

ION EXCHANGE PROCESSES FOR DECONTAMINATING ALKALINE RADIOACTIVE WASTE

by

P. K. Baumgarten, M. A. Ebra,
L. L. Kilpatrick, and L. M. Lee

E. I. du Pont de Nemours & Co.
Savannah River Laboratory
Aiken, SC 29808

ABSTRACT

Improved processes for removing radioactive cesium and strontium from high-level, liquid alkaline wastes are under development at the Savannah River Laboratory. Tracer tests have demonstrated two ion exchange resins for this purpose, a weak-acid phenolic resin for cesium and a chelating polystyrene-DVB resin for strontium. Elution is with formic acid which can be added directly to a glass melter for producing glass bodies for permanent waste immobilization. A high-level shielded facility will permit process demonstration with authentic radioactive waste samples.

INTRODUCTION

An earlier process scheme^{1,2} to remove Cs-137, Sr-90 and other radioisotopes involved the ion exchangers Duolite[®] ARC-359 (Diamond Shamrock Corp., Cleveland, Ohio) and Chelex[®]-100 (Biorad Laboratories, Richmond, California). Duolite[®] ARC-359, a sulfonated phenol formaldehyde resin, removed cesium and plutonium and was eluted with $2M NH_4OH \cdot 2M (NH_4)_2CO_3$. Chelex[®]-100, a finely divided chelating polystyrene-DVB resin, removed strontium and was eluted with $1M HNO_3$. The scheme was demonstrated in high-level

cells with actual supernate samples from waste storage tanks. Cesium removal was also investigated in cold studies with intermediate-size columns 7.5 cm in diameter by 100 cm tall. Removal of 99.99% cesium and 99.9% strontium was demonstrated.

The objectives of current research are to 1) reduce canyon equipment by improved resins and elution schemes, 2) confirm decontamination factors for cesium, strontium, and other radioisotopes, 3) determine effect of recycle streams, and 4) develop engineering information for full-size columns. An improved ion exchange scheme has now been developed with Duolite® CS-100 for cesium removal³ and Amberlite® IRC-718 (Rohm and Haas Co., Pelham Manor, New York) for strontium removal. Duolite® CS-100 is a carboxylic phenol formaldehyde resin,³ and Amberlite® IRC-718 is a chelating macroporous polystyrene-DVB resin. Both resins use formic acid elution and sodium hydroxide regeneration. The use of Duolite® CS-100 instead of Duolite® ARC-359, and the use of Amberlite IRC-718 instead of Chelex®-100 have improved ion exchange cycles, provided better particle hydraulics, and simplified eluate handling with elimination of elutriant recovery equipment. The Duolite® CS-100 may eliminate a zeolite absorption step and directly provide an eluate concentrate low in sodium and compatible with glass melter operation. The glass melter is designed to produce cylindrical glass bodies for permanent storage of the nuclear waste.⁴

ION EXCHANGE PROCESS

The current ion exchange process is shown in Fig. 1. Crystallized salt in waste tanks is dissolved in water and blended with three streams: 1) liquor from dissolving $Al(OH)_3$ sludges in 6N NaOH, 2) liquor from water-washing Al-Fe-U-Ca-Mn-Ni alkaline sludges, and 3) the mother liquor from above the waste salt. The mixture is allowed to settle, and the supernatant solution is filtered to reduce suspended solids from 50 to <1 ppm. An anionic polyelectrolyte is added as a filter aid. The filtrate is passed through two cesium and one strontium ion exchange columns in series, with gamma monitoring after the first cesium column. Goal decontamination factors are 10,000 for cesium and 1000 for strontium. A water rinse follows the feed step. The decontaminated product is concentrated and mixed with sulfate-resistant concrete to produce a solid "saltcrete" composition.

