

TREATMENT OF LOW-ACTIVITY-LEVEL PROCESS WASTEWATERS BY CONTINUOUS COUNTERCURRENT ION EXCHANGE

R. Hall, J. S. Watson, and S. M. Robinson
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831-6044

ABSTRACT

A mobile pilot-scale continuous countercurrent ion-exchange (CCIX) system is being operated at the Oak Ridge National Laboratory (ORNL) for the treatment of wastewaters that contain predominantly calcium, sodium, and magnesium bicarbonates and are slightly contaminated with ^{90}Sr and ^{137}Cs radioisotopes. A demonstration study is being conducted to evaluate the near-steady-state performance and feasibility of a pilot-scale CCIX column for the selective removal of strontium from wastewater. Test results show that the process removes strontium sufficiently from the wastewater to permit discharge while significantly reducing the volume of secondary waste generation. CCIX has the potential for effective use in several applications; however, it has not been frequently utilized by industries to date. The CCIX system could offer an economical alternative for decontamination of wastewaters containing trace amounts of contaminants prior to discharge into the environment.

This paper discusses (a) application of the Thomas model for predicting breakthrough curves from ion exchange column tests, (b) methods for scaleup of experimental small-scale ion-exchange columns to industrial-scale columns, and (c) methods for predicting effluent compositions in a CCIX system.

INTRODUCTION

Alternative methods for reducing secondary waste generation at the Oak Ridge National Laboratory (ORNL) are being developed. Process wastewater that is slightly contaminated with ^{90}Sr and ^{137}Cs radioisotopes has been routinely treated at the ORNL Process Waste Treatment Plant (PWTP) using precipitation and filtration followed by fixed-bed ion-exchange columns containing strong-acid cation resin (1). The objective is to decontaminate process wastewater sufficiently for release to the environment while concentrating the radioactive materials (^{90}Sr and ^{137}Cs) into an immobilized solid waste form that can be safely stored with minimum surveillance.

New federal regulations on discharge limits for ^{90}Sr and ^{137}Cs along with higher costs for disposal of the concentrated secondary liquid low-level radioactive wastes (LLW) produced during resin generation have prompted efforts to improve the efficiency of the PWTP. Therefore, extensive research, development, treatability studies, and analyses of alternatives were conducted to support PWTP upgrades and improvements (2). Studies indicate that calcium and magnesium compete with strontium and other radionuclides for sites on cation-exchange resin, making the efficient removal of strontium from multicomponent mixtures of ions in wastewater extremely difficult. Ion-exchange resins can be selected which will easily separate strontium from monovalent ions found in wastewaters using a fixed-bed ion exchange system. However, fixed-bed ion-exchange systems presently in use cannot efficiently separate strontium from chemically similar divalent cations such as calcium. The separation factor, which is the ratio of distribution coefficients, between strontium and calcium is approximately 2. Large quantities of calcium are often found in waste streams that are only slightly contaminated

with trace quantities of strontium and other radioactive materials. ORNL currently treats process waste by chemical precipitation and ion exchange operated in series. Most of the calcium and magnesium and a portion of the strontium and cesium are precipitated by the addition of sodium hydroxide. The final sludge precipitate is dewatered and packaged for disposal. The remaining cations in solution are removed by ion exchange. The strong-acid ion-exchange resin is regenerated using nitric acid. The regenerate solution from the ion exchange column (primarily calcium salts) is concentrated in an evaporator, forming a concentrated radioactive liquid waste solution. Waste disposal costs for contaminated solids and liquids at ORNL are generally based on radioactivity and total volume. Finding a treatment process that will efficiently separate ^{90}Sr from calcium would be desirable to reduce the volume of secondary waste generated and simplify the process flowsheet.

A pilot-scale continuous countercurrent ion-exchange (CCIX) system marketed by the CSA, Inc., in Oak Ridge, Tennessee, was purchased as a potentially economical, alternative means of treating slightly contaminated process wastewaters. This system has the potential for efficiently removing strontium from the wastewater while simultaneously minimizing secondary waste generation by (a) separating calcium and strontium by regeneration with 1 M and 5 M NaCl solution, (b) precipitating strontium from the recyclable 5 M NaCl solution using a sodium carbonate solution followed by subsequent disposal of strontium-rich solid precipitates, and (c) discharging a nonradioactive calcium-rich stream. One paramount feature of the CCIX process is the ability to selectively remove a preferred component, strontium, from other multicomponent ions, calcium, magnesium, etc., even at conditions where ion-exchange separation factors are near unity (3). To maximize production efficiency and generate low volumes of

secondary waste under conditions of low distribution coefficients, poor separation factors, and high production rates, a CCIX system is often preferred over a fixed-bed ion-exchange system. The CCIX system is more efficient in utilizing the resin exchange capacity. Resin is continuously reacted and regenerated, thus minimizing the amount of resin required for a given amount of liquid processed (4).

