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Separation of Cs-137, Sr-90, and Th-232 in Aqueous Solution by Using a Multistage Countercurrent Batch Contactor Ion-Exchange System

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Abstract

The radioisotopes Cs-137, Sr-90, and Th-232, in simulated high level nuclear liquid waste, were recovered and sequentially separated by using an 8-stage flask simulation of a multistage countercurrent batch contactor (MCBC) ion-exchange system. The solution normality ratio used for the three ions Cs:Sr:Th was 1:1:1. The solution was contacted for 2 h with resin Dowex HCR-W2 initially in the H^+ form. The obtained recovery efficiency of the MCBC and the purity of the separated ions for the three ions were 77 and 60% for Cs^+, 64 and 93% for Sr^{2+}, and 99 and 65% for Th^{4+}, respectively.

INTRODUCTION

The high level liquid waste nitrate solution from nuclear fuel reprocessing operations contains recyclable fissionable materials (U, Pu), Np, and several major soluble solid fission products (*1*).

The waste is separated by a solvent extraction process to recover the recyclable fissile materials and Np, and then the useful radioactive nuclides are recovered by an ion-exchange or solvent extraction process (*1–3*) for use as special purpose radionuclides (*1*, *4*). The recovery also reduces the disposal cost of the remaining waste as well as reducing the environmental hazards associated with the waste (*4*). During solvent extraction, the fissile materials and the bulk of the actinides contained in the organic phase are recovered, leaving the fission products, including Cs-137 and Sr-90, contaminated with small amounts of the actinide elements left behind in the

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aqueous phase. This aqueous solution is in the final step of the recovery process and is separated by an ion-exchange process. The aqueous solution contains several elements, and countercurrent processing is an efficient method for separating them. A batch countercurrent process is especially suitable, because the elements are slow and diffuse rapidly in the resin or have weak and strong affinities for the resin.

The batch countercurrent process used in this work has an 8-stage flask simulation of a multistage countercurrent batch contactor (MCBC) ion-exchange system.

GENERAL CONCEPTS OF ION-EXCHANGE SEPARATION OF Cs^+, Sr^{2+}, AND Th^{4+}

The exchange capability of an ion in solution (solution phase ion) is dependent on the affinity of the ion for the resin. When the affinity of the solution phase ion is greater than that of the counterion which is initially present in the ion-exchange resin (resin phase ion), exchange occurs. While the ion initially in solution diffuses into the resin, the exchanged ion migrates out of the resin into the solution. In this work, hydrogen ion was chosen as the counterion initially present on the resin, because the hydrogen form resin has an advantage in developing an elution process using hydrochloric acid (*5*).

The affinity sequence of the ions analyzed in this work for the resin is in the following order (*5*):

$$H^+ < Cs^+ < Sr^{2+} < Th^{4+}$$

Following the affinity sequence of the ions, the mechanisms of ion exchange between the resin and solution phase ions can be expressed by several ion-exchange equilibrium equations. For this system, the equilibrium equations are:

$$\text{A) } HR + \begin{bmatrix} Cs^+ \\ Sr^{2+} \\ Th^{4+} \end{bmatrix} \rightleftarrows \begin{bmatrix} Cs^+ \\ Sr^{2+} \\ Th^{4+} \end{bmatrix} R + [H^+]_S$$

$$\text{B) } CsR + \begin{bmatrix} Sr^{2+} \\ Th^{4+} \end{bmatrix} \rightleftarrows \begin{bmatrix} Sr^{2+} \\ Th^{4+} \end{bmatrix} R + [Cs^+]_S \qquad (1)$$

$$\text{C) } SrR + [Th^{4+}]_S \rightleftarrows [Th^{4+}]\ R + [Sr^{2+}]_S$$

where R = resin matrix
subscript S = solution phase

Initially, when the resin comes into contact with the solution, the ion-exchange reactions move to the right. As the resin sorbs the Cs^+, Sr^{2+},

and Th^{4+} and the resin phase ions increase, a reversible ion exchange occurs and finally equilibrium between the two phases is reached. Since Th^{4+} has the strongest affinity, the resin phase Cs^{+} or Sr^{2+} may be replaced by Th^{4+} as noted in Eq. (1).

In general, the overall ion-exchange process is composed of two steps. The first step is a loading process in which the solution phase ion is exchanged onto the resin. In the second step, or the elution process, the ion previously loaded on the resin is eluted by using other ions. In the loading process, the hydrogen form resin is used and the H^{+} on the resin is exchanged for the solution phase ions Cs^{+}, Sr^{2+}, and Th^{4+} according to Eq. (1). The exchange process continues until an equilibrium state between the resin and solution phases is reached.

After loading, the elution process is initiated to elute the resin phase ions. Since ion exchange is a reversible process, the eluent hydrochloric acid can elute the phase ions by the law of mass action to regenerate the resin in its original hydrogen form. This elution process is achieved by forcing Eq. (1) to move to the left by using a sufficiently high concentration of the hydrogen form in the eluent.

