663070

DP-1388

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PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION UNDER CONTRACT AT(07-2)-1

Printed in the United States of America

Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161

Price: Printed Copy $4.00; Microfiche $2.25

663070

DP-1388
Distribution Category UC-70

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by

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Publication Date: July 1975

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ABSTRACT

A process for separation and concentration of ^{137}Cs from Savannah River Plant waste supernate by using *Duolite* ARC-359 cation exchange resin was demonstrated with both synthetic and actual wastes. Tracer-level studies showed that *Duolite* resin efficiently sorbed cesium from a solution with composition expected for the plant process and that the resin could be cycled (load-elute-regenerate) repeatedly without damage. In column tests using actual waste supernates, >99.99% of the ^{137}Cs was removed. Column throughput was correlated with feed composition by an empirical model. ^{137}Cs, eluted from the *Duolite* columns, was sorbed on zeolite for final solidification in concrete or glass. The overall volume reduction factor from cesium-salt solution to cesium-zeolite product is about 1400.

Linde AW-500 zeolite sorbed cesium directly from waste salt solutions. Direct sorption is not recommended because 40 times more cesium-zeolite would be produced than by the *Duolite* process.

CONTENTS

LIST OF TABLES AND FIGURES

REMOVAL OF CESIUM FROM SAVANNAH RIVER PLANT WASTE SUPERNATE

INTRODUCTION

Studies are in progress at the Savannah River Laboratory (SRL) to determine methods for possible solidification and storage of Savannah River Plant (SRP) high-level liquid radioactive waste. In one of several options under consideration, solidified waste would be stored in an on-site, retrievable surface storage facility until the waste could be shipped to a federal repository.

An earlier report[1] described in detail the origins and characteristics of SRP waste, the criteria for acceptable solid forms, and potential solid forms for SRP waste. That study was used to formulate the conceptual process outlined in Figure 1.

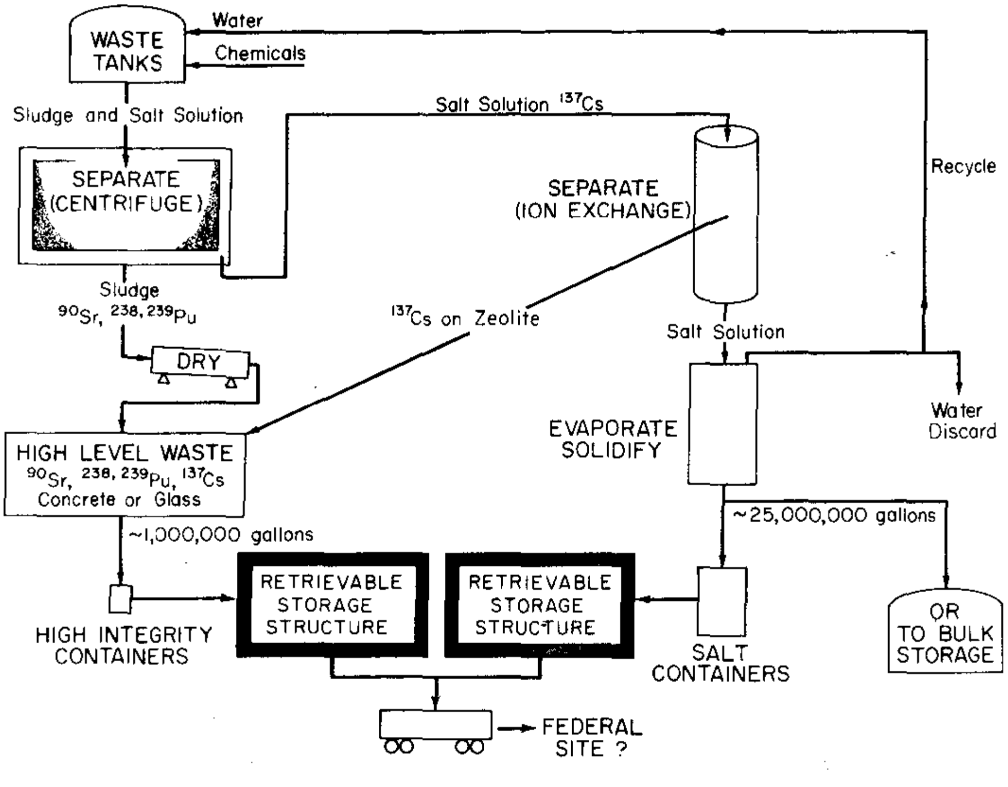

FIGURE 1. Conceptual Waste Solidification Process

SRP waste, stored in underground tanks, consists of an alkaline salt solution, solid salt cake, and an insoluble sludge layer containing large amounts of iron, aluminum, manganese, uranium, and many other elements. In the conceptual process, waste would be removed from a tank by dissolving the salt cake with water and sluicing the slurry of sludge and solution from the tank. Sludge and solution would be separated by centrifugation and filtration. ^{137}Cs, the principal biological hazard in the solution, would be removed by an ion exchange process and sorption on zeolite. Sludge would be washed to remove salts, dried, and blended with the cesium-zeolite for solidification into either concrete or glass.