This report summarizes the modeling results of a pilot-scale demonstration of the CSA CCIX system for treatment of process wastewaters generated from the multipurpose research facilities at ORNL. The ORNL process wastewater essentially consists of tap water and groundwater that are slightly contaminated with ^{90}Sr and ^{137}Cs ; therefore, the data and results discussed in this paper should be widely applicable since many other wastewater systems have similar characteristics.

COMPOSITION OF ORNL PROCESS WASTEWATER

The process waste system at ORNL is used to collect waste streams that are slightly contaminated with radioactivity, such as process wastewater from research laboratories, surface water, and condensate from the evaporation of LLLWs. Approximately 50% vol of the process wastewater is surface water that is slightly contaminated with radioactivity.

ORNL process wastewater contains a number of trace radionuclides, as shown in Table I, and relatively large amounts of competing ions (representative of city water and local groundwater in Oak Ridge, Tennessee), as shown in Table II (5). The major chemical constituents are calcium, sodium, and magnesium bicarbonates, which are introduced by shallow drainage wells. The major radionuclides are ^{90}Sr and ^{137}Cs . The ^{90}Sr is the more hazardous contaminant because of its potential for entering the human and animal food chain. Discharge limits into the environment, as defined by the Code of Federal Regulations, Chapter 10, Part 20 (10 CFR 20), are 11 Bq/L for ^{90}Sr and 740 Bq/L for ^{137}Cs .

The concentrations of ^{90}Sr and ^{137}Cs in the feed to the process waste treatment system average 1000 and 110 Bq/L, respectively. Concentration spikes have occurred occasionally due to drainages from construction sites, leaks in underground piping, and so forth. Feed compositions may vary between 500 and 8000 Bq/L ^{90}Sr and 100 and 1000 Bq/L ^{137}Cs .

ION-EXCHANGE COLUMN MODELING

The experimental data obtained from the ion-exchange column runs were analyzed using a mathematical model originally developed by Thomas (6,7). The Thomas model assumes that a Langmuir isotherm is used and that ion-exchange mass transfer can be approximated by a sec-

TABLE I
Radiochemical Composition of Process Wastewater at ORNL

Radionuclide	Concentration (Bq/L ^a)
Gross alpha	5
Gross beta	2500
^{60}Co	25
^{90}Sr	1000
$^{95}\text{ZrNb}$	50
^{106}Ru	10
^{137}Cs	110

a1 Bq = 1 dis/s = 2.7×10^{-11} Ci.

TABLE II
Chemical Composition of ORNL Process Wastewater (pH = 7.7)

Cation	Concentration (mg/L)	Anion	Concentration (mg/L)
Ca	40	HCO ₃	60
Mg	10	SO ₄	18
Na	20	Cl	6
Si	2	NO ₃	4
K	2	F	1
Sr	0.2	PO ₄	0.2
Al	0.1		
Fe	0.05		
Zr	0.05		
Cu	0.02		
Ni	<0.02		
Cr	<0.02		
U	<0.001		

ond-order kinetic equation and modeled by: (a) T, a throughput parameter; (b) N, column height as transfer units; and (c) R, the separation factor. The value of N was determined from laboratory-scale experimental breakthrough curves and used to predict scaleup for the pilot-scale CCIX system. For dilute solutions such as the ORNL process wastewater, the separation factor, R, is approximately constant and can be assumed to equal 1.

The original Thomas model which was designed for a single fixed-bed ion-exchange column, has been extended by R. M. Wallace to predict the operation of several columns in series. Wallace used a numerical analysis solu-

tion of the Thomas equation with input values of R , N , and K_d (8). In his calculations, a series of columns was loaded until a specified breakthrough occurred. At that time, a fresh column was added to the front (outlet end), and a column was removed from the back (inlet end) of the series. The columns again operated until a specified breakthrough occurred, and the sequence was repeated. This sequence of operations with a series of fixed beds simulates the behavior of a CCIX loading section. In the present study, the Wallace model was expanded to estimate the steady-state performance of the pilot-scale CCIX system (9). The cyclic pulse operation in the CCIX column was modeled as several columns in series where the volume of each column was equal to the volume of freshly regenerated resin per pulse cycle. The model was used to predict distribution coefficients and performance of the CCIX system under various operating conditions.

