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

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by

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A paper prepared for presentation to the
*International Symposium on the Scientific
Basis for Nuclear Waste Management*,
Boston, Massachusetts,
November 27-30, 1979,
and for publication in the *Proceedings*.

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INTRODUCTION

A process is now being developed to solidify and isolate the biologically hazardous radionuclides from approximately 20 million gallons of alkaline high-level radioactive waste accumulated at the Savannah River Plant (SRP) and now being stored in large underground tanks. The waste consists mainly of liquid waste supernate, a damp sodium salt cake, and a gelatinous, insoluble sludge. The process involves dissolving the salt cake in water, separating it from the sludge, washing the sludge, and adding the washings to the dissolved salt cake. The aqueous portion is then treated by ion exchange to remove cesium-137, plutonium, and other actinides, and soluble strontium-90. After elution, the cesium and actinides are concentrated by evaporation and immobilized on zeolite. The strontium is similarly concentrated. The cesium-zeolite and strontium concentrate are combined with washed sludge for calcination. The calcined mixture is melted with a glass frit to form a leach-resistant glass. The final glass is encased in 0.8 m³ metal canisters. The decontaminated aqueous waste is concentrated by evaporation and returned to cleaned underground tanks for storage as a salt cake.

Bench-scale demonstration and initial process studies of the cesium ion-exchange step were reported by Wiley (1978) at the Savannah River Laboratory (SRL). Decontamination factors

* The information contained in this article was developed during the course of work under Contract No. AT(07-2)-1 with the U. S. Department of Energy.

(concentration in feed/concentration in product) of over 100,000 were reported. The tests were made in shielded remote cells ("high-level caves") on actual wastes from tanks, adjusted to standard reference compositions, and slurried with radioactive sludge to assure equilibrium composition. The resin used was Duolite® ARC-359, a gel-type sulfonated phenol-formaldehyde cation exchange resin which had proved in the past (Knoll, 1963) to be particularly selective to cesium at high pH, even in solutions with large sodium concentrations. Duolite ARC-359 resin is a refined version of Duolite C-3 resin used in some of the early tests.

Additional work is now going forward to develop the basic data needed for the design of plant columns and to demonstrate reliable, day-to-day performance. The features of the process are (1) two resin columns in series, with continuous monitoring of cesium concentrations between the column (cesium is too dilute in the second column effluent in the face of relatively high concentrations of short-lived ruthenium-106), (2) downflow feed (exhaustion) and upflow elution and regeneration, followed by water rinses as shown in the schedule in Table 1, (3) periodic backwashing to remove fines, correct channeling, and to regrade the resin, and (4) valveless operation to provide a low-maintenance installation for remote canyon (protective barrier) operation. The countercurrent mode produces better decontamination and uses less eluant/regenerant than cocurrent operation (Abrams, 1973). Separate elution and regeneration are required according to the simplified equations:

where R is the resin. The eluant is a solution of ammonium hydroxide and ammonium carbonate with a pH of 9.5.

Table 1. Cesium Ion Exchange Cycle

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Step	Time, hr	Column Vol/hr ^a	Column Volumes ^b	Direction	Stream
Load	20	1	20	Down	Supernate
1st Rinse	3	1	3	Down	Water
Elution	10	1	10	Up	2M NH ₄ OH; 2M (NH ₄) ₂ CO ₃
2nd Rinse	3	1	3	Up	Water
Regeneration	5	1	5	Up	2M NaOH
Standby	<u>3</u>				
Total	44				

^aLinear velocity = 2.45 m/hr = 1 gal/(min-ft²).

^bColumn volumes are based on a single column.

Included in the program were (1) developing equilibrium and diffusion data on Duolite ARC-359 resin and correlating the effects of hydroxyl and cesium ion concentrations, (2) operating two 7.5-cm-diameter x 1-m-high columns to determine effects of process variables such as feed rate and composition, resin batch, and back-washing, and (3) developing scale-up principles necessary for design of plant columns.

ABSORPTION OF SODIUM IONS

The elution step with the ammonium hydroxide-carbonate solution not only removes the cesium from the columns, but also most of the sodium, and converts the resin to the ammonium form. Characterization of the process, therefore, requires knowledge of the amount of sodium on the resin before elution.

Duolite ARC-359, a phenol methylene sulfonic acid type resin, has two types of replaceable hydrogens; strong acid hydrogens associated with the sulfonic acid group, and very weakly acidic phenolic hydrogens. The capacity of the sulfonic acid hydrogens was determined to be 2.5 gram-equivalents per kg of resin. The excess capacity due to the phenolic groups was measured by equilibrating samples of resin originally in the sodium sulfonate form with sodium hydroxide solutions. The amount of acid consumed when the resins were returned to that form was determined with a mixture of sodium nitrate and dilute nitric acid. Excess capacities

were found to be quite high (Table 2) and are more than double those of the sulfonate groups at high hydroxide concentrations.

