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DEVELOPMENT OF AN IMPROVED ION-EXCHANGE PROCESS FOR REMOVING CESIUM AND STRONTIUM FROM HIGH-LEVEL RADIOACTIVE LIQUID WASTES

by

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DEVELOPMENT OF AN IMPROVED ION-EXCHANGE PROCESS FOR REMOVING CESIUM AND STRONTIUM FROM HIGH-LEVEL RADIOACTIVE LIQUID WASTES

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Processes are being developed to solidify and isolate the biologically hazardous radionuclides from approximately 23 million gallons of alkaline high-level waste accumulated at the Savannah River Plant. The waste consists mainly of a liquid supernate, a damp salt cake, and a gelatinous, insoluble sludge. The reference solidification process involves separation of the water soluble fraction (supernate) from the insoluble fraction, removal of cesium and traces of strontium from the supernate, incorporation of the sludge and the radionuclides from the supernate in glass, and incorporation of the residual salt in concrete.

A previously reported process for treating the supernate consisted of sorbing the cesium and strontium separately on different ion exchange resins.[1] Cesium was sorbed on Duolite* ARC-359, a phenol methylene sulfonate resin. Strontium was sorbed on Amberlite** IRC-718, an iminodiacetate resin. The cesium was eluted with a mixture of ammonium carbonate and ammonium hydroxide, and the strontium was eluted with an EDTA solution. The ammonium carbonate in the eluate was thermally decomposed, leaving a solution that was principally sodium carbonate containing the radionuclides. These were further concentrated by sorption in a zeolite column. The zeolite and the EDTA-strontium eluate were combined with the sludge prior to calcination and incorporation into glass.

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* Trademark of Diamond Shamrock.
** Trademark of Rohm and Haas.

A new process, now being developed, involves sorbing cesium on phenolic resins that contain no strongly acidic sulfonate groups. These resins can then be eluted with formic acid which is not possible with Duolite ARC-359. Duolite CS-100, a phenol-carboxylate resin, and Duolite S-761, a phenolic resin containing methylol groups, were studied initially. CS-100 was chosen for further development because of its greater breakthrough capacity and because it also sorbs strontium to some extent. Strontium sorption by CS-100 was not sufficient to eliminate the need for Amberlite IRC-718. However, the latter resin can also be eluted with formic acid because its functional groups are weakly acidic.

Formic acid elution permits several options to be considered. The preferred option consists simply of mixing the eluate with sludge prior to calcination. Sodium formate, which is formed when the resins in the sodium form are eluted, decomposes rapidly between 450°C and 500°C and will be destroyed in either the calciner or the melter. The resulting sodium oxide would be incorporated into glass. About 60% of the required sodium for glass production would come from this source. Another attractive option is to elute most of the sodium prior to elution of cesium and strontium. This is possible because only small amounts of the radionuclides are eluted until most of the sodium has been removed. They are then eluted rapidly (~99% within 1 column volume of eluate). The sodium formate would be recycled to feed. Both of the above options would eliminate the ammonium carbonate recovery step, would eliminate the zeolite sorption step, and simplify the process by using the same elutriant for both resins. Another possibility is the destruction of formic acid and sodium formate with ozone or hydrogen peroxide prior to vitrification. The separation of sodium formate by sorption of cesium and strontium on zeolite prior to vitrification is also possible. One of these steps might be necessary if the presence of too much formate should cause difficulties with operation of the calciner or melter.

Advantages of the New Process

The principal advantage of the new process is the elimination of a number of process steps. This reduces the amount of canyon space required for ion-exchange to one-third to one-half of its original value and thereby may significantly reduce the cost. A further advantage is that it is more compatible with the production of alternative waste forms than is the present process. Several of these waste forms require incorporation of the radionuclides in a mineral matrix; large amounts of sodium and silica interfere with the production of the most desirable minerals. The product of the new process contains no silica (from zeolite) and potentially much less sodium than the older one.

Basis of the Process

The sorption of cesium on Duolite CS-100 and Duolite S-761 was studied in connection with a continuing investigation of the causes of the high specificity of phenolic resins for cesium. Roberts and Holcomb[2,3] have studied the sorption of cesium and strontium by CS-100 from low-level, alkaline (pH 12) waste waters and their elution with dilute nitric or hydrochloric acid. The sorption of these fission products from highly alkaline high-level waste by weak-acid phenolic resins and their elution with weak acids, such as formic acid, have not previously been studied. The following sections describe the sorption and elution characteristics of Duolite CS-100 and Duolite S-761 for cesium, the sorption and elution characteristics of CS-100 for strontium, and the elution characteristics of Amberlite IRC-718 for strontium.