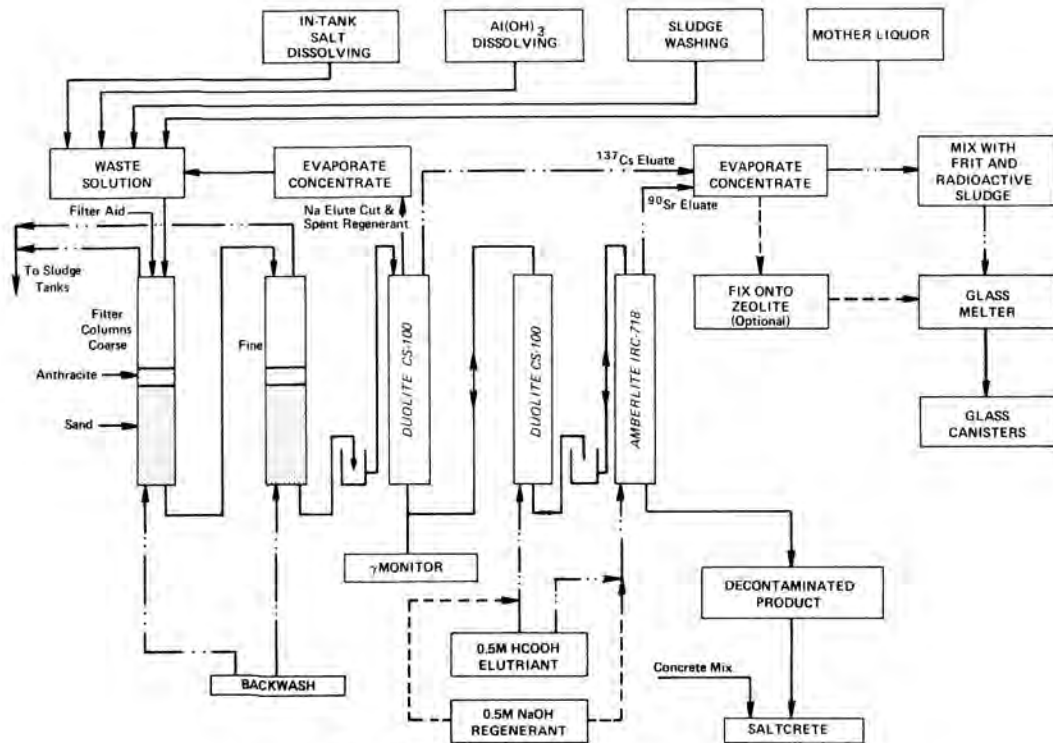


Fig. 1. Ion Exchange Process

Dilute formic acid (0.2 to 0.8M) is used as the elutriant and dilute sodium hydroxide (0.2 to 1M) as the regenerant. The feed/rinse and elute/regenerate steps are run downflow and upflow, respectively, to take advantage of the lower elutriant requirement and cleaner product afforded by countercurrent contacting.⁵ The spent regenerant, plus optionally a first portion of the eluate high in sodium and low in cesium, is concentrated and returned to tankage ahead of filtration for reprocessing. The rest of the eluate can either be sent directly to a slurry-fed glass melter, or first passed through a zeolite bed which preferentially absorbs the cesium. The zeolite is then slurried to the glass melter while the raffinate is reprocessed.

The full-size waste plant will handle about 60 L/min of ion exchange feed. Present plans call for 1.7-m-diameter ion exchange columns each with 1.8 m of resin. An average ion exchange feed composition is listed in Table I. Variations in that composition are expected due to tank-to-tank variations as well as different proportions of liquor from $Al(OH)_3$ dissolving.