Table 2. Excess Capacity of Duolite ARC-359 Resin in Alkaline Solutions

NaOH Concentration, Moles/Liter	Excess Na ⁺ on Resin, Equivalents/kg of Dry Resin ^a
0.0047	0.776
0.0114	1.58
0.0492	2.02
0.0987	2.59
0.1926	3.13
0.4972	3.77
0.9643	4.46
1.975	5.31
4.979	7.97

^aOne kg of dry resin has an expanded bulk wet volume of 340 mL in 1 molar NaOH.

EQUILIBRIUM CESIUM DISTRIBUTION

Previous work by Wiley and Wallace (1975) showed that the distribution coefficient, K_D , for cesium between Duolite ARC-359 resin and aqueous solutions was a function of the sodium ion and hydroxide ion concentrations. The present work revealed that the cesium K_D is also a sensitive function of the cesium concentration.

Distribution coefficients were measured at room temperature for solutions of nearly constant sodium ion concentration (about 5.75M) but varying hydroxide (0 to 5.75M) and cesium (10^{-9} to 0.1M) ion concentrations. Typical results are given in Figure 1. The data were fitted to equations based on models which assumed that two or three different types of sites participated in ion exchange. Each type of site was assumed to have its own capacity and selectivity. A three-site equation fit satisfactorily over the whole concentration range.

The equation derived for the three-site model is:

$$K_D = \frac{C_1 K_1}{1 + K_1 [Cs]} + \frac{C_2 K_2}{1 + K_2 [Cs]} + \frac{C_3 K_3}{1 + K_3 [Cs]}$$

where $[Cs]$ is the cesium ion concentration in solution; K_1 , K_2 , and K_3 are the equilibrium quotients (selectivity coefficients) of the three sites; and C_1 , C_2 , and C_3 are their capacities.

Fig. 1. Distribution Coefficient vs. Cesium Concentration for Duolite® ARC-359 Resin in 4.7M NaNO_3 - 0.95M NaOH .

The C and K values could be fit to sodium hydroxide concentrations between 0.56M and 5.75M (a total of 84 data points) by using a single set of capacity (C) values and assuming that each of the selectivity coefficient (K) values was proportional to the square of hydroxide concentration [OH]. The final values were

$$K_1 = 6.04 + 1.55 [\text{OH}] + 1.31 [\text{OH}]^2$$

$$K_2 = 573 + 122 [\text{OH}] + 197 [\text{OH}]^2$$

$$K_3 = 2.88 \times 10^5 + 2.52 \times 10^4 [\text{OH}] + 9.32 \times 10^4 [\text{OH}]^2$$

$$C_1 = 1.83$$

$$C_2 = 5.98 \times 10^{-2}$$

$$C_3 = 3.44 \times 10^{-4}$$

KINETICS

An important factor in the ion exchange process is the rate at which ions diffuse from solution into the resin. Diffusion parameters were measured at various flow rates by passing simulated supernate solution containing cesium-137 tracer through a shallow layer of resin (~0.05 g). Flow was stopped after a prescribed time and the residual solution was removed rapidly. The resin was then washed with water, and counted for gamma activity. The diffusion parameter (D/a^2) was calculated from the equation

$$D/a^2 = \frac{1}{\pi t} \left(1 - \sqrt{1 - \frac{\pi}{3} U} \right)^2$$

where $\underline{D}$ is the diffusion coefficient, $\underline{a}$ is the particle radius (assuming spherical shape), and $\underline{U}$ is the fractional attainment of equilibrium (Crank, 1975).

A reasonably constant value of the parameter, namely $13.2 \pm 0.7 \times 10^{-6} \text{ sec}^{-1}$ was obtained for times ranging from 0.5 to 2.0 hours for a 1978 batch of Duolite ARC-359 resin at flow rates of 0.57 and 0.88 cm/min (27 and 42 mL/hr). The parameter at a lower flow of 8.8 mL/hr was 10.2 sec^{-1} , which suggests that film-diffusion was a controlling factor in that case.

PROCESS STUDIES

Apparatus, Solutions, and Analysis

The equipment for doing the process studies consists of two glass columns in series (Figure 2). Above each 7.5-cm diameter x 1-m tall resin column, is a 0.9-m backwash column of the same

Fig. 2. Cesium Ion Exchange Process (Schematic).

diameter connected with it through a 2.5-cm i.d. ball-valve and pipe. The valve is closed except during backwash. The feed solution is a filtered synthetic waste liquor dosed with non-radioactive cesium-133.

