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Cesium Removal Demonstration Using Selected Actual Waste Samples from the Hanford Reservation Tank Farm

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Abstract: Approximately 40 million curies of Cs-137 are currently contained in High Level Waste stored in 177 underground storage tanks at the Hanford Nuclear Reservation near Richland, Washington. A series of actual waste, small-scale column tests were performed to evaluate the performance of a selected ion exchange resin for cesium removal from a range of planned feed streams. These tests demonstrated that the selected cationic resin–SuperLig 644$^{®}$-has more than adequate resin capacity to treat each of three potential feed streams. Furthermore, tests indicate an acceptable mass transfer zone for each of the three types of feed material, and that the elution of the resin can be accommodated within the design criteria for the proposed Waste Treatment Plant.

Keywords: Cesium, ion exchange, nuclear waste

INTRODUCTION

The purpose of this work was to confirm the acceptable performance of a cesium ion exchange resin using actual waste samples from the Hanford High Level Waste tank farm. In particular, the objective was to confirm that resin performance meets selected design criteria for the proposed Waste Treatment Plant currently under construction on the Hanford Site.

Approximately 40 million curies of Cs-137 are currently contained in High Level Waste stored in more than 100 underground storage tanks at the Hanford

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Site near Richland, Washington. It is the intention of the Department of Energy (DOE) to vitrify 99.9 + % of this cesium into a final glass waste form (blended with other radioactive constituents) for disposal in the Yucca Mountain repository. However, the cesium bearing caustic stream also contains approximately 40,000 MT of sodium. Incorporation of that quantity of sodium into the HLW glass form for disposal in the repository is not feasible. Therefore, DOE has chosen to pursue separation of the cesium from the sodium to maintain a reasonable quantity of HLW glass canisters. The chosen methodology is ion exchange using organic cation exchange resins.

Best Basis Inventory (BBI) characterization (1) of the waste from the Hanford tanks farm has identified more than 150 different significant cesium bearing individual waste fractions accounting for the vast majority of the available cesium curies. This waste is partitioned between supernate and salt cake phases throughout the tank farms. This material represents the wastes from more than 40 years of production of plutonium and other nuclear materials at the Hanford Site. During those 40 years of operations, multiple processes were employed both for the processing of plutonium and for special campaigns to produce other specific materials. As such, the waste in the tank farm comes from broadly disparate origins and has significant differences in key characteristics relevant to ion exchange performance.

Cesium removal performance is most dramatically affected by other alkaline metals. The alkaline metals most prevalent in HLW are sodium and potassium. Figure 1 provides a comparison of the relative compositions of 150 of the individually identified waste phases (either supernate or salt

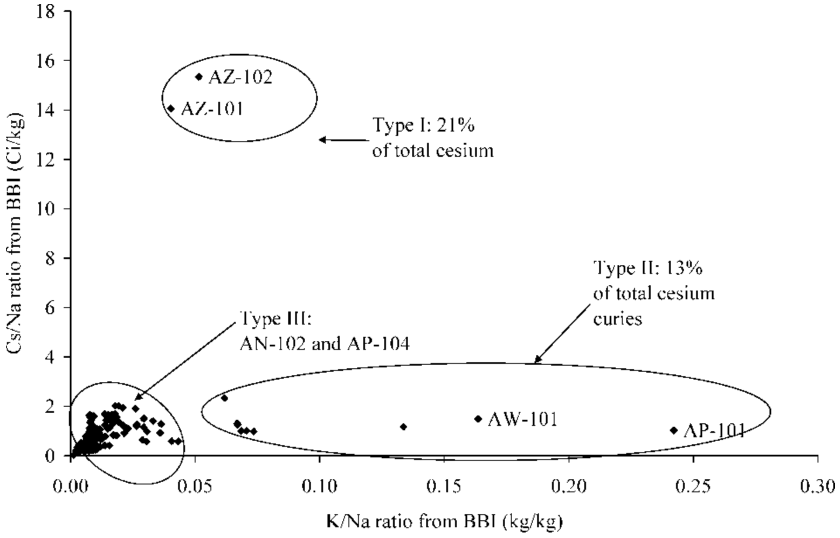

Figure 1. Waste types grouped by K/Na ratio and Cs/Na ratio.