CESIUM TESTS

Cesium ion exchange tests on Duolite® CS-100 have so far been done on a small scale. The tests used a single 0.9-cm-diameter column (resin volume = 30 mL), Cs-137 spiked solutions at $2.5 \times 10^{-4}M$ total cesium concentration, and a fraction collector system to catch periodic samples for gamma-ray count. Tests are planned in 7.6-cm-diameter by 240-cm-tall columns in the tracer-level facility described below. Figures 2 and 3 show performance curves for the cesium feed and elution steps. Assuming a goal of 90% retention in the first column, between 40 and 60 resin volumes (RV) of throughput can be handled at 1.6 column volumes (CV)/hour. By extrapolation to $C/C_0 = 10^{-4}$ (C/C_0 = cesium concentration in the effluent divided by cesium concentration in the feed), second column breakthrough should be between 60 and 80 CV for 40- to 60-mesh (0.25 to 0.42 mm) resin where the CV are based on a single column (1 CV = 0.5 RV). Resin performance improved significantly in going from 20- to 40-mesh (0.42 to 0.84 mm) resin to 40 to 60 mesh. Further particle size reduction did not have a consistent effect. The 60- to 80-mesh fraction did not follow the predicted pattern. This was possibly due to a lower cesium distribution coefficient K_d = (concentration on resin)/(concentration in equilibrated solution) as shown by separate measurements.

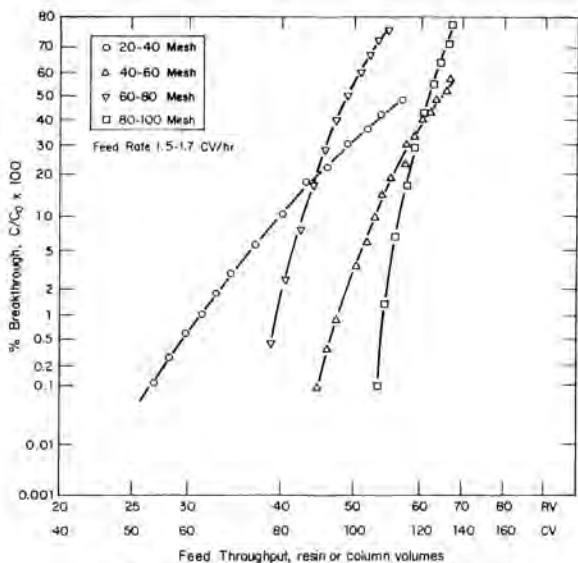


Fig. 2. Cesium Breakthrough Curves

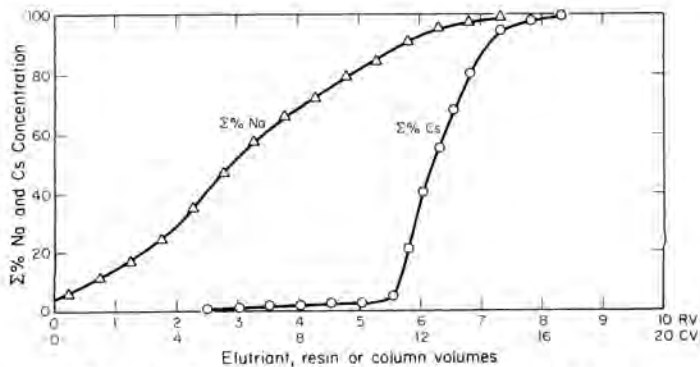


Fig. 3. Cesium Elution with 0.2M Formic Acid

Elution performance of 0.2M formic acid is shown in Fig. 3. The possibility of splitting sodium away from cesium is evident. At 11 CV throughput, 80% of the sodium is diverted to a sodium rich fraction containing less than 2% of the cesium and can be recycled. The remaining 20% amounts to about 7% of the total sodium required by the glass melter to make a leach-resistant glass. This proportion of sodium is entirely reasonable, and a separate zeolite fixation step would not be necessary.