Thomas Equation

The general equation for the reaction kinetics of fixed-bed ion exchange is:

$$\left(\frac{\partial Y}{\partial NT}\right)_N = X(1 - Y) - RY(1 - X) \quad (\text{Eq. 1})$$

and

$$\left(\frac{\partial X}{\partial N}\right)_{NT} = -X(1 - Y) + RY(1 - X), \quad (\text{Eq. 2})$$

where

X and Y = dimensionless concentrations of the solute ion in the fluid and solid phases, respectively;

N = length of the exchange column in transfer units;

NT = time parameter for the system;

R = separation factor; and

T = throughput parameter.

The variable X is defined as C/C_0 , where C and C_0 are the concentrations of the solute ion of interest in the effluent and feed, respectively. The variable Y is defined as q/q^* , where q is the actual concentration in the solid phase and q^* is the concentration in the solid phase at equilibrium with fluid at the inlet concentration, C_0 . When the concentration of the solute ion is small relative to the concentration of the replaceable ion in the feed, R approaches unity and the isotherm is linear. The variable N is defined by the dimensionless expression

$$N = \frac{K'_d \rho_b K_a}{\left(\frac{f}{v}\right)} \quad (\text{Eq. 3})$$

where

K'_d = distribution coefficient when $X = 1$,

ρ_b = bulk density of the ion exchanger,

K_a = mass-transfer coefficient characteristic of the system,

f = flow rate of solution through the column, and

v = overall volume of the sorbent bed, including the void spaces.

The throughput parameter, T , is defined as

$$T = \frac{\left(\frac{V}{v}\right)}{K'_d \rho_b} \quad (\text{Eq. 4})$$

where

V = volume of solution processed through the column,

and

V/v = number of bed volumes of solution that have passed through the bed.

When ρ_b is constant, the volume-based distribution coefficient is defined by the expression

$$K_d = \frac{q_v}{C_0} \quad (\text{Eq. 5})$$

where

q_v = the solute ion concentration per unit volume of sorbent bed (sorbent plus void space);

and

C_0 = the solute concentration in the feed.

Equations (3) and (4) can then be expressed as

$$N = \frac{K_d K_a}{\left(\frac{f}{v}\right)} \quad (\text{Eq. 6})$$

and

$$T = \frac{\left(\frac{V}{v}\right)}{K_d} \quad (\text{Eq. 7})$$

For an ion-exchange system initially free of adsorbate, the boundary conditions are:

$$X = 1 \quad \text{at} \quad N = 0 \quad \text{for all} \quad T, \quad (\text{Eq. 8})$$

$$Y = 0 \quad \text{at} \quad T = 0 \quad \text{for all} \quad N, \quad (\text{Eq. 9})$$

When Equations (1) and (2) are integrated, assuming the above boundary conditions, the solution obtained by Thomas is:

$$\bar{X} = \frac{C}{C_0} = \frac{J(RN, NT)}{J(RN, NT) + [1 - J(N, RNT)] \exp[(R-1)N(t-1)]} \quad (\text{Eq. 10})$$

and

$$V = \frac{q}{q^*} = \frac{1 + J(RN, NT)}{J(RN, NT) + [1 - J(N, RNT)] \exp[(R-1)N(t-1)]} \quad (\text{Eq. 11})$$

where J is a zero order Bessel function (10,11).

Modeling Breakthrough Curves

Breakthrough curves are S-shaped curves obtained by plotting T (or V/v) vs X on linear scales. Plotting these variables on logarithmic-probability scales eliminates the curvature of such plots and allows direct comparison with theoretical curves. For large values of RN , X is ~ 0.5 when T equals 1 and is independent of RN . Therefore, K_d is approximately equal to V/v at the point where X is ~ 0.5 . Experimental data can be used to construct breakthrough curves of X vs T (or V/v). Values of R and N can be obtained from the experimental data by repeated iterations of Eqs. 7 and 10 or by comparing the experimental breakthrough curves (plotted on logarithmic-probability paper) with theoretical values available in many reference books (10,12,13). These values can then be used to estimate performance at increased residence times and for columns in series (12).

Scaleup

The scaleup of small ion-exchange systems to industrial units can be performed once values of R , N , T , K_d ,

and K_a are obtained. These values can be used to predict the performance of columns at different operating conditions. The breakthrough curve at the new set of conditions will pass through the stoichiometric point ("center of mass," i.e., the value of X at $T = 1$ for which the area below and to the left of the breakthrough curve equals the area above and to the right of the breakthrough curve), but the slope of the breakthrough curve will change. The slope of the new curve at each X value will be proportional to that at the central X point and is determined by two factors: (a) how N changes with the new conditions and (b) how the slope ratio changes with N . It can be seen from Eq. (6) that the value of N will vary with K_a , K_d , v , and f . During scaleup, the rate parameter, (i.e., the mass-transfer mechanism) cannot change. For linear isotherms ($R = 1$) and constant-sorption material, K_d is constant. Therefore, N becomes a function of v and f only.