cake) in the Hanford tank farm (1). Inspection of this figure indicates that, with respect to cesium removal performance, the waste can be broadly separated into three basic groupings; high cesium bearing waste (Type I: consisting of only 2 tanks but containing more than 21% of the cesium curies), tanks with relatively high potassium quantities (Type II: consisting of 8 tanks containing 13% of the cesium curries) and tanks with relatively consistent potassium/sodium and cesium/sodium ratios (Type III). The intent of this paper is to validate the performance of a selected ion exchange media against each of these three waste groups using selected actual waste samples. In addition, ancillary performance issues will be identified.

DOE has commissioned a team led by Bechtel National, Inc.(BNI) to build a facility capable of treating slightly less than 16 gpm of Type II and Type III waste (the target for Type I waste is approximately 4 gpm). BNI has chosen a four column carousel arrangement (depicted in Fig. 2). For this carousel arrangement to be effective, the combined post-loading treatment time (feed displacement, rinse, elution, and regeneration) must be balanced with the loading cycle time. The intent of this cesium removal process is to remove sufficient cesium so that the residual effluent stream can be turned into a low level waste glass form suitable for a contact handling facility. To meet this requirement, approximately 99.98% of the cesium must be removed from the feed stream and recovered in the eluant.

Prior testing had indicated that several cationic resins had sufficient selectivity to successfully remove cesium from sodium- and potassium-bearing streams (2). DOE selected SuperLig® 644, produced by IBC Advanced Technologies of American Fork, Utah. The selectivity (as measured by the relative distribution coefficients between resin and solution) of this resin broadly is as follows: $K_{d,H} \sim K_{d,Cs} > K_{d,K} > K_{d,Na}$. Cesium is extracted under caustic conditions and eluted under acidic conditions. It is important to note that the resin contains three different ion exchange sites, only one of which is selective for

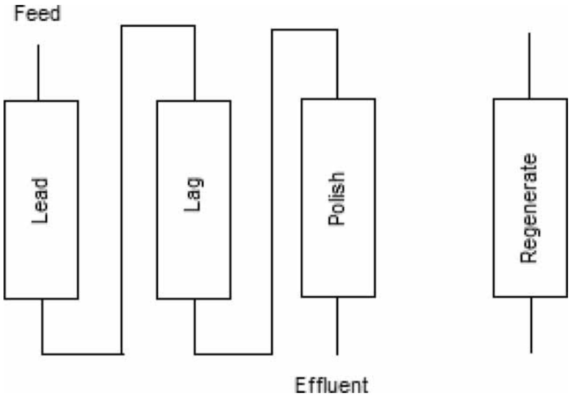

Figure 2. Planned operational sequence for WTP ion exchange system.

cesium. The other two hold primarily sodium ions under the ion exchange conditions of interest. As such, eluted resin will generally be referred to as hydrogen form resin while the regenerated resin will generally be referred to as sodium form resin.

BACKGROUND

Figure 3 shows a typical breakthrough curve for a nominal (Type III) simulated waste feed at the end of the expected resin lifetime (after greater than 10 load/elute cycles) (3). Note that during these tests, repeated cycling of the resin resulted in gradual loss of resin bed capacity. Inspection of this figure indicates that the resin has the capacity to treat approximately 96 bed volumes of feed material (as defined by Eqn (1). The capacity (in terms of bed volumes processed) is defined by the integrated volume to the left of the breakthrough curve:

$$Capacity = \sum_{i=1,n} \left(1 - \frac{y_{i-1} + y_i}{2}\right) \cdot (x_i - x_{i-1}) \qquad (1)$$

where y_i is the ith cesium breakthrough measurement (in fraction breakthrough) and x_i is the bed volumes processed.

