min. These data show insignificant difference between the three velocities, Figure 4.9. This would indicate that the data obtained from the laboratory 200 mL ion exchange columns can be used to directly scale-up to large-scale processing columns. This has been previously demonstrated at West Valley Nuclear Service Co., West Valley, NY when the results of the PNL 200 mL columns were used to directly scale-up the WV 3-foot by 10 feet high zeolite columns being used for the removal of cesium from PUREX alkaline waste (Kurath 1989d).

FIGURE 4.4. CS-100 Cesium Loading Test - Column A; 1,200 mL/hr

FIGURE 4.5. CS-100 Cesium Loading Test - Columns I, J, K; 600 mL/hr

FIGURE 4.6. CS-100 Cesium Loading Test - Columns C, D, E; 1,200 mL/hr

FIGURE 4.7. CS-100 Cesium Loading Test - Columns O, P, Q; 1,800 mL/hr

FIGURE 4.8. CS-100 Cesium Loading Results - Cs Breakthrough as a Function of Flow Rate

FIGURE 4.9. CS-100 Cesium Loading Results - Cs Breakthrough as a Function of Flow Velocity

4.2.2 NaOH Washed BIB-DJ Loading Studies

The initial cesium loading test with NaOH Washed BIB-DJ resin was completed with a single column (Test-2, Column B) at 6 cv/hr, Figure 4.10. The initial detectable cesium breakthrough ($C/Co = 0.0001$) occurred at 23 cv. The Cs 0.5 C/Co value was 80 cv (versus 30 cv for CS-100 under the same conditions, Figure 4.4) but does not agree with the 180 cv value that was predicted from the batch distribution data, Figure 4.3. Further multiple column tests (Section 4.2.3) were placed on hold until the apparent loss in capacity of the resorcinol-formaldehyde resin was understood.

4.2.3 Batch Distribution Studies to Determine BIB-DJ Resin Characteristics

In 1987, Dr. Jane Bibler, WSRC, provided PNL with a liter sample of research-grade resorcinol-formaldehyde resin (BSC-187) to complete a series of laboratory ion exchange column (200 mL) tests (Bibler 1989). Dr. Bibler also had a large quantity of the resin made commercially by Boulder Scientific Co. (BSC), which was shipped to WSRC in a number of 55 gallon drums. To initiate the FY 1992 program for WHC, PNL purchased several cubic feet of resin directly from BSC from material left over from production of the multi 55-gallon Bibler order. However, this material had a very poor Cs batch distribution value as compared with earlier Bibler analytical samples (BSC-187). We then asked Dr. Bibler to send us material from one of the 55 gallon drums in storage. Since this was difficult to do in a short time period, a one gallon sample was withdrawn from a 55 gallon drum by WSRC and sent to PNL. This material was treated with 2M NaOH (12-21-92) and immediately used for batch distribution studies (Bray et al 1992). This also provided the material that was later (March, 1993) used for the first 200 mL ion exchange column test (Figure 4.10), which indicated that the material had degraded since it was first treated for the batch tests.

To determine differences between the one gallon sample, the 55 gallon drum, and the initial resin (BSC-187), 0.1g samples of the organic resins were batch contacted (in duplicate) at 25°C for 72 hrs with synthetic NCAW, Table 3.1. The Cs K_d values for various pretreatment conditions show that the 1-gallon and the 55-gallon BIB-DJ materials appear to be the same, Table 4.2. The 1987 (BSC-187) material appears to have degraded. No pretreatment

FIGURE 4.10. BIB-DJ Cesium Loading Test - Column B; 1,200 mL/hr

provided the highest Cs K_d values for the resin in the drums. Water appears to degrade the resin. However, soaking the water treated resin in NaOH for ~16 hrs partially restored the resin to the "as received" values. Based on

TABLE 4.2. Cesium Batch Distribution Studies for BIB-DJ

Conditions: 0.1g samples in duplicate, 25°C, 72 hrs contact, synthetic NCAW (Table 3.1)

<u>Pretreatment Conditions</u>	<u>BIB-DJ Cs K_d Values</u>		
	<u>55 gal Drum</u>	<u>1 gal Drum</u>	<u>BSC-187 (1987)</u>
5 min, 2M NaOH ²	870, 906	856, 880	237, 252
60 min, 2M NaOH	989, 980	939, 969	275, 330
16 hrs, 2M NaOH	959, 947	765, 803	210, 184
68 hr H ₂ O, 5 min, 2M NaOH	506, 533	499, 492	209, 249
68 hr H ₂ O, 60 min, 2M NaOH	493, 491	506, 467	191, 171
68 hr H ₂ O, 16 hrs, 2M NaOH	761, 780	920, 915	261, 233
No H ₂ O, no NaOH	1035, 1054	1060, 1033	355, 308

this information, the 55 gallon drum was again tested by varying the pretreatment conditions. The results again show that the best material in the 55 gallon drum is 10 inches into the drum with no pretreatment, Table 4.3. That the original resin (1-gallon) that was 2M NaOH treated, water washed and air dried (12/21/92) had degraded, causing the poor ion exchange performance (Section 4.2.2). To test this theory, the BIB-DJ ion exchange column studies were resumed by using as received resin.