STRONTIUM TESTS

Selection of Resin

Amberlite® IRC-718 was selected as resin for strontium removal after considering results of equilibrium measurements, availability, particle properties, and results of column tests comparing it with the previous resin, Chelex® 100. These tests were conducted at the Savannah River Laboratory (J. R. Wiley). One concern was whether other cations such as barium, calcium, and lead might interfere with strontium sorption. These cations are present in the radioactive waste at a much higher concentration than strontium. The affinity series (Table II) shows that strontium distribution coefficients are substantially higher than those of the competing ions even in the presence of sulfate and carbonate anions. The Amberlite® is readily available in this country and has satisfactory particle properties. It comes in the 16- to 50-mesh size range, flows readily because of its spherical shape, and expands only about 50% from its hydrogen to its sodium form (vs. 100% for Chelex® 100).

Experimental

Strontium tracer tests used 2 to 3 millicuries of the gamma-emitter ⁸⁵Sr (half-life = 65 days) per experiment. The tests were made in a glass column 7.6-cm I.D. by 106 cm high. A backwash column (7.6-cm I.D. x 91 cm high) above the resin column facilitated initial resin installation and provided for elimination of air pockets and fines. The two columns were connected by a 2.54-cm ball valve, which was ordinarily closed. Sodium iodide detectors monitored the strontium in both eluate and decontaminated product. The counting chamber for the eluate (44 mL) was a coiled 4-mm-I.D. Teflon® (E. I. du Pont de Nemours & Co., Wilmington, Delaware)

TABLE I

Ion Exchange Feed Compositions

	Component	Average Concentration, M	Expected Concentration Range, M
Cations	Cs ⁺ (a)	1.3 x 10 ⁻⁴ (b)	0.5 to 3 x 10 ⁻⁴
	Sr ⁺⁺ (a)	1.6 x 10 ⁻⁷ (c)	1 to 6 x 10 ⁻⁷
	Na ⁺	5.75	5 to 6
Anions	AlO ₂ ⁻	0.52	0.3 to 0.6
	ClO ₃ ²⁻	0.21	--
	NO ₃ ⁻	1.67	--
	NO ₂ ⁻	0.94	--
	OH ⁻	1.65	1.2 to 2
	SO ₄ ²⁻	0.22	--
	Specific Gravity	1.25	1.22 to 1.28
Dissolved Solids, %	28	--	

a. All isotopes.

b. 2.2 curies/gal = 2.1 x 10¹⁰ becquerel/L ¹³⁴Cs, ¹³⁵Cs, and ¹³⁷Cs.

c. 0.004 curies/gal = 3.9 x 10⁷ becquerel/L ⁹⁰Sr.

TABLE II

Amberlite® IRC-718 Affinity Series in 1.0M NaOH - 4.75M NaNO₃

Ion(a)	Concentration in Feed to Equilibrium Test		Distribution Coefficient, K _d (b)
	ppm	M	
Sr	0.8 x 10 ⁻⁶ to 80	1 x 10 ⁻¹¹ to 1 x 10 ⁻³	3250
Sr + 0.2M SO ₄ ²⁻	0.8 x 10 ⁻⁶	1 x 10 ⁻¹¹	2430
Sr + 0.2M CO ₃ ²⁻	0.8 x 10 ⁻⁶	1 x 10 ⁻¹¹	1420
Hg	31	1.5 x 10 ⁻⁴	840
Yb(c)	49	2.8 x 10 ⁻⁴	670
Ca	15	3.8 x 10 ⁻⁴	290
Ba	54	3.0 x 10 ⁻⁴	180
Ag	29	2.7 x 10 ⁻⁴	89
Cr	41	7.0 x 10 ⁻⁴	53
Cu	59	9.3 x 10 ⁻⁴	38
Pb	230	1.1 x 10 ⁻³	28

a. All added as nitrates except for Sr tracer added as 10⁻¹¹M chloride.

b. K_d = (eq/kg dry resin)/(eq/L liquid).

c. Believed representative of all lanthanides.

tube. The counting chamber for the product (1000 mL) consisted of annular and end spaces between concentric Teflon® and polypropylene closed-end tubes. The highly radioactive components of the ion exchange installation were in a ventilated enclosure. The product counter was located at some distance to reduce extraneous radiation.