Further inspection of the figure indicates that the mass transfer zone (from minimal breakthough–[40 BV for this illustration] to 99% breakthrough [140 BV for this illustration]) is approximately 100 bed volumes. However, to ensure that the breakthrough curve is contained within the lag column, the exit criteria for the lead column was selected as 50% breakthrough

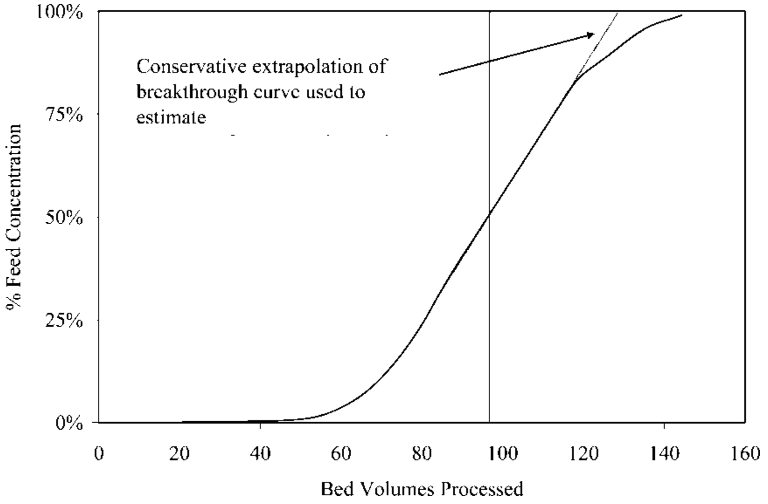

Figure 3. Typical breakthrough curve after repeated 10 load elute cycles.

(95 BV for this illustration). Thus, using the 50% breakthrough criteria, the "effective" mass transfer zone is 55 bed volumes. Based on this information, the designers for the waste treatment plant then conservatively designed the column to accommodate a longer 75 bed volume effective mass transfer zone to ensure that the mass transfer zone is contained within one column length. That is, when the exit concentration from the first column is 50% of the feed concentration, the exit concentration from the second column will not have reached measureable breakthrough.

As indicated above, for continuous loading of the feed, the time duration of the loading segment must be equal to or greater than the time of the sum of post loading steps. Figure 4 demonstrates the timeline of a typical series of loading and post loading steps. The total required cycle time for resin regeneration is approximately 25.5 hours. Designers conservatively set the allowable resin regeneration cycle to 33 hours, this allows adequate time to ensure that the bed can be replaced periodically without a significant disruption to processing.

Figure 5 shows a typical elution curve (corresponding to the loading curve shown in Fig. 3). The first two bed volumes of acid are associated with the conversion of the cationic resin from the sodium form to the hydrogen form, indicated by the pH of the effluent from the column. Immediately after conversion to the hydrogen form, the resin gives up 99+% of the cesium over the next three bed volumes processed. The additional bed volumes of elution are required to remove sufficient residual cesium to allow reuse of the resin bed in the polishing position.