Therefore, the ion-exchange process needed to separate a mixture of the ions Cs^{+}, Sr^{2+}, and Th^{4+} from the chloride solution will involve one loading process and a series of three separation processes, as shown in Fig. 1. Each process will use an 8-stage multistage countercurrent batch contactor (MCBC).

In the loading process, three ions are loaded on the resin. The loaded resin is transferred to the elution process in which the separation of the ions Cs^{+}, Sr^{2+}, and Th^{4+} is conducted by contacting the resin with three different concentrations of the eluent hydrochloric acid. The Cs^{+} will be preferentially separated from the loaded resin by the lowest normality hydrochloric acid. The resin passed through the first MCBC is transferred to the second MCBC in which the Sr^{2+} is separated by using the low hydrochloric acid. Finally, Th^{4+} is separated by using the highest concentration of hydrochloric acid in the third MCBC. In general, the mode of contact is countercurrent, in which the solution phase ions can be continuously exchanged and the loaded resin can be sequentially treated to recover all of the Cs^{+}, Sr^{2+}, and Th^{4+} on the resin. Therefore, the products of each MCBC can be periodically collected. This is one of the advantages of the MCBC.

EXPERIMENTALS

1. Materials and Analysis

Preparation of Resin

The ion-exchange resin used was Dowex HCR-W2, obtained from the Dow Chemical Company, St. Louis, Missouri. Dowex HCR-W2 is the new

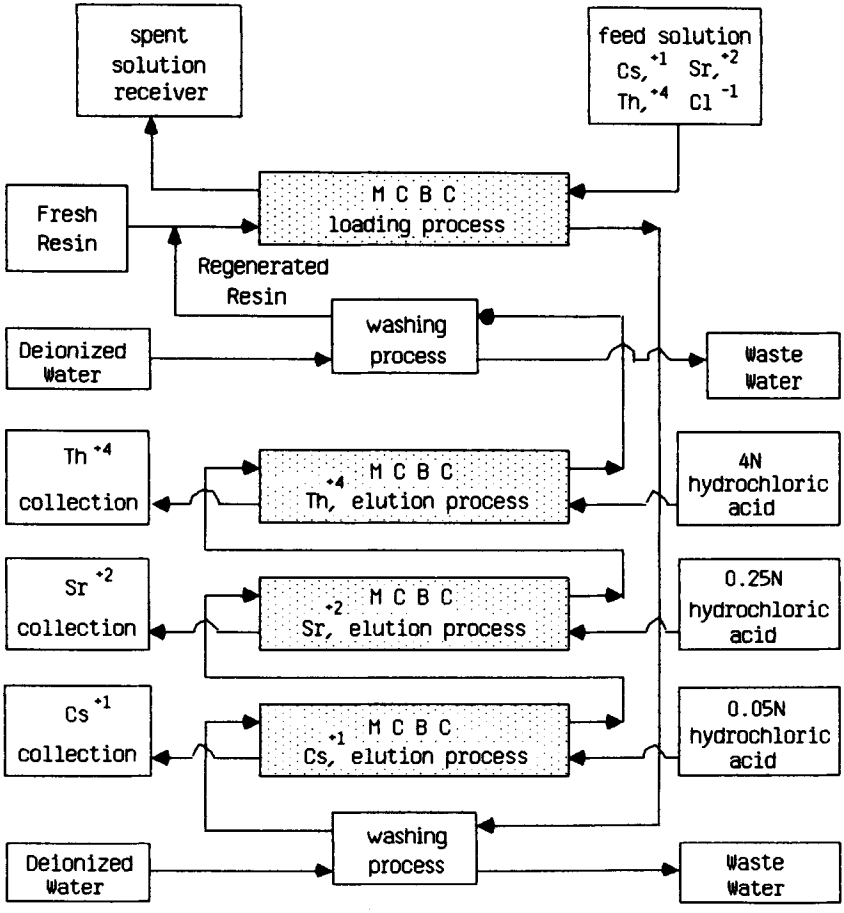

FIG. 1. Block diagram of a multicomponent (Cs^{+}, Sr^{2+}, Th^{4+}) loading and sequential separation process using a multistage countercurrent batch contactor ion-exchange system.

trade name for Dowex 50W-X8 with resin particles in the range of 20 to 50 mesh. Dowex HCR-W2, as received, was in the wet hydrogen form. To insure that the resin was completely converted to the hydrogen form, the resin was preconditioned in a glass chromatographic column by washing with 5% hydrochloric acid (*6*). The hydrochloric acid was passed from the top of the column at a flow rate of 0.5 mL/min. The volume of 5% hydrochloric acid used for preconditioning was about 30 times the resin volume. After preconditioning, the resin was again washed with demineralized water.