COLUMN TESTS

Bench-scale column tests were performed to determine distribution coefficients and separation factors for calcium and strontium from breakthrough curves using a Dowex cation-exchange resin in the sodium form and ORNL process wastewater feed (14). The purpose of these tests was to obtain data to determine the feasibility of efficiently separating strontium from calcium using ORNL process wastewater feed in a fixed-bed column. The resulting data were then used to establish operating conditions for the pilot-scale CCIX tests.

Bench-Scale Breakthrough Curves

A fixed-bed ion-exchange column (7 mm id, 76 mm long) was packed with glass wool (to eliminate end effects) and then loaded with 3 mL (1.5 g) of Dowex HGR-W2 sodium-form resin [20 to 50 mesh (0.84 to 0.30 mm), resin capacity equals 2.2 meq/mL wet resin] (15). ORNL process wastewater with a composition of 10.5 mg/L Sr, 53 mg/L Ca, 10 mg/L Mg, and 10.5 mg/L Na was fed to the top of the column at a flow rate of 3 mL/min (1 bed volume per minute). Effluent samples were collected at the bottom of the column and analyzed at intervals to produce concentration profiles (breakthrough curves) for calcium, strontium, and magnesium. These breakthrough curves, shown in Fig. 1, were obtained by plotting the mean throughput vs fractional breakthrough (i.e., effluent concentration divided by feed concentration). The distribution coefficient, K_d , is a volume-based (mL solution per mL resin) distribution approximately equal to the number of bed volumes that have been processed at 50% breakthrough. Distribution coefficients are often given in terms of the proportion of a metal adsorbed or not adsorbed (mL solution per gram of dry resin) by an ion-exchange resin (16). Distribution coefficients of 879 mL solution per mL resin (1730 mL solution per gram of dry resin) and 631 mL solution per mL resin

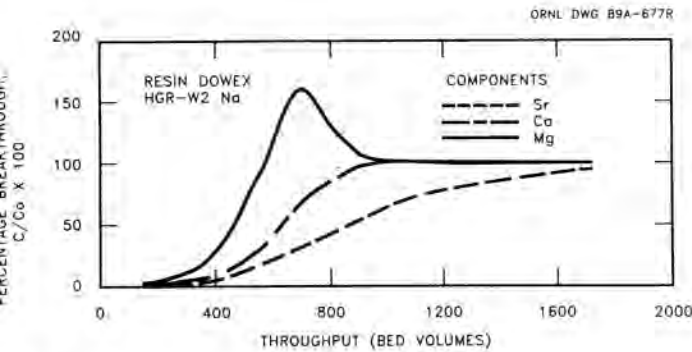


Fig. 1. Breakthrough Curve for Bench-Scale Column Using ORNL Process Wastewater and Dowex HGR-W2 Sodium-Form Resin.

(1245 mL solution per gram of dry resin) were measured for strontium and calcium, respectively, during continuous loading on the ion-exchange resin.

Results from these tests indicated that a separation factor [ratio of distribution coefficients (K_dSr/K_dCa)] of only 1.4 between calcium and strontium had been realized. As shown in the breakthrough curve, magnesium and other components in the process wastewater tend to offer little competition for sites on the resin and are easily displaced by calcium. Therefore, the multicomponent system can be modeled as a binary system consisting of calcium and strontium. The strontium breakthrough data (plotted on logarithmic paper) were modeled to obtain the Thomas model parameters given in Fig. 2.

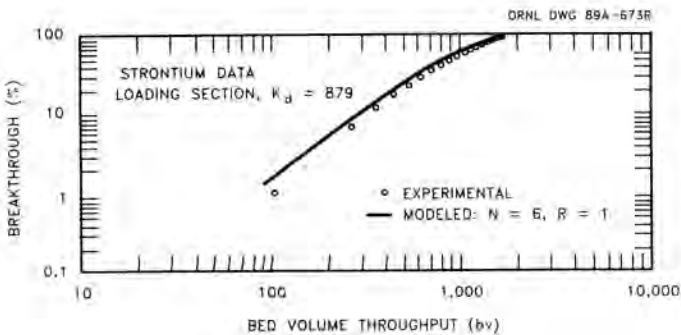


Fig. 2. Modeling of Bench-Scale Column Breakthrough Curve Using Thomas Model.