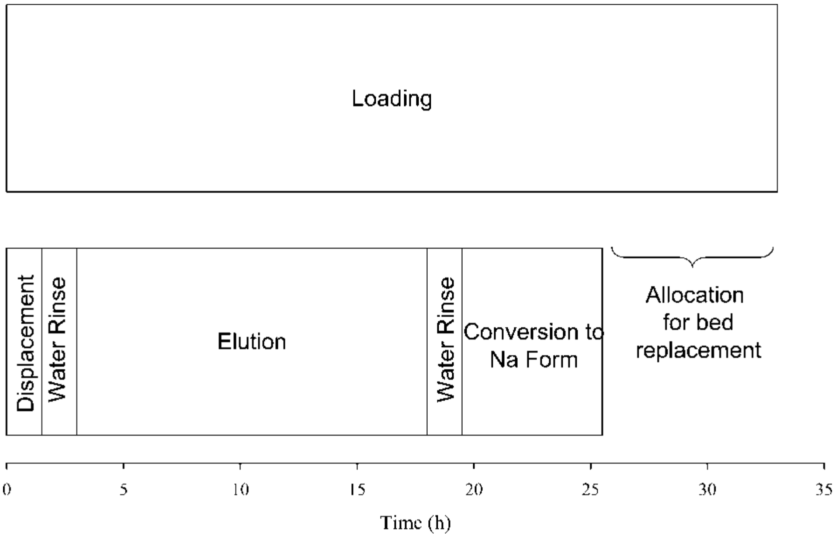

Figure 4. Nominal time sequences for various process steps.

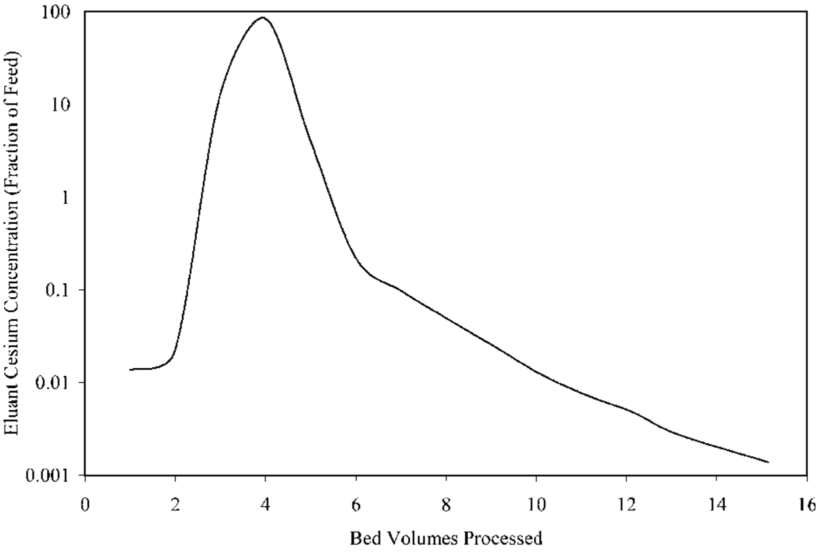

Figure 5. Typical elution curve.

The purpose of this work was to confirm the adequate performance of a cesium ion exchange resin using actual waste samples from the Hanford High Level Waste tank farm. In particular, the objective was to confirm selected design criteria for the proposed Waste Treatment Plant currently under construction on the Hanford Nuclear Reservation.

An experimental plan was established to confirm that resin performance met the selected design criteria using actual waste samples obtained from the Hanford Tank Farm with at least one waste sample from each of the three classes of waste. Of particular importance was confirmation of the resin capacity for treatment of the selected wastes and the ability of the regenerated resin to perform in the lag/polish column position. To this end the mass transfer zone of the resin for the selected waste samples was evaluated.

EXPERIMENTAL

SuperLig® 644 was obtained from IBC of American Fork Utah from Batch 010319SMC-IV-73. A 212 to 425 μm particle size fraction was obtained by dry sieving. The test configuration consisted of two 1.46 cm ID columns. The valve systems for the columns were arranged such that columns could alternate between the lead and lag position so that the columns could be regenerated independently. Each column was loaded with approximately 10 mL of resin as expanded in the Na form (2.4 gram of sodium form resin on a dry weight basis). After loading, the resin underwent a pretreatment consisting of conversion to hydrogen form and back to sodium form.

Prior to the start of testing with actual waste samples, a simulant experiment was performed with AW-101 simulant. Tests were then performed with actual waste samples from AP-101, AN-102, AZ-102, AZ-101 (twice) and AP-104 (twice) (4). Table 1 provides a listing of key components present in each of these feed materials.

A total of eight column experiments were performed with this set of ion exchange columns. The columns were rotated in position between each ion exchange test (with the exception of the first simulant test). The column in the load position for the first test (designated column A) was in the lead position 5 times while the other column (designated column B) was in the lead position for the other 3 column tests. Table 2 lists the testing conditions for each of the column tests.