Preparation of Solution

All chemicals used in this work were analyzed by the companies supplying them. They were all of more than 99% purity and used without any further analysis. The chemicals used were $SrCl_2 \cdot 6H_2O$, CsCl, $ThCl_4 \cdot 8H_2O$, HCl, and thorin. Thorin was used for the detection of thorium. Deionized water was used for the preparation of the solutions. The resistance of the deionized water was 10 to 15 MΩ/cm. The solution used were prepared by mixing the proper amount of chemicals with the correct amount of deionized water to obtain the desired normality and amount.

Analysis of Samples

The Cs^+ and Sr^{2+} concentrations in the experimental solutions were determined by tagging the solutions with radioisotopes Cs-137 and Sr-85 as tracers, respectively. The Cs-137 and Sr-85 were purchased from Nuclear England Nucleus, and the concentrations of the radioactive materials added to the solutions were about 0.03 μCi/mL for each isotope considering the selection criteria described in Reference 7. An exact amount of added activity was not necessary because relative measurements were used.

The samples (0.2 mL) taken from the experiments were analyzed with NaI(Tl) detector and a multichannel analyzer to measure the Cs-137 and Sr-85 tracers. Since the NaI(Tl) detector has poor peak resolution, the two peaks at 514 keV for Sr-85 and at 661 keV for Cs-137 overlapped. To minimize these possible interferences, the energy windows for each peak were set so that the overlap region was not included in the results.

To determine the concentration of thorium in a sample by the use of thorin, the optimum conditions for detecting a color change of thorin due to thorium concentration in solution by a spectrophotometer were examined (7). A solution pH of 1.2 and a 540-nm wavelength were selected as the optimum conditions to determine Th^{4+} concentration. The spectrophotometer used was a B&L Spectrophotometer Spectronic 200.

2. MCBC Experiment

An experiment similar to the multistage countercurrent batch contactor used in this work can be found in the literature (*8*, *9*). It employs the periodic movement of both solutions in one direction and the materials in the opposite direction, as shown in Fig. 2.

The MCBC was simulated with an 8 flask system. The operation of the MCBC is schematically shown in Fig. 3. The 8 flasks were initially supplied with fresh resin, and they were contacted with solution for loading the ions in bulk solution on the resin. After the loading process, the loaded resin in the 8 flasks was contacted with eluent for separating the loaded ions.

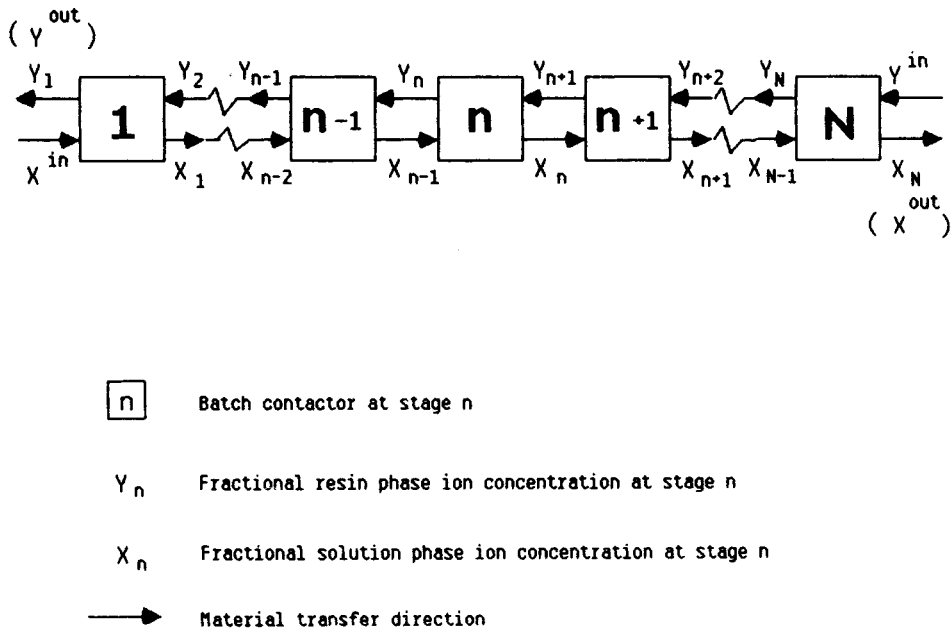

FIG. 2. Multistage countercurrent batch contactor.

The operation procedures in both loading and separation processes were the same, and they are explained in the following sections.