Bench-Scale Elution Curves

A test was performed to compare the separation factor for elution of strontium and calcium from the loaded resin. Strontium and calcium were removed by scrubbing (eluting) with 1M NaCl solution or 5 M NaCl at a flow rate of 1 mL/min (one-third bed volume per minute) (17). The elution curves (Fig. 3) were obtained by plotting the concentration in the effluent divided by the mean concentration on the resin. The 1 M NaCl eluent yielded volume-based distribution coefficients of 11.5 and 3.8 for strontium and calcium, respectively, and a separation factor of 3 between strontium and calcium. The test using 5 M NaCl eluent yielded strontium and calcium distribution coefficients which were Hence, the separation factors (ratio of distribution coefficients) between strontium and calcium were found to vary from 3 in 1 M NaCl to <1 in 5M NaCl.

These results suggest that most of the calcium in the process wastewater can be separated from strontium on the loaded resin using the appropriate volume of 1 M NaCl solution. Strontium can then be removed from the resin using the 5 M NaCl solution. Ultimately, an efficient separation between calcium and strontium can be achieved by using repeated volumes of dilute and concentrated salt solutions in a CCIX system.

Pilot-Scale CCIX System

A schematic of the pilot-scale CCIX column operated at ORNL to test the selective removal of strontium from ORNL process wastewater prior to discharge into the environment is shown in Fig. 4. The stream compositions given here are based on experimental results obtained dur-

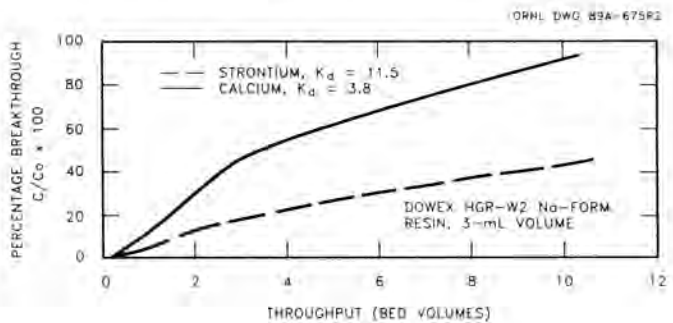


Fig. 3. Elution Curve for Removal of Strontium and Calcium from Dowex HGR-W2 Sodium-Form Resin Using 1 N NaCl in a Bench-Scale Column.

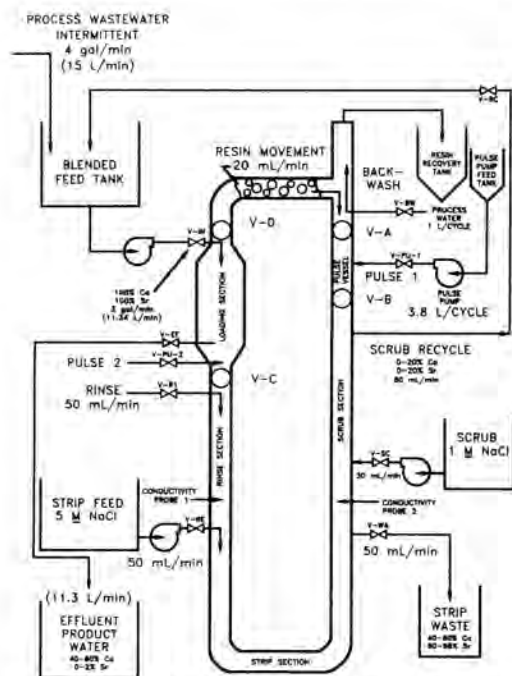


Fig. 4. Schematic of Pilot-Scale CCIX Column Tested Using ORNL Process Wastewater. Percentages are Relative to Blended Feed Composition.

ing pilot testing (18). This system is mounted on a mobile trailer bed to allow easy transport to remedial sites. A Dowex HGR-W2 cation exchange resin (10% cross-linkage) was chosen to perform the separation between the multicomponents based on the resin's affinity for calcium and strontium relative to sodium, cost and availability, and high-throughput capability. The pilot CCIX column is sized to treat 3 gal/min (11 L/min) of process wastewater as a test demonstration. The column is 27 ft (8.2 m) high and composed of four subsections -- loading, pulse, scrub, and strip/rinse -- each connected in a closed loop separated by air-operated valves (19).