There was insufficient waste volumes to run all of these tests to 100% breakthrough. The AZ-101 and AP-104 feeds were each used for two tests, as indicated by the two feed rates. Two of the tests (AZ-102 and the first AZ-101) were run to greater than 50% breakthrough to give an accurate measure of the effective mass transfer zone. The first AP-104 test was terminated prior to any significant breakthrough and did not provide any information on capacity/effective mass transfer zone.

RESULTS

Capacity

Table 2 provides a summary of the capacities as defined in Equation (1) (as measured in BV of feed processed) for this resin with these waste samples. Note that for most of these samples, a linear extrapolation of the loading curve to 99% loading was employed. This provides a conservative estimate of the total capacity of the resin since more cesium could be taken up by the resin at higher (~90% of the feed) cesium concentrations than this

Table 1. Major cations and anions present in feed solutions

Component	AW-101 simulant	AP-101	AN-102	AZ-102	AZ-101	AP-104
Na (*M*)	5.0	4.97	4.8	4.6	4.85	4.92
K (*M*)	0.43	0.76	0.024	0.17	0.12	0.046
Cs (*M*)	6.4E-5	3.68E-5	5.99E-5	5.21E-4	4.48E-4	6.88E-5
Feed type	II	II	III	I	I	III
Feed rate (BV/h)	2.6	2.8	2.7	1.4	1.5/2.6	2.6/3.9
Lead column	A	A	B	A	B/A	B/A

Table 2. Summary of capacities as defined in equation 1

	AW-101 simulant	AP-101	AN-102	AZ-102	AZ-101	AZ-101	AP-104
Lead column	A	A	B	A	B	A	A
Waste type	Type II	Type II	Type III	Type I	Type I	Type I	Type III
Capacity (BV)	190	145	204	94	121	121	198
Feed rate (BV/h)	2.6	2.8	2.7	1.4	1.5	2.6	2.6/3.9
Design Required Capacity (BV)	75	75	55	25	25	25	75
Mass transfer Zone (to 50% C/C_o)	NM	33 BV[a]	NM	15 BV	24 BV	38 BV*	31 BV*

[a] Estimated based on extrapolation of the breakthrough curve to 50% breakthrough.

analysis would imply as seen in Fig. 3. Inspection of this table indicates that all of the tests demonstrated resin capacity in excess of that required to support the design assumptions. In fact, the data suggest that the resin has at least nearly double the capacity required to meet the design criteria.

Effective Mass Transfer Zone

The lengths of the "effective" mass transfer zones were roughly estimated based on the initial breakthrough, the capacity measured in batch contacts and a straight line extrapolation of the breakthrough curve. For the purposes of this work this is adequate to assess the mass transfer performance of this resin. Effective mass transfer zone lengths (here defined as initial to 50% breakthrough) were measured or estimated for 5 of the tests. These effective mass transfer zones were within the targets for type I, II and III feeds. As indicated in Table 3, shorter effective mass transfer zones were observed for the slower processing rates. Also note that because the effective mass transfer zones are small relative to the capacity of the resin, the length of the effective mass transfer zones will not limit operation of the process as the lag column will not experience initial breakthrough prior to full loading of the lead column.

Elution Performance

Also of interest was the extent of elution required to allow re-use of the resin bed as a polishing column. On six different instances, columns were eluted and

Table 3. Lag column effluent cesium concentration

Cesium loaded on resin (moles Cs/g resin)	Elution volume BV	Lag column effluent Cs concentration (M)	Lag column designation
2.23E-05	19.3	8.50E-09	A
1.88E-05	18.9	7.44E-09	B
2.20E-04	21.3	3.72E-08	A
2.38E-04	14.3	3.66E-07	B
2.04E-04	15.9	1.10E-07	A
2.43E-04	42.7[a]	6.88E-09	B

[a] Achieved through two elution steps. Note that a small amount of cesium was loaded onto the column between these two elution steps.

then placed into the lag position as the polishing column. Table 3 summarizes the load/elution conditions for these six transitions and the resultant effluent concentration from the lag column immediately after being placed in service as the lag column.