Loading Process

The 8 flasks containing fresh resin were numbered 1 through 8 and they constituted stages 1 through 8 of the MCBC. Only Flask 1A was contacted with fresh feed solution. This process is shown as Phase A in Fig. 3. After a fixed period of contact time (2 h) between resin and solution, the spent solution in Flask 1A was transfered to Flask 2B and the resin in Flask 1A was again contacted with fresh feed solution. This contact step constituted Phase B. The process could be repeated until Phase D was reached. While the operation continued up to Phase D, the resin remained in the same initial stages and only the solution was moved from Stage 1 to Stage 4: the single current process occurred up to Phase D. But beginning with Phase E, a countercurrent process began. After a fixed period of a contact time in Phase D, the solution in Flask 4D was transfered to Flask 5E and the solution in Flask 3D was transfered to Flask 4E. The process of transition from Phase D to Phase E was finished when the solution in Flask 1D was transferred to Flask 2E. Then Flask 1 was out of the system and was left

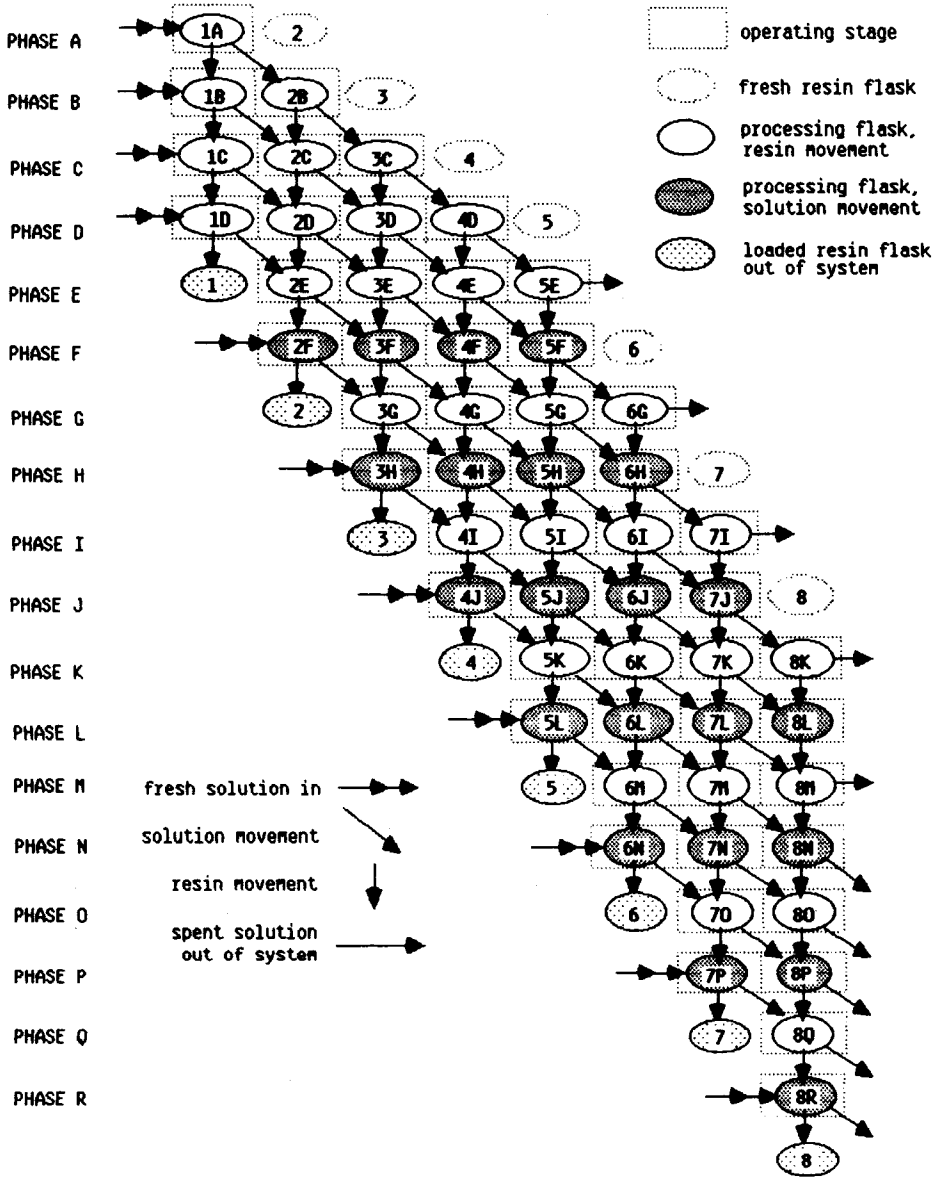

FIG. 3. Flask movement for an 8-stage MCBC conducted in this experiment.

unattended until the elution process began. After Phase E, the flasks remained in the same stages of the MCBC and only the solutions were transferred.

To transfer the solution, the solution in Flask 5E was first drained off and the solution in Flask 4E was transferred to shaded Flask 5E. The solutions in Flasks 3E and 2E were moved to shaded Flasks 4E and 3E, respectively. In Phase E, the resin moved in one direction while the solution moved in the opposite direction. Thus, a countercurrent process occurred. The above procedure for transferring the flasks and solutions continued through Phase K. Then Flask 8 was removed from the system and the loading process was finished. Flask 8 experienced 8 contacts with the solution. Such a flask transferring procedure is also explained in the literature (*10*, *11*).