The studies described in this report demonstrate the feasibility of removing ^{137}Cs from supernate by ion exchange and subsequent sorption on zeolite. Future reports will describe removal of other nuclides, such as ^{90}Sr and plutonium, from supernate, solidification of sludge and zeolite in concrete and glass, and demonstrations of other parts of the conceptual process.

SELECTION AND PROPERTIES OF ION EXCHANGE RESIN

*Duolite** ARC-359, a phenolsulfonic acid cation exchange resin, was selected for cesium removal from SRP waste. Workers at Hanford[2] found *Duolite* to be

- Reasonably selective for cesium
- Easy to elute
- Stable in alkaline solutions
- Undamaged by expected radiation exposure

Sodium-form, 20-50 mesh, *Duolite* resin (analytical grade) was used for the work described in this report. Total ion exchange capacity was determined by equilibrating 1 gram of *Duolite* resin, as received, with 1M NaOH, washing, and equilibrating with standard acid. The residual acid was then titrated with standard base. Duplicate determinations of resin capacity were 2.33 and 2.36 meq/g.

Bulk density of wet resin was determined to be 0.63 g/cm^3 for the Na^+ form and 0.74 g/cm^3 for the NH_4^+ form. The ammonium form was obtained by equilibrating resin with 2M $(NH_4)_2CO_3$ - 2M NH_4OH.

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* *Duolite* is a trademark of Diamond Shamrock Chemical Co.

EFFECTS OF FEED COMPOSITION ON CESIUM SORPTION

Although Hanford results[2] indicated that *Duolite* ARC-359 resin sorbs cesium from solutions of widely varying compositions, quantitative understanding of feed composition effects is important for a plant process. Sodium, which competes with cesium for ion exchange resin sites, and hydroxide can affect cesium sorption; both are present in significant concentrations in plant waste. A systematic study of effects of these ions on cesium sorption was made.

Measured distributions of Cs^+ between resin and solutions containing 1 to 10M Na^+ and 0.5 to 5M OH^- were used to develop an empirical model that can be used to predict breakthrough of Cs^+.

Distribution Coefficients

The distribution of Cs^+ between solution and resin was determined in batch equilibrium experiments. The distribution coefficient is

$$K_d = \frac{(\overline{Cs})}{(Cs)_{eq}} = \left[\frac{(Cs)_o - (Cs)_{eq}}{(Cs)_{eq}}\right] \left[\frac{\text{ml of solution}}{\text{g of resin}}\right]$$

where $(\overline{Cs})$, $(Cs)_o$, and $(Cs)_{eq}$ are the cesium concentrations in the resin phase, initial solution, and equilibrated solution, respectively. K_d is closely related to the number of column volumes of feed required to produce 50% breakthrough[3] (cesium in instantaneous effluent = 50% of cesium in feed).

K_d was determined in solutions containing 2×10^{-4}M Cs^+, 10^5 dis/(min)(ml) ^{137}Cs, and varying concentrations of NaOH and $NaNO_3$. At ambient temperature, 10 ml of solution was equilibrated by shaking overnight with 1 g of *Duolite* ARC-359 resin (Na^+ form). As shown in Table 1, K_d decreased as Na^+ increased; K_d increased as OH^-/NO_3^- increased at constant Na^+.

Empirical Model

Values of K_d can be empirically fitted to the equation

$$\log K_d = n \log [Na^+] + \text{constant}$$

Logarithmic plots of K_d against [Na^+] are linear with a slope of n. Plots of the data in Table 1 are shown in Figure 2. For simple ion exchange replacement of Na^+ by Cs^+, n = -1. However, the measured slope is steeper than -1 and becomes steeper as OH^- increases. At high OH^- concentrations, K_d is enhanced, possibly because anion-cation associations in the concentrated test solutions affect the activity coefficients of Na^+ and Cs^+ differently. However, no completely satisfactory explanation of these results can be presented at this time.