Inspection of this data suggest that the lag column effluent concentration is a strong function of both the eluant volume and the quantity of cesium loaded on the resin bed. This data can be fit with a simple empirical logarithmic model and the result is given in Equation (2). Based on a statistical analysis of the data, the confidence interval on this model is greater than 95%.

$$\ln(c_{\text{effluent}}) = -4.88 - 0.123 * \text{BV}_{\text{Elution}} + 1.05 * \ln(C_{\text{resin}}) \qquad (2)$$

Based on this equation and the maximum cesium tolerated in the effluent, it is possible to estimate the minimum quantity of eluant volume required. Table 4 provides this summary.

Inspection of this table indicates that the estimated eluant requirements are well within the design requirements of 15 BV. It is important to note that this condition is based on the minimum acceptable processing conditions. As shown in Table 2, it is possible to load more than the designated volume of

Table 4. Elution requirements

	Type I	Type II and Type III
Maximum cesium concentration in feed (M)	5.21E-4	6.88E-5
BV Loaded/cycle	25	75
Dry bed density (g/mL)	0.24	0.24
Total cesium loaded (moles Cs/g resin)	5.4E-5	2.1E-5
Elution effluent Cs target (*M*)	8.3E-8	2.1E-8
Estimated elution BV	9	12

feed material onto the resin, however this then requires more time for elution and as such, an infinite number of loading/elution combinations exists. The significance of this analysis is that at the design basis conditions the process is balanced and is anticipated to perform as expected. Figure 6 highlights this point. Figure 6 contains a plot of the required and available elution times for Type I and Type II and III wastes. Inspection of the graph indicates that increasing the loading time (BV processed) provides more than ample time to achieve the required elution. In fact, increasing the loading time above the baseline loading cycle appears to significantly increase the operating margin of the regeneration cycle. Note, however, that due to the significant radiation field that will generate from loaded resin, optimization of the resin cycle will have to account for the impact of extended loading cycles on resin lifetime. Insufficient data was available from this set of tests to adequately determine the extent of radiolytic and chemical degradation occurring over the limited number of load/regenerate cycles that were performed.

CONCLUSIONS

A series of actual waste ion exchange tests were performed to evaluate the performance of a selected ion exchange resin over a range of planned feed streams. These tests demonstrated that the selected cationic resin–SuperLig

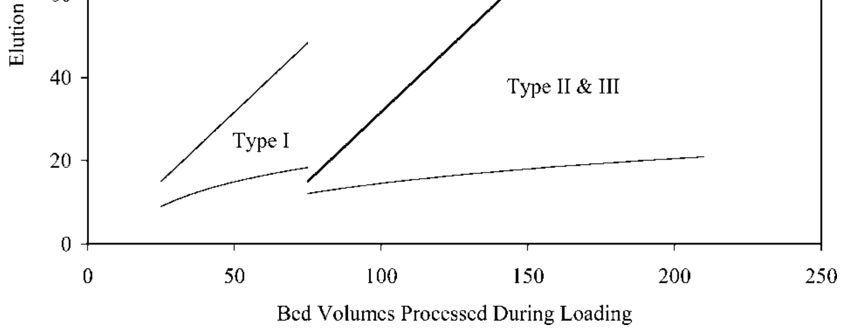

Figure 6. Available and required elution time as a function of bed volumes processed.

644®, has more than adequate resin capacity to treat each of the three proposed feed streams. Further, tests indicate an acceptable mass transfer zone for each of three types of feed material, and that the elution of the resin could be accommodated within the design criteria for the proposed Waste Treatment Plant. Future work should address the optimization of the load/elute cycles and evaluation of the chemical and radiolytic degradation of the resin performance upon extended operation beyond the 4 cycles performed during this test program.

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