Resin [20 to 50 mesh (0.84 to 0.30 mm)] is initially charged into the CCIX column. During a loading cycle, the column loading section contains a fixed volume of resin [maximum volume is ~ 12.3 L, i.e., the volume of a 5-ft (150-cm)-long, 4-in. (10-cm)-ID PVC pipe]. Process wastewater is intermittently blended with the scrub recycle in a 200-gal (756-L) blended feed tank. The blended feed is continuously fed to the column at a constant flow rate of 3 gal/min (11 L/min) in a countercurrent direction with respect to the resin flow during a loading cycle. The loading cycle usually requires 30 to 40 min. At the end of each cycle, a small volume (~ 600 ml) of resin, loaded primarily with strontium and calcium as indicated by the breakthrough curve in Fig. 1, is pulsed from the top of the column loading section around the column loop as a freshly regenerated volume of resin is simultaneously introduced in the bottom of the loading section. Normally, there is a maximum inter-

val of 10 s between the end of one loading cycle and the start of the consecutive loading cycle. This interval is the intermittent, semicontinuous operating cycle for the CCIX system.

Strontium and calcium are separated in the scrub section [a 9-ft (2.7-m) long, 2-in. (5-cm)-ID PVC pipe] using a 0.5 to 1.0 M NaCl solution countercurrent with respect to the resin flow. Approximately 80 to 100% of the strontium remains on the resin. The resulting solution is collected in the scrub recycle stream and blended with the process wastewater feed. Strontium loaded on the resin is ultimately removed in the strip section [a 14 ft (4.3 m) length, 2 in. (5 cm) ID PVC pipe] using a 3.5 to 5 M NaCl solution countercurrent with respect to the resin flow. After strontium has been removed, the resin is washed with clean rinse water prior to entering the bottom of the loading section. Strontium-rich eluate collected in the strip waste tank is precipitated as the carbonate by adding of sodium carbonate. Strontium and any residual calcium precipitates are then filtered and ultimately disposed of as solid waste.

PILOT-SCALE CCIX RESULTS

Data obtained from the near-steady-state operation of the pilot CCIX system for less than 50 of continuous operation have indicated that maximum removal efficiency ($> 99.7\%$) of the strontium from the blended feed stream can be achieved. Typically, the blended feed composition was in the range of 0.1 to 0.3 mg/L (300 $\mu\text{g/L}$) total strontium and 900 to 1200 Bq/L ^{90}Sr , 40 to 60 mg/L Ca, 10 mg/L Mg, 20 to 40 mg/L Na, 100 to 120 Bq/L ^{137}Cs , and 2000 to 3000 Bq/L gross beta. The effluent stream from the CCIX contained < 0.005 mg/L total strontium and ~ 3.4 Bq/L radioactive strontium, which is below the federal discharge limit of < 11 Bq/L for radioactive strontium.

Results of the Wallace model suggested that approximately 20 to 25 operating cycles (10 to 12 h of semicontinuous operation for a 30-min loading cycle) was required to reach steady state under conditions where the composition of the blended feed was constant and the resin entering the bottom of the loading section was thoroughly stripped (100% removal of strontium and calcium, leaving only sodium ions on the resin). The value of N ($N = 6.6$) for the pilot-scale column was estimated from bench-scale data using Eq. (6). The bench-scale column and pilot-scale CCIX columns had diameters of 7 and 102 mm ID, respectively. The columns had length-to-diameter ratios of 11 and 15, respectively. The feed flow rate was constant with a 1 min residence time in each column. Mass-transfer coefficients, K_a , and the value of K_d were assumed to be constant during scaleup. The actual value of N ($N = 4$) for the pilot-scale column was determined from the pilot-scale breakthrough data. Thus, the scaleup equation predicted a higher value of N than was observed. The pilot-scale data

suggest that a combination of controlling mass transfer mechanisms may occur. Consequently, more fundamental mass-transfer data are needed to accurately predict the CCIX column performance.

One key feature of the CCIX system is its potential to eliminate secondary waste streams generated in the treatment process. The strip waste stream in the CCIX system generates the only radioactively contaminated secondary waste stream. The strip waste stream would contain 40 to 60% of the calcium and 90 to 99% of the strontium originally in the blended feed. Results of preliminary batch precipitation tests show that 88 to 99% of the strontium and 90% of the calcium in the strip waste stream were chemically precipitated by stoichiometric addition of sodium carbonate (with 0.3 N excess sodium carbonate) to form a carbonate sludge waste. The radioactivity in the supernate solution (strip feed solution) was analyzed to be in the range of 390 Bq/L to 1800 Bq/L gross beta and would require further treatment before recycling as strip feed solution to minimize the potential addition of radioactivity in the column effluent stream. The CSA Company, of Oak Ridge, Tennessee, performed tests using similar ORNL feed solutions and estimated that the remaining strontium could be removed using a Duolite C-467 phosphonic resin (1). However, no further tests were performed at ORNL to verify additional removal of strontium using the Duolite resin. An industrial-scale CCIX flowsheet based on ORNL pilot-scale data and CSA data is given in Fig. 5. This flowsheet includes a zeolite column for ¹³⁷Cs removal.