Column Test

The model was evaluated in a laboratory test in which a solution containing 4.75M $NaNO_3$, 1M NaOH, 2 x 10^{-4}M Cs^+, and 10^5 dis/(min)(ml) ^{137}Cs was passed through a 25-ml column (1.3-cm diameter) of *Duolite* ARC-359 resin at 1 column volume (CV) per hour. Breakthrough was 50% at 30 column volumes. The product of K_d times the resin bulk density is approximately equal to throughput at 50% breakthrough.[3] For 5.75M Na^+ and 1M OH^-, K_d obtained from Figure 2 is 39 (39 x 0.63 = 25 CV, in reasonable agreement with the experimental result of 30 CV). The relation between feed composition and column performance was further confirmed in tests with actual waste supernates (p 13).

TABLE 1. Effects of Feed Na^+ and OH^- on Cs^+ Sorption by *Duolite* ARC-359 Resin

Na^+, M	OH^-, M	K_d
1	0.5	343
2	0.5	142
3	0.5	78
4	0.5	57
5	0.5	40
1	1.0	462
2	1.0	199
3	1.0	100
4	1.0	70
5	1.0	45
2	2.0	371
3	2.0	176
4	2.0	110
5	5.0	347
6	5.0	205
7	5.0	132
8	5.0	90
9	5.0	66
10	5.0	48

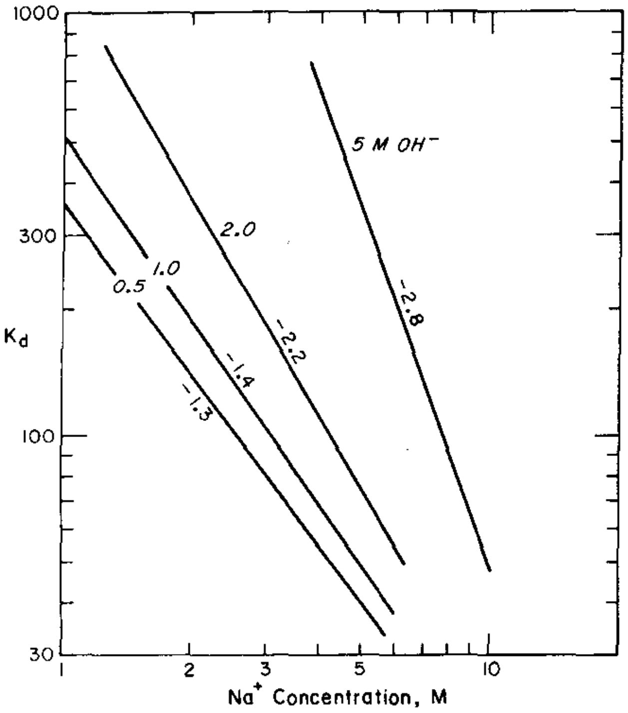

FIGURE 2. Cesium-*Duolite* Distribution Coefficients

TRACER-LEVEL COLUMN TESTS

Column tests were made using ^{137}Cs tracer to determine cesium decontamination factors (DF)* as a function of column throughput and to determine the effects of several sorption-elution-regeneration cycles on cesium DF.

Simulated waste supernate with a composition (Table 2) similar to that expected for dissolved salt cake was used in these tests.[1]

TABLE 2. Composition of Simulated Supernate

Component	*Concentration, M*
$NaNO_3$	2.2
$NaNO_2$	1.1
NaOH	0.75
$NaAlO_2$	0.5
Na_2SO_4	0.3
Na_2CO_3	0.3
$CsNO_3$	0.0002

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* $DF = \dfrac{^{137}\text{Cs in feed}}{^{137}\text{Cs in effluent}}$

The apparatus (Figure 3) used in these tests consisted of two 1.3-cm-ID glass columns filled with 25-ml of Na^+-form, 20-50 mesh, *Duolite* ARC-359 cation exchange resin. The same type of apparatus was used in column tests using actual SRP waste supernate (page 13).

Simulated waste containing actual plant waste supernate as a tracer, 4.4×10^5 dis/(min)(ml) ^{137}Cs, was pumped downflow through the columns at 1 CV/hr.* Effluent from the first column was monitored with a GeLi gamma detector; ^{137}Cs activity in the monitor loop was calculated hourly by a PDP-15 computer. Effluent from the second column was collected with a fraction collector and subsequently analyzed for ^{137}Cs by gamma counting.