Separation Process

The separation process was the reverse of the loading process shown in Fig. 3. Hence, if the resin and solution designations shown in Fig. 3 are replaced by solution and resin, respectively, Fig. 3 explains the operating procedure for the separation process. As can be seen from Fig. 1, for the separation of loaded ions on the resin, the low concentration eluent (HCl) first contacted the loaded resin to elute the least tightly bound ion (Cs^+). After the cesium elution process was completed, the strontium elution process began. Then, the final elution process of thorium followed. In each separation process, the fresh eluent contacted the loaded resin in Stage 1. Next, the resin in Stage 1 was moved to Stage 2, where it was contacted with fresh eluent. Additional loaded resin was added to Stage 1 and contacted with the old eluent transferred from Stage 1. Likewise, the operating procedure for the movement of the flasks in the separation process was exactly the same as in the loading process. After the cesium elution process was completed, the strontium elution process began. Then, the final elution process of thorium was followed.

RESULTS AND DISCUSSION

1. Elution of Cs^+, Sr^{2+}, and Th^{4+} from the Resin

The elution of Cs^+, Sr^{2+}, and Th^{4+} from the resin can be accomplished by the reverse ion-exchange reaction expressed by the first equation in Eq. (1), which occurs when the hydrogen ions in the eluent are increased. Since Cs^+, Sr^{2+}, and Th^{4+} are held on the resin with different affinity strengths, different hydrogen ion concentrations must be used to elute them. To

determine the hydrogen ion concentrations necessary to elute the three ions from the resin, the gradient elution technique was employed (*5*, *12*). The resin loaded with the three ions was contacted for 2 h with eluents of different hydrogen ion concentrations in the range 0.001 to 7 *N*, which was conducted in the batch process described in Reference *7*. The elution phenomena of Cs^+, Sr^{2+}, and Th^{4+} are plotted as a function of normality of the hydrogen acid in Fig. 4. The figure shows narrow band gaps between two adjacent ion concentration peaks. This means it would be difficult to obtain a nearly pure solution of one ion, but it is possible to obtain high purity of a particular ion at the particular concentration of the eluent (*5*). By observing the concentration profiles of the eluted ions shown in Fig. 4, the following points can be understood. If 0.05 and 0.25 *N* hydrochloric acid are chosen for eluting Cs^+ and Sr^{2+}, respectively, about 70% pure Cs^+ and 95% pure Sr^{2+} can be predicted for MCBC operation. After eluting the Cs^+ and Sr^{2+}, almost pure Th^{4+} remains on the resin. For more pure Cs^+ and Sr^{2+}, hydrochloric acid lower than 0.05 *N* may be used for eluting Cs^+. Figure 4 also shows a large amount of Th^{4+} can be eluted at 4 *N* (this was also examined by the conducting column process).

Based on the above observations, 0.05, 0.25, and 4 *N* hydrochloric acid were used as the eluents for eluting Cs^+, Sr^{2+}, and Th^{4+}, respectively.

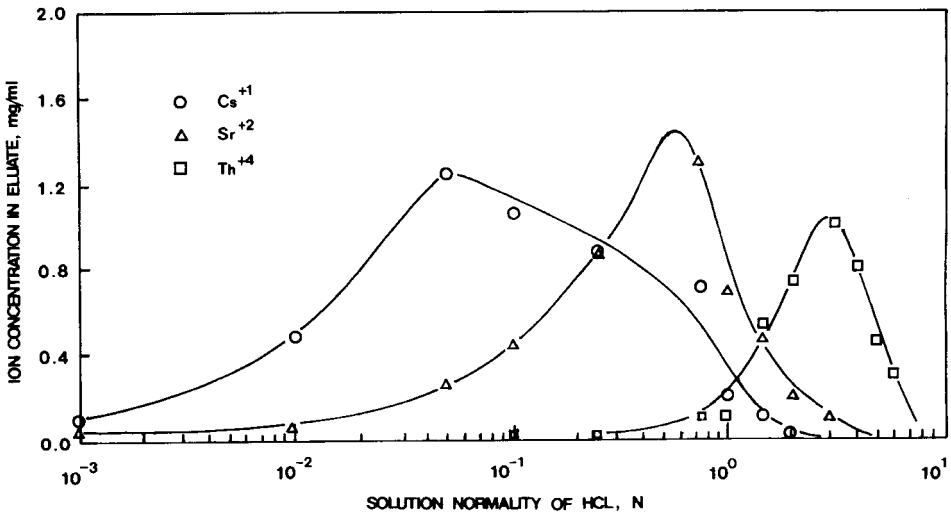

FIG. 4. Elution phenomena of Cs^+, Sr^{2+}, and Th^{4+} as a function of normality of hydrochloric acid.