Product streams are sampled in an isolation box to avoid contamination. Effluents containing less than 1 part per million cesium are analyzed by isotope dilution-mass spectrometry using a special technique within the instrument in which the cesium is separated from the large quantity of sodium salts. Solutions containing cesium above 1 ppm, i.e., mainly for first column effluent, elution, and regeneration streams, are analyzed by flame emission in a Jarrell-Ash spectrophotometer. Because the mass spectrometer detection limit is about 1 part per billion, or about 7.5×10^{-9} molar, and feed concentrations are 2 to 8×10^{-4} molar, a decontamination factor (DF) of between 10^4 or 10^5 can be demonstrated.

Three feed compositions representative of three different flowsheet conditions were used. The streams consisted mainly of solutions of sodium aluminate, nitrate, nitrite, hydroxide, carbonate, and sulfate. Traces of calcium, iron, nickel, and manganese ions were also present, but limited by solubility. Elutriant was prepared by dissolving NF-grade ammonium carbonate in water, and then adding concentrated aqueous ammonia. During the endothermic ammonium carbonate dissolution step, temperature was maintained by steam-heating.

Cesium Breakthrough Curves with 1978 Resin

Three ARC-359 resin batches (Table 3) were used. The best results were obtained with 1978 resin and equaled or exceeded Wiley's (1978) demonstration results. As shown in Figure 3, the goal of 0.01% breakthrough (DF = 10,000) was reached in Column 2 effluent after >60 column volumes (CV) throughput at feed rates of both 1 and 3 CV/hr. 53% breakthrough was obtained in Column 1 effluent after 60 CV's at 3 CV/hr, and after >60 CV's at 1 CV/hr. The 53% breakthrough point corresponded to the effective stoichiometric feed volume, i.e., the feed volume at which the resin would be in equilibrium with the concentration of cesium in the feed solution (Perry and Chilton, 1973).

Percent breakthrough ($100 \times$ effluent concentration, C /feed concentration, C_0) plots (Figure 3) as a straight line vs. throughput (column volumes of solution fed) on log-probability paper, once the effluent concentration exceeds the mass spectrometer detection limit. The straight line plot would be expected from J-function prediction as discussed by Perry and Chilton (1973). Development of a promising computer code using basic kinetic and equilibrium data is underway.

Fig. 3. Typical Breakthrough Curves for 1978 Resin.

Table 3. Resin Batches Used in Process Tests (Duolite® ARC-359)

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Mfr's Date	Vol % in Size Range, U.S. Mesh ^a		Sodium Capacity, g/L ^b	Moisture Absorption, ^b %	Comments
	>16	<50			
1973	17	2	1.08	50.4	Used by Wiley in 1975; lost cesium retention capacity between 1975 and 1979.
1977	24	0.8	1.15	51.8	Coarse resin, low cesium capacity.
1978	0	0.6	-	-	Fine resin, high cesium capacity.

^aWet analysis.^bManufacturer's data.

Column 1 breakthrough curves for 2 and 3 CV/hr were essentially the same, while 1 CV/hr performance was significantly better. Near the beginning of the runs, Column 1 effluent sometimes exceeded the detection limit, presumably because of incomplete elution after the previous run. All Column 2 results were at the detection limit for up to 60 column volumes throughput, which was as far as the runs were carried.

Resin and Feed Effects

Appreciable resin batch and feed differences were found as shown by Figure 4. The main effect was a change in resin capacity as indicated by the relative position of the 53% C/C₀ point. Little change occurs in the kinetics as indicated by the relatively constant slope of the breakthrough curve on log-probability paper. Feed 2 (5.6M Na⁺, 1.0M OH⁻) performed appreciably better than Feed 1 (5.6M Na⁺, 1.7 OH⁻) as would be expected from K_D data on the effect of increasing hydroxyl ion concentration. No difference could be found between Feeds 2 and 3, the latter containing added sodium carbonate.

The 1973 resin which had been used by Wiley (1978) in studies in shielded facilities showed less than half the capacity of the 1978 resin in the process tests. Bench-scale tests with radioactive tracer showed that the 1973 resin had deteriorated between 1975,

Fig. 4. Effect of Resin Batch and Feed Type.
Column 1 Performance: $C_0 = 2 \times 10^{-4}M$.