Figure 4 shows typical breakthrough curves from both columns. ^{137}Cs could not be detected in effluent from Column 2 with less than 25 CV (625 ml) feed throughput.

After 25 to 30 CV of feed was passed through the columns, they were washed downflow with 5 CV of distilled water at 1 CV/hr. The columns were then heated to 55°C and eluted upflow at 1 CV/hr until all of the ^{137}Cs was removed. ^{137}Cs in the eluate was monitored with the GeLi detector and PDP-15 computer. Figure 5 shows a typical elution curve. Very little ^{137}Cs eluted initially; its concentration in the eluate then increased abruptly and declined. After 12 CV of elutriant was pumped through the columns, ^{137}Cs was not detectable in the eluate.

Figure 5 also shows the results of one test in which eluate samples were analyzed for sodium. About 25% of the Na^+ preceded the Cs^+; this sodium fraction could be recycled to feed and thus increase the Cs^+/Na^+ ratio in the eluate. This could reduce the total volume of cesium-zeolite by about 25%.

After elution, the resin was regenerated at ambient temperature with 5 CV of 2M NaOH. After seven complete load-elute-regenerate cycles were made, there was no noticeable deterioration in resin performance.

These tests showed that ^{137}Cs can be efficiently removed from simulated waste supernate by sorption on *Duolite* ARC-359 resin. An overall DF of $>10^4$ was obtained with 25 CV of feed (625 ml) using the two-column arrangement. Higher DFs could be attained by using additional columns.

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* CV = 1 column volume, 25 ml.