Absorption Studies

Equilibrium distribution coefficients (K_d) for cesium between the resins and solutions containing 4.75M $NaNO_3$, 1M NaOH are shown in Table 1. The dry H^+ form was used as the mass basis for K_d. The sorption characteristics of Duolite CS-100 and S-761 are very similar to the sorption characteristics of ARC-359; the distribution coefficients were a very sensitive function of cesium concentration. Both weak acid resins were as good for cesium sorption as the best samples of Duolite ARC-239 previously tested when K_d's were compared at a cesium concentration of 2×10^{-4}M. At cesium concentrations lower than 2×10^{-4}M, the sorption characteristics of CS-100 and S-761 were better than ARC-359.

Breakthrough curves were run using columns containing 25 mL of resin when in equilibrium with 1M NaOH. The feed was designed to simulate the supernate expected in actual plant operation. The feed contained: 5.65M Na^+, 2.36×10^{-4}M Cs^+ (with ^{137}Cs tracer), 1.67M NO_3^-, 0.94M NO_2^-, 1.67M OH^-, 0.52M AlO_2^-, 0.21M CO_3^{2-} and 0.22M SO_4^{2-}. Columns were fed at a rate of 1.25 column volumes per hour. The results of these tests are shown in Figure 1. The ratio of the ^{137}Cs activity in an effluent sample to that in the feed (C/C_0) is plotted as a function of throughput in column volumes (CV). Results of the tests show that CS-100 is better than S-761 as far as breakthrough capacity is concerned. The principal reason for the superiority of CS-100 over S-761 is its greater bulk density in equilibrium with feed solutions.

Figure 2 shows the results of column tests in which $^{85}Sr^{2+}$ was sorbed on CS-100 from simulated supernate run at 1.25 CV/hour. Although strontium sorbs well as indicated by the midpoint of the breakthrough curve at greater than 30 CV, the rate of sorption appears to be too slow for this resin to be effective in removing strontium in the plant process; the initial breakthrough occurred after only 5 CV.

Elution Studies

Although the sorption characteristics of Duolite CS-100 and S-761 are not greatly different from ARC-359, they offer a distinct advantage in elution. Because these resins are weak acids, they can be eluted by a stronger acid. However, ARC-359, which contains a strongly acidic sulfonate group, can be eluted only with a high concentration of an ion, such as ammonium ion, that tends to replace cesium. Formic acid was chosen for study as an elutriant because: (1) it is a weak-acid that is relatively strong and therefore should convert the resin to the hydrogen form; (2) it should not damage the resin as would nitric acid if it were used; (3) it would have a smaller impact on subsequent operations in the vitrification plant than any other organic acid; (4) it should not interfere with the ion exchange process if some were recycled; and (5) it would be fairly easy to destroy in aqueous solution if that were necessary.

Table 2 gives the results of measurements of distribution coefficients of $^{137}Cs^+$ tracer between several resins and a solution containing 2M $(NH_4)_2CO_3$ - 1M NH_4OH and one containing 2M formic acid. These studies were made to indicate conditions that will be favorable for elution; low K_d's indicate favorable conditions. The results indicated that: cesium should elute from CS-100 and S-761 more efficiently with ammonium carbonate than from ARC-359. Cesium should elute from CS-100 and S-761 with 2M formic acid more efficiently than with ammonium carbonate, but it should not elute well from ARC-359 with formic acid. The elution performance of S-761 should be slightly better than CS-100 with both elutriants.

Tests of the elution performance of the resins were run in 1 cm ID columns with the feed introduced down-flow. The columns were eluted down-flow at a rate of 1.25 CV/hour. Down-flow elution was used because it was easier experimentally and because it is a more severe test of elution performance than the up-flow elution used in the reference process.[1] The eluates were collected in 0.25 CV fractions. Figure 3 shows the results of a test of cesium elution from CS-100 with 2M formic acid. One curve gives the % of the total cesium activity originally on the column eluted with each of the 0.25 CV fractions, the other is the cumulative % eluted. Virtually all of the activity was removed within 4 CV, but very little was removed in the first few fractions (1.75 CV); most of the activity is then removed in the next 1 CV. It appears that very little cesium is removed until after the bulk of the sodium has been eluted and the resin is converted to the hydrogen form. It should therefore be possible to separate much of the sodium from the cesium should it prove desirable. The elution curve for cesium from Duolite S-761 with 2M formic acid was nearly the same as that from the CS-100. Elution of Cs from Duolite CS-100 with 2M $(NH_4)_2CO_3$ - 1M NH_4OH resulted in a broader curve than that shown in Figure 3.