Results

Breakthrough curves for different flow rates with and without sodium oxalate are shown in Fig. 4. Eighty-three CV of feed could be passed at a feed rate of 0.9 CV/hr, and 35 CV at a feed rate of 2.14 CV/hr before reaching $DF = 1000$. After breakthrough the curves are almost straight lines on log probability paper. The original flowsheet parameters were to be flow rate = 3.3 CV/hr and throughput = 40 CV, with the strontium column half the size of the cesium columns. These parameters are clearly overoptimistic and now a strontium column of the same height as the cesium columns (1.8 m) is to be used to reach $DF = 1000$ at 40 CV with flow rate = 1.7 CV/hr. The 0.0033M oxalate concentration had a negligible effect. The oxalate is one of the minor components that was expected to interfere with strontium ion exchange.

The resin was originally planned to be eluted by a 0.01M Na_4EDTA (ethylene diamine tetraacetic acid) solution with the advantages that contraction/expansion between the sodium and acid forms of the resin is avoided, and that no separate regeneration stream is required. However, preliminary runs indicated that one of the minor constituents in waste liquor, barium at $3 \times 10^{-4}M$ concentration, fouled the resin. $EDTA$ elution did not regenerate the resin after fouling, whereas either nitric or formic acid elution did. Formic acid elution is preferred and was used in subsequent runs because this acid is used for the cesium resin and because it can be directly added to the glass melter. Other cations such as $2 \times 10^{-4}M$ Pb, $5 \times 10^{-4}M$ Hg, and $1.65 \times 10^{-5}M$ Yb (representative of lanthanides) did not affect resin performance, even though their concentrations were >30 times that of the Sr ($= 5 \times 10^{-7}M$). Review of the waste composition calculation from radioactive decay indicated that barium concentration will be less than $1 \times 10^{-5}M$. Thus, barium should not interfere with performance either.

Strontium elution by formic acid was usually complete by 5 or 5.5 CV (Fig. 5). The elution peak occurred between 1.5 and 2 CV. EDTA elution was somewhat slower. No problems were encountered with the hydraulics of the resin.

INTEGRATED SUPERNATE PROCESSING FACILITY

To get a complete picture of all the processing steps involved in supernate decontamination, a high-level shielded cell processing facility was designed and built. Reasons for the new equipment were: 1) need for more representative tank samples including crystallized salt and mother liquor, 2) need to determine effect of various recycle streams such as sodium cuts from Duolite® CS-100 or zeolite, 3) need for data on trace isotopes, especially plutonium, technetium, and tin-126, and 4) new processing steps such as in-tank settling and addition of cesium and strontium-rich formic acid eluate to the glass melter. The Integrated Supernate Processing Facility (ISPF) was designed to include all the processing steps shown in Fig. 1 except for salt-crete preparation and addition to a glass melter (these can be done in adjoining cells). The facility has now been installed in two cells after extensive checkout in a mockup shop. Initial testing with an authentic waste stream is in progress.

The ISPF consists of eight 70-liter stainless steel tanks, two sand filters, four glass ion exchange columns, and a horizontal 3-kW evaporator. Decontaminated product from the first cesium column is continuously gamma-counted with a germanium-lithium detector. A multichannel analyzer with microcomputer capability allows display, analysis, data storage, and hard-copy output of the gamma spectrum. Various offline analytical procedures have been tested and are available for detailed analysis of feeds and product streams. Controls for pumps, valves, and heaters are mounted on a 0.9- by 1.8-m-wide graphics panel depicting the process. Filtration is set up for a flow rate of 100 mL/min, while cesium and strontium ion exchange are set up for 7 mL/min. Radioactive waste arrives in 40-liter containers, sufficient for three ion exchange runs at 50-CV throughput.