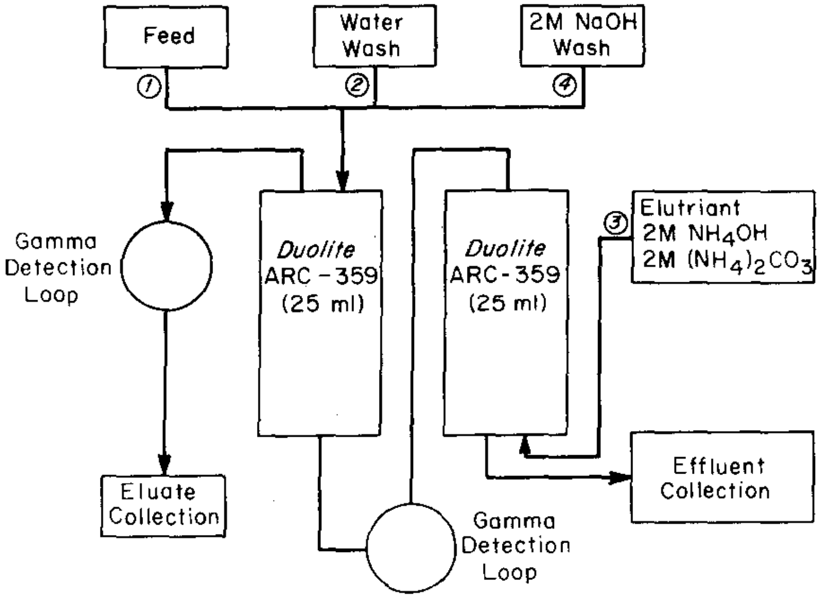

FIGURE 3. Apparatus for Column Tests

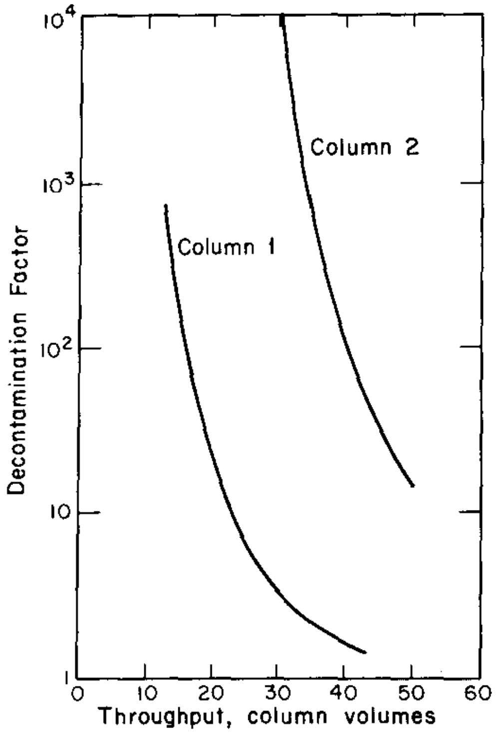

FIGURE 4. Sorption of Cesium on *Duolite* Columns in Series

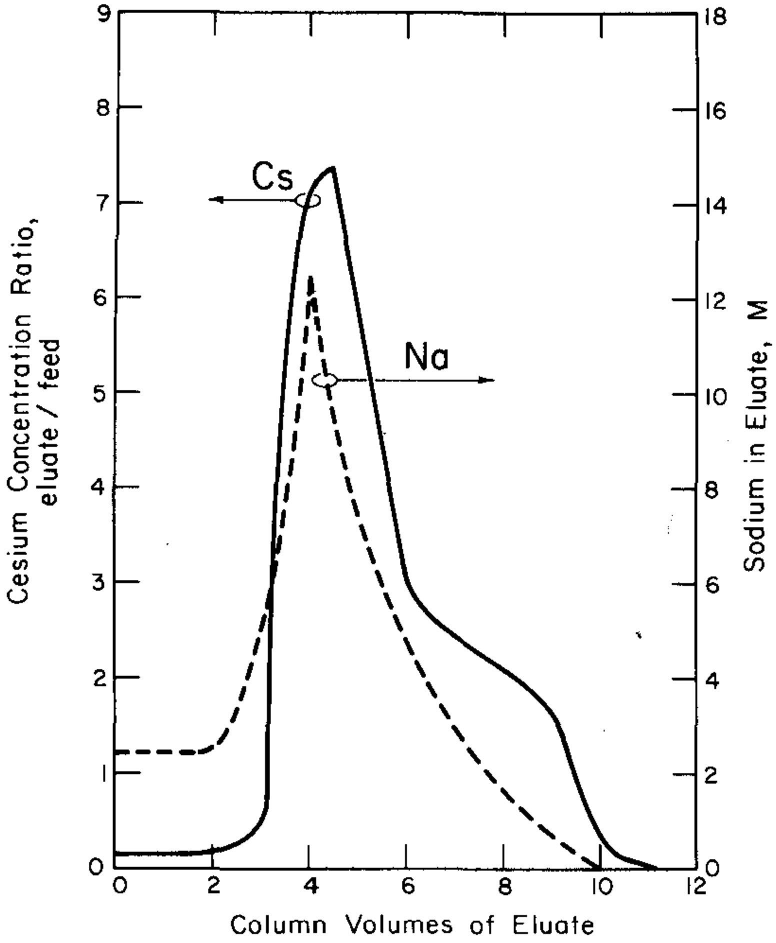

FIGURE 5. Elution of Cesium and Sodium from *Duolite* Resin

EFFECT OF POTASSIUM ION ON CESIUM SORPTION

Studies at Brookhaven National Laboratory using *Linde* AW-400* zeolite showed that potassium interfered severely with cesium removal.[4] Similar tests with *Duolite* resin were therefore made. Addition of 0.01M KNO_3 to simulated supernate had very little effect on cesium removal; 0.06M KNO_3 reduced by about 20% the number of column volumes that could be processed. Plant wastes are expected to average 0.01M K^+. Thus, K^+ should not significantly interfere with cesium removal by *Duolite* resin.

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* *Linde* is a trademark of Union Carbide Corporation.

COLUMN TESTS WITH PLANT WASTE

Based on the previous tests with synthetic waste supernate, column tests were made to determine ^{137}Cs DF using actual plant waste. Because waste supernate composition varies from tank to tank, samples from four waste tanks were obtained.

Supernate samples from F- and H-Area SRP waste tanks were obtained to verify that *Duolite* ARC-359 could efficiently sorb cesium from actual plant waste. These samples contained high ^{137}Cs activity and concentrations of other ions and radionuclides spanning the range of concentrations of waste tank supernates.[5] Compositions of samples obtained are given in Table 3. Tank 24 supernate was diluted to 1.5 times its original volume with water before processing in an attempt to match its concentration to that of simulated supernate. The other samples were untreated.

Tests were conducted in a shielded cell facility with an apparatus similar to that described on page 10. Supernates were drawn through a coarse (ASTM 40-60) filter funnel to remove possible particles and then pumped at 1 CV/hr (25 ml/hr) through the columns by CCl_4 displacement from the feed reservoir. Pressure drop across the columns was normally about 1 psig. The pressure drop did not increase during these four tests; therefore, it is unlikely that the number of resin fines increased significantly. This indicates that the resin was not damaged by the very alkaline supernates or by radiation.