2. Optimum Contact Time between Resin and Solution for Loading and Elution Process

For the batchwise process used in MCBC to be conducted successfully, the resin and solution must have the optimum contact time, which is defined as the length of time required for exchanging a significant fraction of ions between the resin and solution phases.

The optimum contact time for loading ions on the resin was determined from the batch ion-exchange experiment conducted previously (*7*): it was 2 h. At 2 h after initial contact, the solution phase ion concentrations of Cs^+, Sr^{2+}, and Th^{4+} were slightly different from those at equilibrium (about 48 h). The differences between the concentrations at 2 h and at equilibrium were less than 2%. The optimum contact time for eluting the resin phase ions was also examined by eluting the resin phase Cs^+, Sr^{2+}, and Th^{4+} with 0.05, 0.25, and 4 *N* HCl, respectively. The concentrations of Cs^+ and Sr^{2+} in the eluent were about constant after 1 h, but the concentration of Th^{4+} increased slowly up to and beyond 35 h after initial contact. To elute 90% of the total resin phase Th^{4+}, about 66 h of contact with the eluate was necessary. The determined optimum contact time was 1 h for eluting Cs^+ and Sr^{2+}, and 48 h for Th^{4+}.

3. Results of MCBC

The history of Flask 7 in the MCBC process was analyzed to understand the ion-exchange interactions between Cs^+, Sr^{2+}, Th^{4+}, and the resin in 8 stages which Flask 7 had passed through in the loading and elution processes.

Loading Process

The experimental conditions for the loading process are given in Table 1. The variations of Cs^+, Sr^{2+}, and Th^{4+} concentrations in the solution in each stage are shown in Fig. 5.

In the first two solution inlet stages (Stages 1 and 2), some amount of resin phase Cs^+ was displaced from the resin by Sr^{2+} and Th^{4+}. As a result, the displaced Cs^+ was stored in the first three stages (Stages 1, 2, 3) of the MCBC, and the concentration of Cs^+ thus exceeded the initial concentration of Cs^+ in the feed solution. The Cs^+ concentration in the solution was increased to a 2.5-fold build-up over its initial concentration. After the first three stages, the remaining Cs^+ in solution was completely recovered in Stages 3 through 8. Therefore, some amount of Cs^+ was led to the internal circulation in the MCBC.

Sr^{2+} was slightly displaced by Th^{4+} at the solution inlet stage (Stage 1) and then completely recovered in Stages 2 and 3. Thus, Sr^{2+} also exhibited

TABLE 1
Experimental Conditions of MCBC for Loading and Elution Processes

Flask no.	1	2	3	4	5	6	7
Loading Process							
Dry weight of resin (g)	2.995	3.016	3.025	3.024	3.022	3.029	3.033
Ion-exchange capacity (meq)	7.515	7.567	7.590	7.690	7.528	7.547	7.710
Resin	Dowex HCR-W2 in H^+ form						
Solution	Chloride salt solution of Cs^+, Sr^{2+}, and Th^{4+} in a 1:1:1 ratio in solution normality						
Total solution normality	0.1						
Total meq ratio between solution and resin phases	Solution phase:resin phase = 16:15						
Amount of each ion in solution	Sr^{2+}, 1.4602 mg/mL; Cs^+, 4.429 mg/mL; Th^{4+}, 1.906 mg/mL						
Volume of feed solution	80 mL						
Contact hours	2						
Elution Process							
Amount of absorbed ion in loaded resin (meq):							
Cs^+	0.66	0.29	0.74	0.87	0.87	1.38	0.96
Sr^{2+}	1.68	2.57	3.75	3.75	3.75	3.46	3.75
Th^{4+}	5.11	4.38	3.32	2.68	2.68	3.12	2.85
Concentration of eluent HCl	0.05 *N* HCl for Cs^+, 0.25 *N* HCl for Sr^{2+}, 4 *N* HCl for Th^{4+}						
Volume of eluent	80 mL						
Contact hours	2						

small internal circulation at the solution inlet stage. However, all Th^{4+} was recovered in the first two resin outlet stages, with most of Th^{4+} absorbed in the first stage.

Therefore, Stages 4 through 8 were not necessary to the recovery of Cs^+. Consequently, to increase the effective operational process of recovery for the Cs^+, Sr^{2+}, and Th^{4+} in the loading process, only three stages are necessary.