Elution curves were also run for $^{85}Sr^{2+}$ from CS-100 and Amberlite IRC-718 with 2M formic acid as an elutriant. Strontium elutes well from both resins with formic acid and the shapes of the curves are similar to those obtained with cesium. This suggests that a sodium/strontium separation is also possible. Because formic acid can be used to elute both cesium and strontium from Duolite CS-100, and to elute strontium from Amberlite IRC-718, there does not appear to be any reason why these resins could not be mixed together in the same column, should that prove desirable.

Future Program

The gross features of the new process have been demonstrated but a few questions remain. These include: (1) Will plutonium be sorbed by CS-100? (2) How well can sodium and cesium be separated during formic acid elution? (3) What reactions will occur between formic acid or sodium formate in the vitrification process? (4) What will be the effect of sodium formate on the ion exchange sorption of strontium and cesium if some formate must be recycled? (5) How can formate ion best be destroyed in aqueous solution if the need should arise? These problems are currently under investigation.

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Table 1

DISTRIBUTION COEFFICIENTS (K_d) OF Cs^+ BETWEEN 4.75M $NaNO_3$ - 1M NaOH AND VARIOUS RESINS AS A FUNCTION OF Cs^+ CONCENTRATION

Duolite CS-100		Duolite S-761	
Equilibrium Cs^+ Conc., M	K_d	Equilibrium Cs^+ Conc., M	K_d
8.67×10^{-2}	9.41	8.65×10^{-2}	10.4
7.31×10^{-3}	15.9	7.18×10^{-3}	25.2
3.74×10^{-4}	54.0	5.90×10^{-4}	57.4
2.85×10^{-5}	159	3.22×10^{-5}	150
1.84×10^{-6}	265	2.25×10^{-6}	212
0	402	0	317

Table 2

DISTRIBUTION COEFFICIENTS (K_d) OF Cs^+ AT TRACER LEVEL BETWEEN VARIOUS RESINS AND ELUTRIENTS

	Cs^+ K_d	
Resin	2M $(NH_4)_2CO_3$ - 1M NH_4OH	2M Formic Acid
Duolite ARC-359	6.95	535
Duolite CS-100	2.13	1.45
Duolite S-761	1.24	0.78