In each test, about 600 ml of supernate was pumped downflow through the columns. The resin was then washed with 3 CV of water at 1 CV/hr, and then 7 more CV at 4 CV/hr. This ensured that all $NaAlO_2$ present in the feed was removed from the resin. Otherwise precipitation of $Al(OH)_3$ could occur during elution and plug the column.

TABLE 3. Composition of SRP Waste Supernate

Concentration, M									*Activity, dis/(min)(ml)*			
Tank	Na^+	OH^-	NO_3^-	NO_2^-	$Al(OH)_4^-$	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}	^{137}Cs (10^{10})	^{106}Ru (10^{8})	^{90}Sr (10^{5})	Gross α (10^{4})
1	11	7.6	1.8	3.4	0.8	0.01	0.13	0.06	1.01	1.2	4.3	8.0
2	13	9.4	1.4	2.3	0.9	0.01	0.09	0.07	1.27	1.1	1.8	0.7
10	9	3.6	3.0	2.2	1.3	0.02	0.18	0.01	0.45	1.7	0.9	0.5
24	4	2.6	1.5	0.5	0.3	0.01	0.13	0.02	0.07	<0.1	0.6	0.5

Figure 6 shows ^{137}Cs decontamination factors obtained in these tests. In all of the tests, ^{137}Cs DFs of 10^4 to 10^5 were obtained with 10 CV of feed. After 10 CV, DFs for the four supernates are in the order expected according to their Na^+ concentration. Tank 24 supernate, which had the lowest Na^+ concentration, gave the highest DF, followed in sequence by tanks 10, 1, and 2. This result agrees with predicted feed concentration effects (page 7).

There is no theoretical reason why the curves in Figure 6 should intersect. Accepted ion exchange models predict concentric curves as the feed composition changes.[3,6] The intersections of the curves at high DFs are possibly a result of ^{137}Cs cross-contamination between tests.

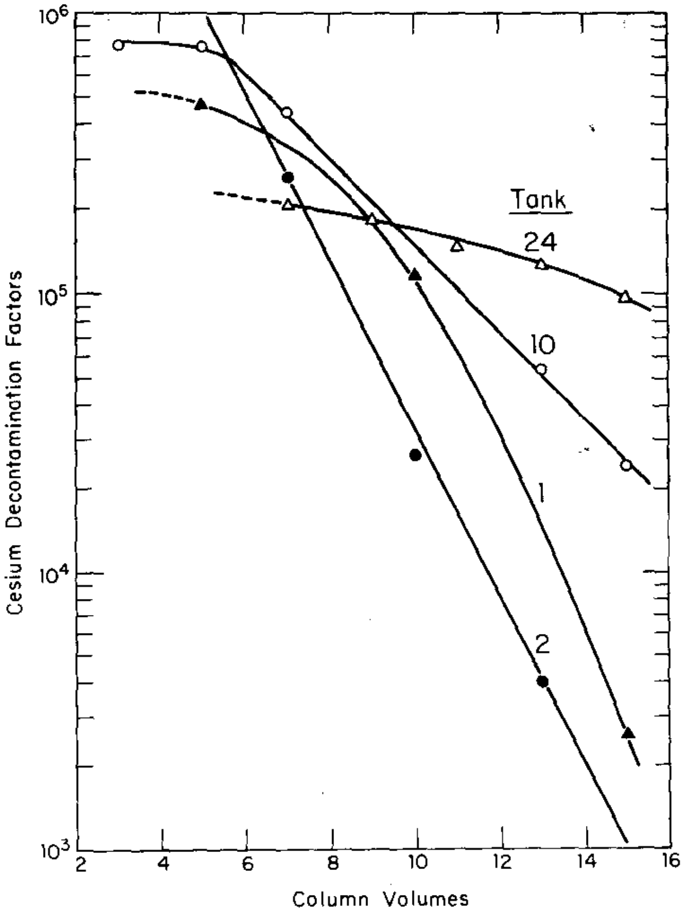

FIGURE 6 Cesium Decontamination Factors for SRP Waste Supernate

In all of the tests, ∿95% of the ^{137}Cs was eluted with 8 CV of 2M $(NH_4)_2CO_3$ - 2M NH_4OH elutriant. Elutions (1 CV/hr) were performed at 25 and 55°C; no differences in elution characteristics were noticed, and ambient temperature elution will suffice for the plant process. Figure 7 shows a typical elution curve.

After elution of ^{137}Cs, the resin was regenerated at ambient temperature, downflow, with 10 CV of 1M NaOH at 1 CV/hr.