Elution Process

The initial conditions for the elution process are given in Table 1. The elution histories for three ions are shown in Fig. 6. When Cs^+ was eluted by using 0.05 *N* HCl eluant, a large amount of Sr^{2+} was also eluted and therefore the purity of the separated Cs^+ was reduced. The separated Cs^+

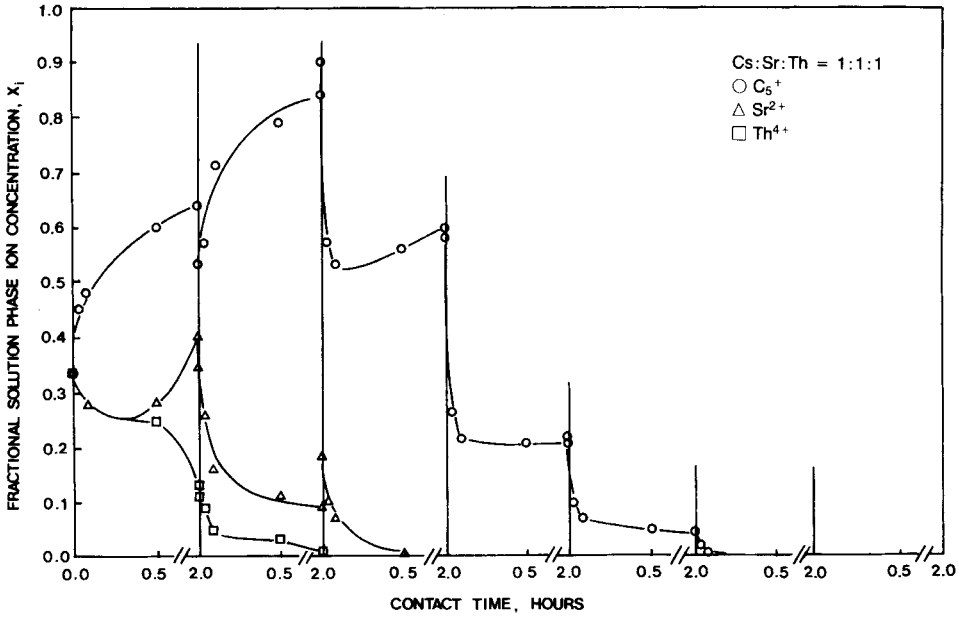

FIG. 5. Fractional meq solution phase ion concentration in each stage of Flask 7 as a function of contact time for loading process.

was 60% pure. Th^{4+} was not detected in the Cs^+ eluant. It can therefore be concluded that 0.05 *N* HCl was still too high a concentration to elute and separate pure Cs^+.

When Sr^{2+} was eluted by using 0.25 *N* HCl, high purity Sr^{2+} was obtained. The purity was 93%. The 7% contaminated ion was Cs^+. Th^{4+} was not detected.

Th^{4+} was eluted using 4 *N* HCl and was more than 65% pure. It was contaminated with Sr^{2+}.

The elution efficiencies (percentage of total meq of ion in eluant to initial total meq of resin phase ion) of Cs^+, Sr^{2+}, and Th^{4+} were about 100, 61, and 58%, respectively. The low elution efficiencies of Sr^{2+} and Th^{4+} indicate that large amounts of Sr^{2+} and Th^{4+} remain on the resin and that larger amounts of eluants (>80 mL) are necessary.

The separation efficiencies (Eff) of the MCBC conducted in this work for the three ions are shown in Fig. 7. These calculations were based on