Fig 1

ABSORPTION OF Cs⁺ ON *DUOLITE* CS-100 AND S-761 FROM SIMULATED SUPERNATE

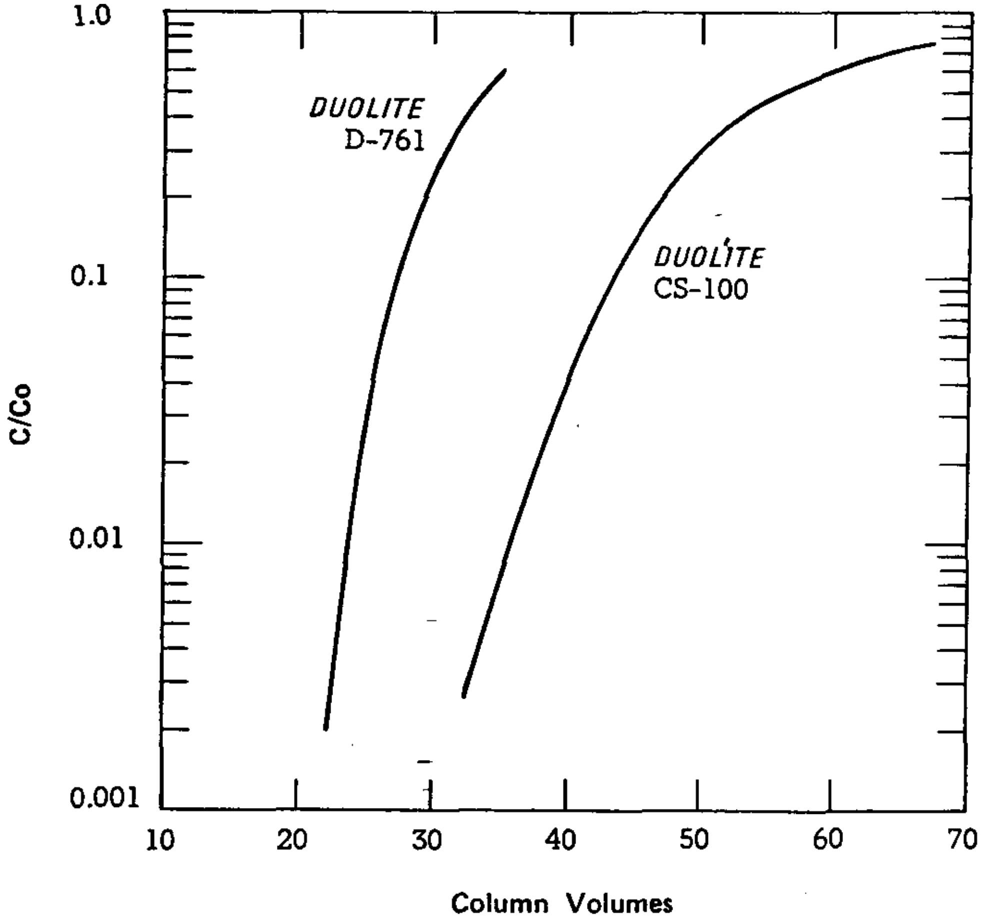

Fig 2

ABSORPTION OF Sr^{2+} FROM SIMULATED SUPERNATE BY *DUOLITE* CS-100

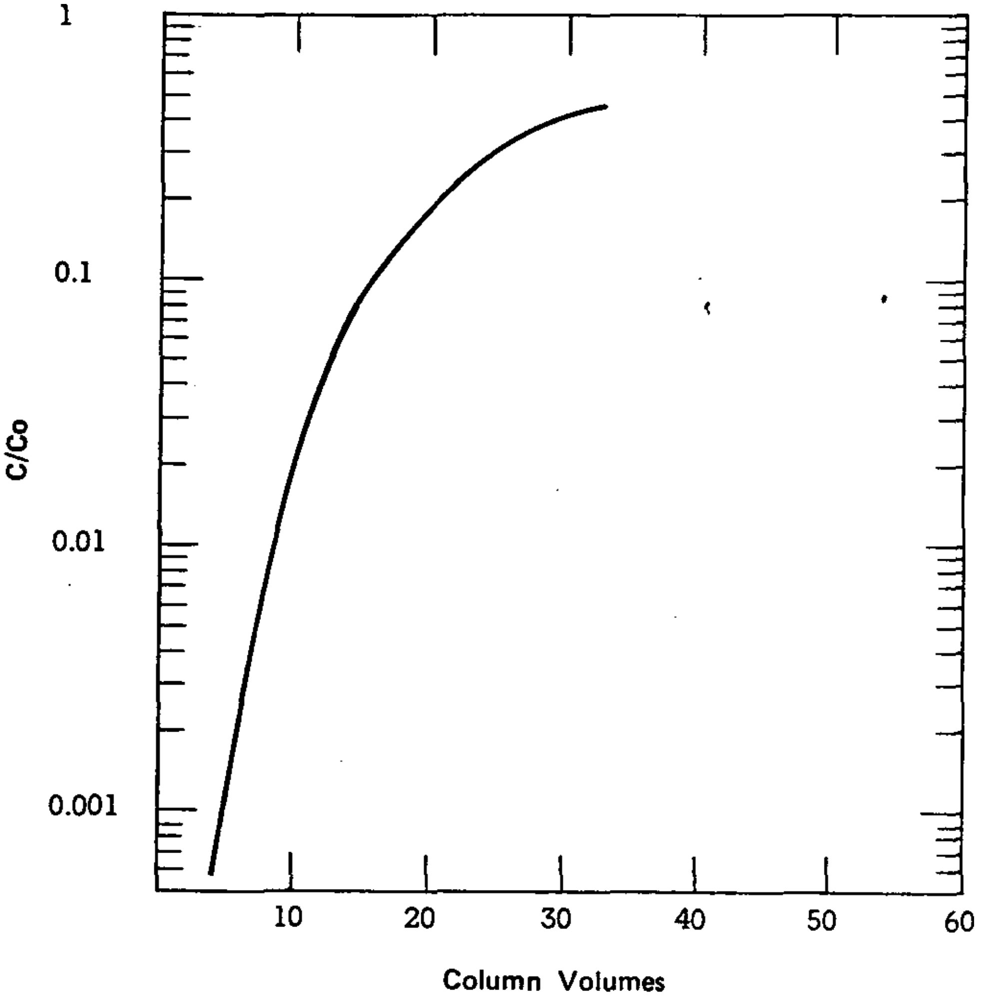

Fig 3

ELUTION OF Cs FROM *DUOLITE* CS-100 WITH 2M FORMIC ACID