COMPARISON OF DISPOSAL COSTS FOR CCIX AND ORNL CURRENT PROCESS WASTE TREATMENT METHODS

The industrial-scale CCIX system (Fig. 5) produces three types of solid wastes: spent zeolite, resin, and sludge. Precipitation of the raffinate stream (strip waste stream) by addition of sodium carbonate produces sludge containing 60% of the calcium and 90% of the strontium originally in the feed. Disposal costs for the CCIX process are estimated to be in the order of \$100,000/year (plus the disposal cost for zeolite).

A flow diagram of the current PWTP system at ORNL is shown in Fig. 6. The PWTP generates both concentrated and dilute LLLW, as well as solid sludge precipitates that consist primarily of calcium carbonate. The dilute waste is generated during column regeneration with nitric acid and totals approximately 5800 gal/year. Dilute waste is evaporated in the LLLW evaporator and disposed at a cost of \$7/gallon. The concentrated waste (4200 gallons/year) is combined with LLLW evaporator concentrate and stored for future processing. The disposal cost for concentrated LLLW is \$50/gal. Approximately 3900 ft³ of sludge is generated at the PWTP each year as a result of the clarifier

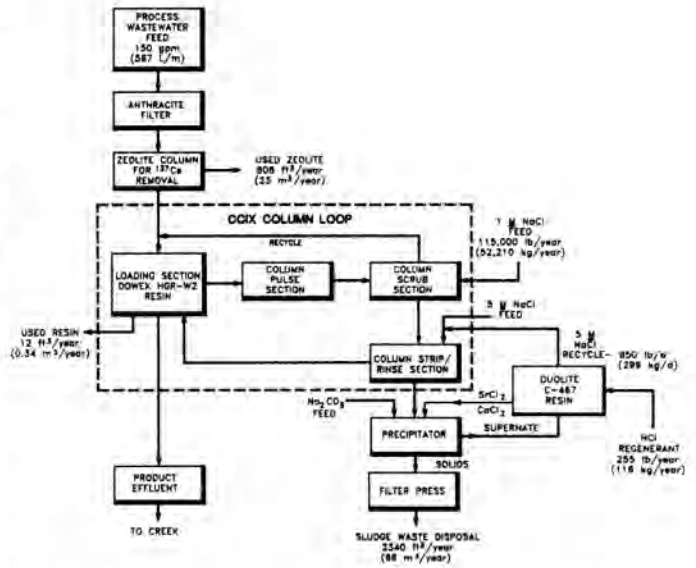


Fig. 5. Flowsheet for Industrial - Scale CCIX System Based on Experimental Pilot-Scale Results.

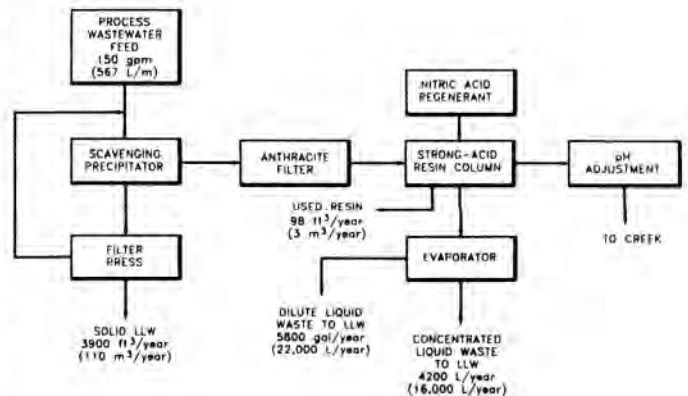


Fig. 6. Flowsheet for ORNL Process Waste Treatment Plant.

precipitations. Sludge is disposed of at a cost of \$40/ft³. Disposal costs for the currently used treatment plant are in the order of \$500,000/year (plus the disposal cost for zeolite).