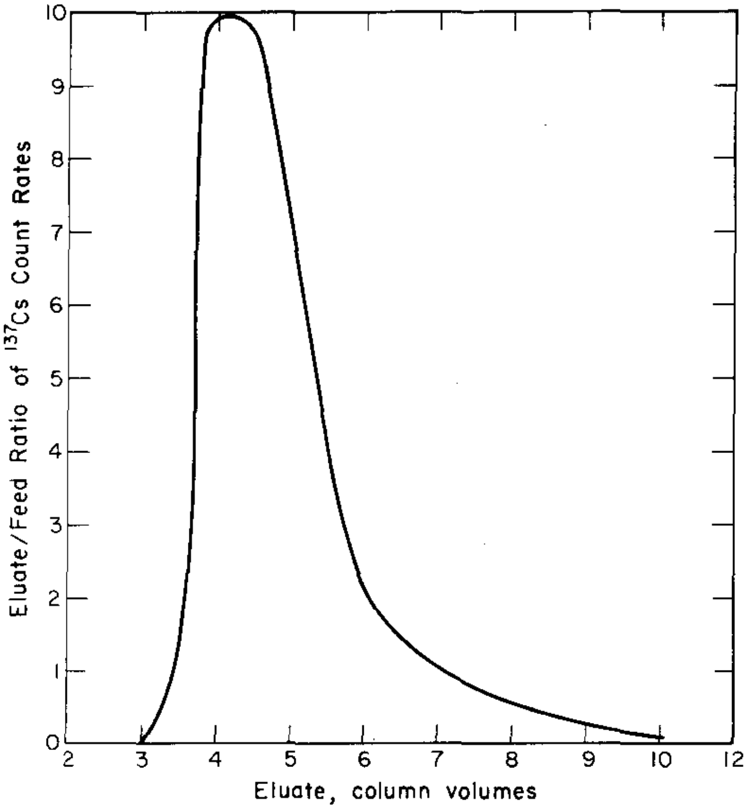

FIGURE 7. Elution of ^{137}Cs at Ambient Temperature

DISSOLUTION OF *DUOLITE* RESIN

Spent resin from the *Duolite* columns must be disposed of by some method. Residual radioactivity on the ion exchange resin may preclude disposal in the burial ground. Because of this, a test was made to determine whether *Duolite* ARC-359 resin would dissolve by a known procedure.[7]

In this test, *Duolite* resin was digested in 0.1M HNO_3 - 6% H_2O_2 at 80°C; the resin completely dissolved in about 1 hr. After neutralization, this aqueous solution would be suitable for disposal with other liquid waste in the carbon steel waste tanks used at SRP.

SORPTION OF ELUTED CESIUM ON ZEOLITE

Eluate from the *Duolite* resin will be concentrated by steam-stripping NH_3 and CO_2 and evaporating the remaining solution to approximately 2M Na_2CO_3 - 0.007M Cs. Cesium from this solution is sorbed on zeolite for subsequent mixing with sludge and solidification in glass or concrete. This sorption step was demonstrated by tracer-level column tests.

To ensure conversion to Na^+ form, 25 ml (19.5 g) of *Linde* AW-500, 20-50 mesh zeolite was washed with 3M $NaNO_3$. The resin was rinsed with water and transferred to a 1.3-cm-ID column. 2M Na_2CO_3 - 0.007M $CsNO_3$ [with 1.7×10^5 dis/(min)(ml) ^{137}Cs] was pumped downflow through the column at 1 CV/hr at ambient temperature. 2% breakthrough (Cs in column effluent = 2% Cs in feed) occurred after 70 CV; 20% breakthrough occurred after 76 CV. The zeolite was then washed with water at 1 CV/hr. Effluent ^{137}Cs was reduced to 1% of that in the Na_2CO_3 feed after 7 CV of wash water and was not detectable after 10 CV.

These results show that it will be possible to sorb at least 70 CV of concentrated *Duolite* column eluate on one zeolite column. After an initial water wash, further contact with water will not leach appreciable ^{137}Cs from zeolite.

DIRECT CESIUM REMOVAL BY ZEOLITE

Because direct sorption of ^{137}Cs on zeolite would eliminate the *Duolite* columns, reduce costs, and also remove some plutonium and ^{90}Sr from waste supernate, tests were made to determine the feasibility of this approach.

Equilibrium Tests

Batch equilibrium measurements of the cesium-zeolite distribution coefficient, K_d, showed that *Linde* AW-500 zeolite sorbs cesium from wastes of varied concentration.