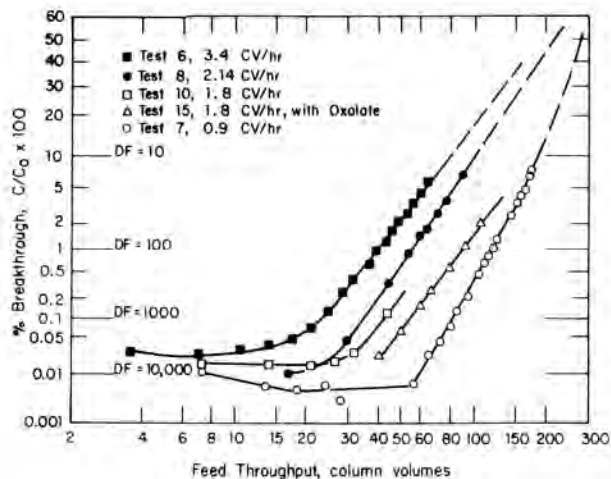


Fig. 4. Effect of Feed Rate on Strontium Breakthrough

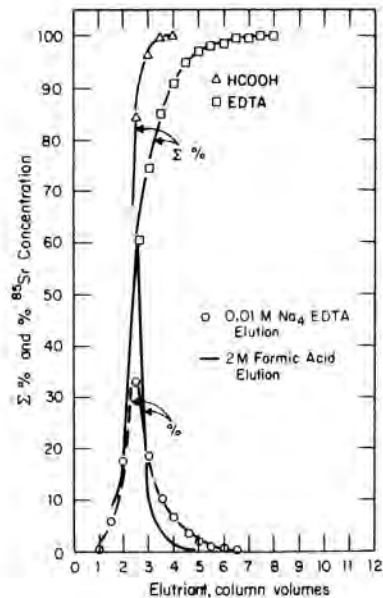


Fig. 5. Strontium Elution Curves

CONCLUSION

Several advantages result from the use of two new cesium and strontium ion exchange processes for the decontamination of high-level liquid alkaline waste. With the weak-acid phenolic resin Duolite® CS-100, up to 60 CV of feed can be processed in a 2-column train using 40- to 60-mesh particles and a flow rate of 1.6 CV/hr. Formic acid elution permits splitting off a sodium-rich stream. The eluate can then be added directly to a glass melter preparing glass bodies for permanent waste storage. As shown by full-height tracer level tests, the chelating resin Amberlite® IRC-718 satisfactorily decontaminates feed containing relatively high proportions of competing bivalent ions. The process was kinetics-limited, and a resin bed larger than previously envisioned will be necessary.

ACKNOWLEDGEMENT

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

REFERENCES

1. P. K. Baumgarten, R. M. Wallace, D. A. Whitehurst, and J. M. Steed. "Development of an Ion-Exchange Process for Removing Cesium from High-Level Radioactive Liquid Wastes," Scientific Basis for Nuclear Waste Management 2, Clyde J. M. Northrup, Jr., et al., ed., pp. 875-884, Plenum Press, Boston (1980).
2. J. R. Wiley. "Decontamination of Alkaline Radioactive Waste by Ion Exchange." Ind. & Eng. Chem., Process Des. & Dev. **17** (1), 67-71 (1978).
3. R. M. Wallace, and R. B. Ferguson. "Development of an Improved Ion-Exchange Process for Removing Cesium and Strontium from High-Level Radioactive Waste," presented at the International Symposium on the Scientific Basis of Nuclear Waste Management, Boston, MA (November 16-20, 1980).
4. M. J. Plodinec. "Improved Glass Compositions for Immobilization of SRP Waste." Scientific Basis for Nuclear Waste Management 2, Clyde J. M. Northrup, Jr., et al., ed., pp. 223-229, Plenum Press, Boston (1980).
5. I. M. Abrams. "Countercurrent Ion Exchange with Fixed Beds." Industrial Water Engineering **10**, 18-26 (1973).