SUMMARY AND CONCLUSIONS

The CCIX system employs use of a well-known, often-used water softening technique to perform a relatively difficult separation between strontium and calcium and other multicomponent ions (¹³⁷Cs, Mg, Na, etc.) found in ORNL wastewaters. Removal of strontium from the process wastewater via CCIX, coupled with a zeolite process for removal of ¹³⁷Cs would reduce secondary waste disposal costs to one-fifth of those presently incurred if recycle of regeneration solutions can be accomplished. Recycling of the 5 M NaCl regeneration stream used in the strontium removal needs to be demonstrated. Studies to date have partially confirmed the potential of the CCIX system; however, more fundamental studies are needed to accurately model the CCIX system and predict optimum performance.

REFERENCES

1. E. D. COLLINS et al., "An Improved Ion-Exchange Method for Treatment of Slightly Contaminated Wastewaters," Proc. Am. Nuclear Soc. Int. Meeting on Low-, Intermediate-, and High-Level Waste Manage. and Decontamination and Decommissioning, Niagara Falls, N.Y. (1986).
2. S. M. ROBINSON, "Initial Evaluation of Alternative Flowsheets For Upgrade of the Process Waste Treatment Plant," ORNL/TM-10576, Oak Ridge National Laboratory (in press).
3. R. E. BLANCO and J. T. ROBERTS, "Separation of Lithium Isotopes by Batch or Continuous Ion Exchange With Decalco or Dowex-50 Media," Progress in Nuclear Energy, Series IV, Vol. 4, Technology Engineering and Safety (1961).
4. I. R. HIGGINS and M. S. DENTON, "CSA Continuous Countercurrent Ion Exchange (CCIX) Technology," Sep. Sci. Technol., 22(2&3), 99 (1987).
5. S. M. ROBINSON et al., "Treatment of Radioactive Wastewaters by Chemical Precipitation and Ion Exchange," presented at the Am. Inst. Chem. Eng. Spring Natl. Meet., Houston, Tex., March 29-April 2, 1987; AIChE Symp. Ser., 83, 52 (1987).
6. H. C. THOMAS, J. Am. Chem. Soc., 66, 1664 (1944).
7. I. LANGMUIR, J. Am. Chem. Soc., 40, 1361 (1918).
8. E. D. COLLINS, D. O. CAMPBELL, L. J. KING, J. B. KNAUER, and R. M. Wallace, "Development of the Flowsheet Used for Decontaminating High-Activity-Level Water," In "The Three Mile Island Accident, Diagnosis and Prognosis," ACS Symp. Ser., 293, 212 (1986).
9. R. HALL, J. S. WATSON, and S. M. ROBINSON, "Pilot-Scale Demonstration of Strontium Removal from Low-Level Radioactively Contaminated Process Wastewater Using Continuous Countercurrent Ion Exchange (CCIX)," ORNL/TM-Draft, Oak Ridge National Laboratory (in preparation).
10. N. K. HIESTER and T. VERMEULEN, "Saturation Performance of Ion-Exchange and Adsorption Columns," Chem. Eng. Prog., 48, 505 (1952).
11. K. S. MILLER, Partial Differential Equations in Engineering Problems, Prentice-Hall, New York, 178 (1972).
12. H. K. S. TAN, "Programs for Fixed-Bed Sorption," Chem. Eng., 91(26), 57 (1984).
13. N. K. HIESTER, T. Vermuelen, and G. KLEIN, Chemical Engineers' Handbook, 6th ed., J. H. Perry et al., Eds., McGraw-Hill, New York, Chap. 16, 1984.
14. I. R. HIGGINS, "Treatment of ORNL Low-Level Wastewater for Selective Removal of Strontium-90," Job No. 263-CT162, CSA, Inc., Oak Ridge, Tennessee.
15. DOW CHEMICAL CORPORATION, "Physical and Chemical Properties," Midland, Michigan.
16. A. RINGBOM, Complexation in Analytical Chemistry, Interscience Publishers, John Wiley & Sons, New York, Chap. VI (1963).
17. R. E. TREYBAL, Mass-Transfer Operations, 3rd ed., University of Rhode Island, McGraw-Hill, New York, Chap. 11 (1980).
18. R. HALL et al., "Operation of a Mobile Pilot-Scale Continuous Countercurrent Ion Exchange System for Treatment of Low-Level Radioactive Wastewater," In "Proceedings of 62nd Annual Water Pollution Control Federation Conference," San Francisco, California (1989).
19. I. R. HIGGINS and M. S. DENTON, "Model 42 CCIX Pilot Unit Installation, Operation and Maintenance Manual," CSA Document No. 263-050, Rev. 0, CSA, Inc., Oak Ridge, Tennessee (May 1988).
20. I. R. HIGGINS, "Treatment of ORNL Low-Level Wastewater for Selective Removal of Strontium-90," Job Nos. 263-CT162, CSA, Inc., Oak Ridge, Tennessee.