Results shown in Figure 8 fit the equation

$$\log K_d = n \log [Na^+] + \text{constant}$$

and show the same trends as in Figure 2. Increased hydroxide concentration initially favors cesium sorption; however, zeolite is damaged by >5M hydroxide. 0.01M K^+ does not affect cesium sorption.

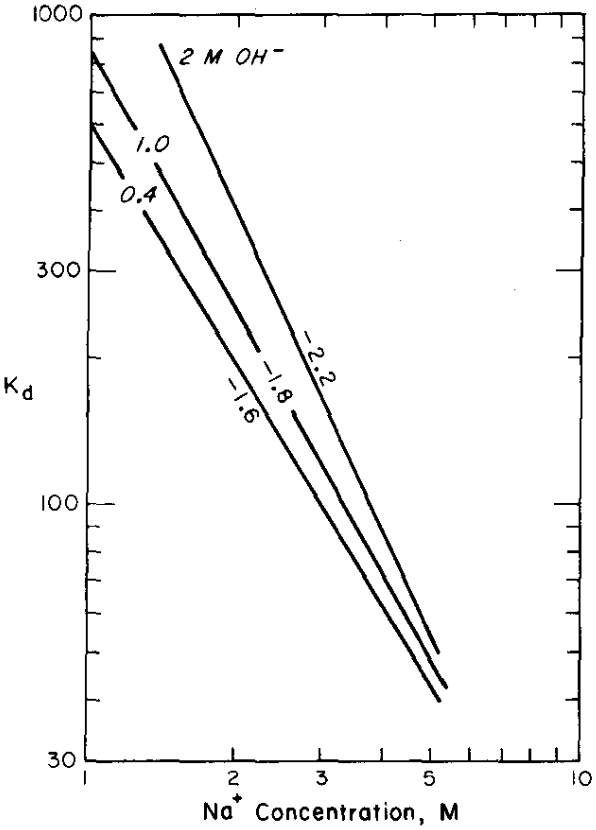

FIGURE 8. Cesium-Zeolite Distribution Coefficients

Column Tests

Tests were made to determine the number of column volumes (CV) of synthetic supernate that could be processed through a zeolite bed before cesium breakthrough. In a plant process, supernate would flow through two zeolite columns in series. At cesium breakthrough, the first column would be emptied. The partially loaded secondary column would replace the primary column, which would be loaded with fresh zeolite and used as the new secondary column.

In the tests, two 1.3-cm-ID columns were filled with 25 ml of *Linde* AW-500, 20-50 mesh zeolite, which was converted to Na^+ form by washing with 10 CV of 1M NaOH. Synthetic supernate containing 10^5 dis/(min)(ml) ^{137}Cs tracer was pumped downflow through the columns at 1 CV/hr. Initially with 2 fresh columns, detectable ^{137}Cs (DF = 10^4) appeared in the effluent after 71 CV. Using a partially loaded primary column reduced throughput to about 35 CV for DF = 10^4. Column efficiency was not improved by either decreasing the feed rate or increasing column temperature.

These tests showed that cesium can be removed from waste supernate by direct sorption on zeolite. However, since only ∿35 CV of supernate can be processed before zeolite is replaced, direct sorption would give a cesium concentration factor of about 35. The *Duolite* process would give a cesium concentration factor of about 1400 (20 by ion exchange and evaporation and 70 by sorption on zeolite). Because of the 40-fold increase in the amount of zeolite to be solidified in concrete or glass, direct sorption of cesium on zeolite is not recommended.

CONCLUSIONS AND FUTURE WORK

Tests demonstrated ^{137}Cs removal from SRP waste supernate by the two-column *Duolite* ion exchange process. Feed composition parameters affecting cesium sorption were identified and fitted to an empirical model. The entire ion exchange cycle was demonstrated successfully with both synthetic and actual waste. Direct sorption of cesium on zeolite is feasible, but this would generate 40 times more zeolite to be solidified in concrete or glass.

In future work, studies will be made to remove residual nuclides, such as plutonium and ^{90}Sr, from SRP waste supernate. Also, effects of flow rate and column diameter will be determined. Finally, waste supernate separated from actual waste sludge by centrifugation and filtration will be processed.

ACKNOWLEDGMENT

Unpublished results of J. S. Buckingham, Atlantic Richfield Hanford Company, were used as a basis for the beginning of this work. His work and suggestions are gratefully acknowledged.

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