4.2.4 BIB-DJ Loading Studies - No Pretreatment

Three ion exchange columns were operated in series (R, S, and T). The columns were each filled with 200 mL of BIB-DJ resin obtained from approximately 10-inches below the surface of the resin in the 55-gallon receiving drum. The object was to determine if the resin in the 55-gallon drum had deteriorated as compared with sodium-washed resin prepared (12/21/92) and tested earlier (Figure 4.4). The flow rate through the first column in

² Followed by water washing and air drying. Weighed sample of air dried resin was heated to 105°C and used to adjust the air dried weights.

TABLE 4.3. Cesium Batch Distribution Studies for BIB-DJ, 55 gallon Drum
 Conditions: 0.1g samples in duplicate, 25°C, 72 hrs contact,
 synthetic NCAW (Table 3.1)

<u>Pretreatment Conditions</u>	<u>Cs K_d Values, 55 gal Drum</u>
Top of drum, 6M NaOH, 72h No H ₂ O wash	1249, 1229
Top of drum, 6M NaOH, 24h H ₂ O wash, vacuum dry	1226, 1221
Top of drum, air dry, 24h	1021, 998
10 inches into drum, no pretreatment	1294, 1271
Resin treated with NaOH, H ₂ O, and air dried on 12-21-92 used for batch distribution studies (Bray et al, 1992), 1-gallon BIB-DJ	247, 262

series was 1,800 mL/hr or 9 cv/hr. The initial detectable cesium breakthrough ($C/C_o = 0.0001$) was 100 cv. The column volumes of feed which passed through the first column (R) at Cs $C/C_o = 0.5$ was 190 and agrees well with that predicted (180 cv) from the batch distribution data, Figure 4.3. In each case, the column volumes of feed passed through the system (R, S, and T) at Cs $C/C_o = 0.5$ was 190, 380 and 570 for the three columns in series, Figure 4.11. There was no detectable breakthrough of the succeeding column prior to 0.95 C/C_o breakthrough of the initial column. The resin in the 55 gallon drum (10-inches below the surface) was comparable to the initial batch distribution studies. The data in Table 4.3 confirms that the resin on the surface may be degraded, but that resin 10 inches into the drum is protected by the surface resin.

Columns in series (R, S, and T) can also be viewed as three single columns, i.e., R (200 mL), RS (400 mL) and RST (600 mL). A flow rate of 1,800 mL/h through this series was used to obtain data at three residence times, i.e., 9 cv/h, 4.5 cv/h and 3 cv/h. The column volumes at which the initial

FIGURE 4.11. BIB-DJ Cesium Loading Test - Columns R, S, T; 1,800 mL/hr

detectable cesium breakthrough ($C/Co = 0.0001$) was noted varied from 100 cv, 140 cv and 160 cv as the flow rate varied from 9, 4.5 to 3 cv/hr, respectively. However, all of the breakthrough curves merged at $\sim 0.5 C/Co$ of 190 cv as expected, Figure 4.12. The results show that the BIB-DJ resin has a cesium capacity approximately 6.3 times that of CS-100 under similar conditions.

4.3 ION EXCHANGE ELUTION STUDIES

Cesium elution experiments were performed using the CS-100 and BIB-DJ cesium loaded resins (Section 4.2). The experiments were designed to determine the effect of flow rate, temperature, and type of acid eluate on the cesium elution characteristics of the resin being tested. The acid types were limited to nitric acid and formic acid. The concentration of the nitric acid was limited to 0.1 molar due to the concern for auto catalytic reactions with the resin at higher acidities. Tests completed are shown in Table 4.4.

TABLE 4.4 Cesium Elution Experiments

Column (Test)	Resin	Eluent	Flow Rate (mL/hr)	cv/hr (200 mL/col.)	Temp., °C
A(1)	CS-100	0.1M HNO_3	1,200	6	25
C(3)	CS-100	0.05M HNO_3	1,200	6	25
D(3)	CS-100	1N $HCOOH$	1,200	6	25
E(3)	CS-100	0.5N $HCOOH$	1,200	6	25(not shown)
I(5)	CS-100	0.1M HNO_3	1,200	6	40
J(5)	CS-100	0.05M HNO_3	1,200	6	40(not shown)
K(5)	CS-100	1N $HCOOH$	1,200	6	40
O(7)	CS-100	0.1M HNO_3	200	1	25
P(7)	CS-100	0.05M HNO_3	200	1	25
Q(7)	CS-100	1N $HCOOH$	200	1	25
R(8)	BIB-DJ	0.1M HNO_3	200	1	25
S(8)	BIB-DJ	1N $HCOOH$	200	1	25
T(8)	BIB-DJ	0.5N $HCOOH$	200	1	25