Feed 1. 5.6M Na^+ ; 1.7M OH^-
 Feed 2. 5.6M Na^+ ; 1.0M OH^-
 Feed 3. 5.6M Na^+ ; 1.0M OH^- ; added Na_2CO_3

the time of Wiley's tests, and 1978, the time of the process tests. The cause of the deterioration will be studied further. We are working with the resin manufacturer to explore the relation of manufacturing conditions, sodium capacity, and moisture absorption to cesium capacity. The 1977 resin showed about the same capacity as the 1973 resin, but poorer kinetics due to the coarser particle size. The reason for the initial low cesium capacity of this resin relative to the 1978 resin is still not explained.

The effect of increasing the cesium concentration in the feed was to reduce relative resin capacity. With the 1973 resin at 53% breakthrough, 19.5 CV's were achieved at $C_0 = 2 \times 10^{-4}$ molar whereas 16 CV's were obtained at $C_0 = 7.7 \times 10^{-4}$ molar. Note that the absolute quantity of cesium absorbed was higher in the higher C_0 run, namely, 0.0566 mole vs. 0.0179 mole for the two columns.

Effect of Repeat Cycles and Backwashing

Backwashing is used to eliminate airpockets and size-classify the resin, which in turn minimizes channeling. No significant effects of 7 repeat cycles or a subsequent backwash step were found with the 1977 resin at 3 CV/hr using 70% bed expansion and the separate backwash columns shown in Figure 2. Further tests of repeatability and effect of backwashing are planned. Because of the relatively small throat represented by the pipe connecting the columns, repeated expansion and settling was necessary to obtain reasonably good classification.

Because separate backwash columns also have mechanical drawbacks in hot canyon operation, combined resin-backwash columns with gravity feed will be investigated in future studies. The separate backwash columns were first selected to minimize the amount of liquids remaining above the resin between cycle steps and to permit pressure operation.

Elution

The 2M ammonium carbonate - 2M ammonium hydroxide elutriant was adopted based on earlier studies (Knoll, 1963). In one typical experiment, with 60 column volumes fed during the load step, the eluted cesium band appeared after 1 column volume of the upflow elutriant had been fed. The band peaked at 18.5 times the feed concentration (C_0) at 4.5 CV's and was down to 3.5% of C_0 at 10 column volumes. Additional elution time would reduce this further, but a balance must be struck between the time required by the whole ion exchange cycle and the purity of the decontaminated supernate.

The purity of the elutriant must also be considered because in the proposed waste processing plant the elutriant is to be recycled by evaporating the ammonia and carbon dioxide gases from the cesium concentrate. In tests to determine the required overhead purity, cesium ion was intentionally added to the elutriant. Results showed that the cesium ratio between eluate and evaporator overhead may be as low as 4000:1. Standard demisters should provide such clean-up without difficulty.

Regeneration

Complete regeneration with NaOH is important, otherwise aluminum hydroxide will precipitate. This is due to sodium aluminate in the ion exchange feed contacting ammonia residues on or surrounding the resin particles. An initially contemplated 3-CV regeneration step was insufficient to convert all the resin from the ammonium form to the sodium form. Pluggage of the column resulted from aluminum hydroxide precipitation; therefore, the length of the regeneration step was increased to 5 CV's. The extent of regeneration was followed by measuring the pH, electrical conductivity, and the concentrations of sodium and ammonium ion in the regenerant effluent. Electrical conductivity rises tenfold at the end of the regeneration step at which point the ammonium ions in the effluent have been reduced to 1% of the elutriant ammonium concentration. Electrical conductivity can be more reliably monitored than pH in the plant and will, therefore, be used to follow the extent of regeneration and prevent precipitation of aluminum hydroxide.

PROPOSED SCALE-UP TESTS

An intermediate-scale (~1/13) semiworks is now being designed to demonstrate the cesium and strontium ion exchange flowsheet and performance on an expanded scale. The particular size was selected on the basis of ability to demonstrate distributor design, valveless operation, and resin handling. The facility will use 3000 and 10,000 gallon tanks at the SRL semiworks. Startup of this unit is proposed for 1981.

CONCLUSIONS

- Methods to determine resin characteristics, i.e., cesium equilibria and diffusion rates, were developed. These parameters can now guide resin selection and aid in interpreting column performance. The K_D cesium ion concentration relation gives evidence of three different types of ion exchange sites.

- The countercurrent load/elution/regeneration cycle for the removal of cesium by ion exchange repeatedly reached the goal decontamination factor (DF) of 10,000 at throughputs up to 60 column volumes.
- Resin backwashing appears feasible, but further development of column geometry will be required.
- The proposed ammonium elutriant is satisfactory. Regeneration end-point can be controlled by electrical conductivity monitoring.

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