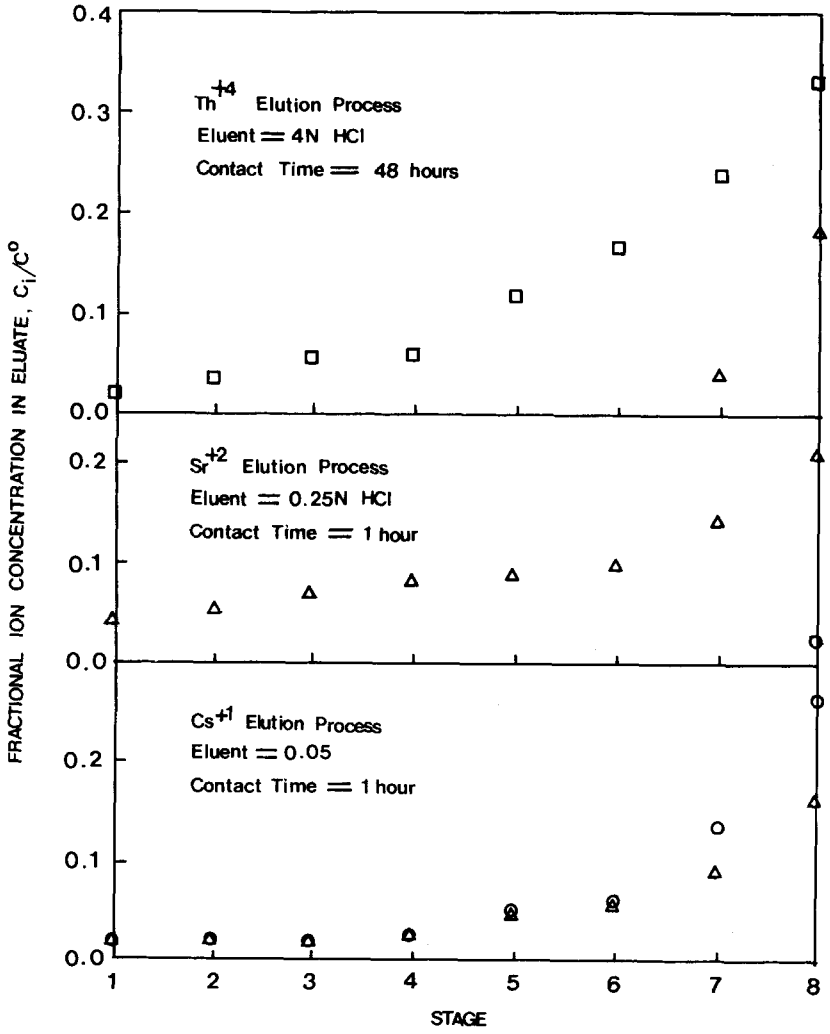

FIG. 6. Elution history of Cs^+, Sr^{2+}, and Th^{4+}: (○) Cs^+, (△) Sr^{2+}, (□) Th^{4+}.

a feed solution of 81 mL and were completed by using the following relation:

$$\text{Eff} = \frac{\text{amount of ion in eluant in Flask 7}}{\text{amount of ion in feed solution of 81 mL}} \times 100 \qquad (2)$$

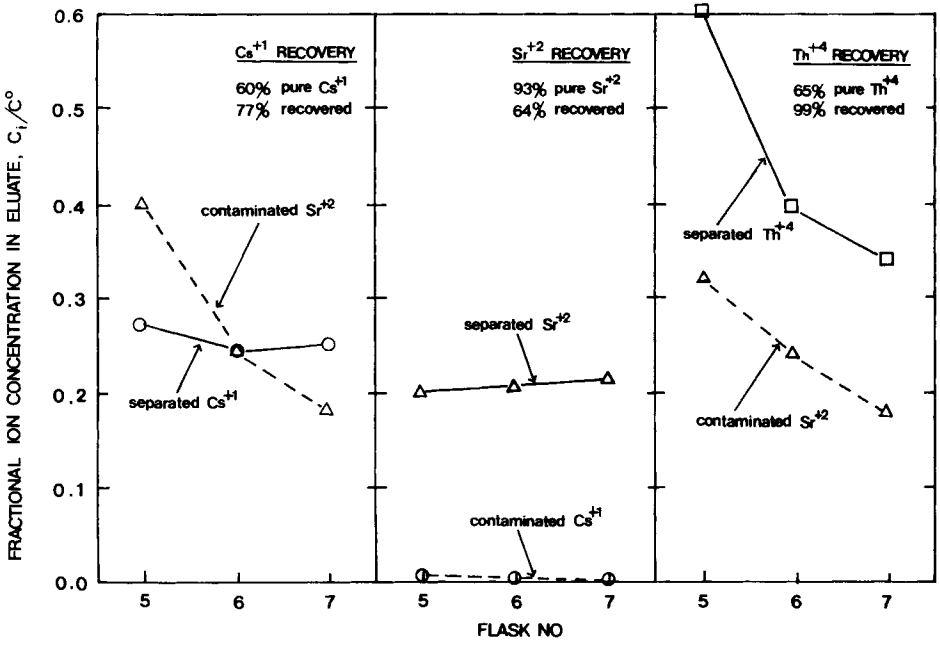

FIG. 7. Results of recovery process for Cs^+, Sr^{2+}, and Th^{4+}. The purities of the separated ions as given in the figure were determined by analyzing Flask 7.

Figure 7 shows that the capability for recovering Cs^+, Sr^{2+}, and Th^{4+} from the waste stream by using a sequential ion-exchange separation 8-stage countercurrent batch contactor is high.

More than 99% of the total amount of thorium in the feed solution was recovered. Cesium and strontium were recovered at levels of more than 77 and 64%, respectively, of the total amount of each in the feed solution. Figure 7 shows that if more than 7 flasks are used for the elution process, the purities of the ions are increased.

CONCLUSION

The overall recovery efficiencies of the 8-stage MCBC for the separation of Cs^+, Sr^{2+}, and Th^{4+} were 77, 64, and 99%, respectively. The purities of the separated ions were 60% for Cs^+, 93% for Sr^{2+}, and 65% for Th^{4+}. To increase the recovery efficiencies and the purities of the separated ions, Cs^+ should be collected after the 3rd stage in the loading process, since all the Sr^{2+} and Th^{4+} were adsorbed in the first 3 stages and the Cs^+ remaining in solution after the 3rd stage would be 100% pure.

The Cs^+ hydrochloric acid eluant concentration, 0.05 *N*, was too high to produce high purity Cs^+. The 0.05 *N* hydrochloric acid eluted a significant amount of Sr^{2+} which contaminated the Cs^+.

This work shows it would be possible to increase the recovery efficiencies and purities of the three ions if 3 stages were used for the loading process and if a hydrochloric acid concentration lower than 0.05 *N* were used for eluting Cs^+.

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