FIGURE 4.12. BIB-DJ Cesium Loading Results - Cs Breakthrough as a Function of Flow Rate

4.3.1 CS-100 Elution Tests

Elution tests were initiated for CS-100 and ion exchange columns O, P, and Q at 1 cv/hr and 25°C using nitric or formic acid, Figure 4.13. The initial resin had been loaded to a value equal to the cesium contained in 30 column volumes of NCAW (Loading Test #7). The 1N HCOOH very efficiently eluted the cesium in 6 cv of acid, concentrating the cesium 5-fold. However, the elution results for 0.05 (Figure 4.14) and 0.1M HNO₃ show that 5 to 12 cv of dilute influent acid will pass through the column before the effluent was acidic as noted by the change in pH. This is the result of the column containing residual hydroxide from the column post wash. This effect is not observed in the 1N HCOOH case because of the higher concentration of hydrogen ion, Figure 4.15. Discounting this potential recycle stream, the amount of 0.05 or 0.1M nitric acid required before reaching a C/Co value of ~0.001 was 9 cv and 13 cv of acid respectively, concentrating the cesium ~3-fold.

When the above series of elution tests was repeated at a higher flow rate (6 cv/hr versus 1 cv/hr), the volume of 1N HCOOH or 0.1M HNO₃ required to obtain the same elution efficiency doubled, Figure 4.16. The volume of the more dilute acid (0.05M HNO₃) did not change with flow rate. When several tests were repeated at a higher temperature (40°C versus 25°C) no change in acid requirement was observed, Figure 4.17.

4.3.2 BIB-DJ Elution Tests

Elution tests were initiated for BIB-DJ resin and ion exchange columns R, S, and T at 1 cv/hr (25°C) using nitric or formic acid, Figure 4.18. The double peak for the HCOOH elutions has not yet been identified. Analysis of the acid eluate may reveal that K, Rb, and Na are also being eluted in this region causing this observation. Each resin column had been loaded to a value equal to the cesium contained in 190 cv of NCAW (Loading Test #8). No acid tested removed the cesium down to a C/Co level of 0.01 as was demonstrated for CS-100, Figures 4.19 and 4.20. After passing 25 cv of 0.1M HNO₃ through column R, 45% of the cesium was eluted. After passing 31 cv of either 0.5 or 1M HCOOH through Columns T and S, 97% of the cesium was eluted. Since 190 cv of NCAW had originally been loaded on to the columns, even a 97% elution allows 5.7 cv of cesium to remain on the resin. The relatively poor elution

behavior of BIB-DJ may be due to the ~35% volume shrinkage during elution when $\text{Na}^+ - \text{K}^+ - \text{Cs}^+$ is replaced with H^+ . There is a visible void space between the resin and the wall of the ion exchange column during elution. The tests were all carried out using downflow elution. It may be possible to improve the elution with upflow of the acid, such that the bed is fluidized, or by vibrating the column to break up the resin. This may not be a problem in a larger column where the weight of the resin is much greater. These and other suggestions for improved elution characteristics will be evaluated in FY 94.

FIGURE 4.13. CS-100 Elution as a Function of Acid Concentration - 1 cv/hr, 25°C

RUNCE-PH.SPS 03/08/93

Figure 4.14. CS-100 Elution with 0.05M HNO₃ as a Function of pH

RUNDE-PH.SPS 03/08/93

Figure 4.15. CS-100 Elution with 1M HCOOH as a Function of pH

FIGURE 4.16. CS-100 Elution as a Function of Flow Rate - 1 to 6 cv/hr, 25°C

FIGURE 4.17 CS-100 Elution as a Function of Temperature - 6 cv/hr, 25°C - 40°C

FIGURE 4.18. BIB-DJ Elution as a Function of Acid Concentration - 1 cv/hr, 25°C

FIGURE 4.19. Elution of CS-100 and BIB-DJ Resins with $0.1M HNO_3$ - 1 cv/hr, $25^\circ C$

FIGURE 4.20. Elution of CS-100 and BIB-DJ Resins with 1N Formic Acid - 1 cv/hr, 25°C

5.0 FUTURE STUDIES

Future work will center on the resorcinol-formaldehyde resin (BIB-DJ). Loading and elution studies will be continued to evaluate the current resin and new commercial resin being manufactured by Boulder Scientific Co (ordered for delivery 9/93). In addition, engineering evaluation of the data to provide a scale-up model will be completed. Radiation damage is currently being studied and will be reported. Other types of waste and conditions will be evaluated in FY 94.

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