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Separation of Cesium and Strontium by Electrodialysis

H.C. Hershey, R.D. Mitchell, and W.H. Webb

Department of Chemical Engineering and Chemistry

University of Missouri

School of Mines and Metallurgy

Rolla, Missouri

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The processes for the recovery of fertile and fissionable materials from spent reactor fuel have been well established, but the technology for the recovery of the useful radioactive fission products from waste solutions is less well-developed. Bub, Vie, and Webb (2,5) separated some of the fission elements into three fractions by an electrodialysis process. In the presence of fluoride ion, strontium and cesium were transferred as positively charged ions (Sr^{++} , Cs^{+}) to the cathode cell of a three cell electrodialyzer, while the negatively charged ion (ZrF_6^{-2}) was transferred to the anode cell. The rare earth elements remained in the feed cell in the form of radiocolloidal fluorides.

The purpose of this investigation was to separate individual elements from the above fractions. Quantitative electrodialytic separation of two species is practical only when their ionic charges in solution are opposite or when one species is neutral. A method of changing the ionic charge of an ion in solution is to form a stable complex with another ion of opposite charge. Chelating agents such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) form strong complexes with many cations in solution.

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A careful study of the solution chemistry of strontium and cesium indicated that EDTA or DTPA could be used for their separation by electrodialysis. Durham and Ryskiewich (4) showed that above a pH of 10 the following reaction occurs between strontium and DTPA:

where Y is DTPA with the five replaceable hydrogens removed. The stability constant (pKsc) for strontium and DTPA (defined as the logarithm of the thermodynamic equilibrium constant for the above reaction) is 9.68. The following reaction occurs between strontium and EDTA above a pH of 10:

where Y is EDTA with the four replaceable hydrogens removed. The stability constant for this reaction is 8.63 (1). Although these ligands form such stable complexes with metal ions that they will combine to some extent with sodium and lithium, they will not combine with the other alkali metals including cesium. Therefore, in the presence of these chelating compounds, strontium and cesium exist in basic solution as negatively and positively charged species, respectively.

EXPERIMENTAL

Electrodialysis studies in this laboratory were performed with two and three cell electrodialyzers as described by

Bub and Webb (3), and Bub, Vie, and Webb (2). In the two cell electrodialyzer, the cathode cell, which served as a feed cell, was separated from the anode cell by an anion exchange membrane (Permutit 3148). In the three cell unit, the center feed cell was separated from the anode and cathode cells either by two cation exchange (Permutit 3142) or by two anion exchange (Permutit 3148) membranes. The two cell electrodialyzer continuously recycled the contents of each cell using a Brosites positive displacement pump. This action reduced diffusional effects, provided cooling, and enabled the feed solution pH to be monitored continuously. The temperature in the three cell electrodialyzer was controlled by passing cold water over the exterior surface. No pumping was attempted. The membrane area of the two cell unit was 41.8 cm^2 and that of the three cell unit was 20.3 cm^2 .

Analyses of the initial and final concentrations of strontium and cesium were made by standard radioactive tracer techniques. Carrier solutions of both natural strontium and natural cesium were added to each initial feed solution. Radiostrontium was added and the electrodialysis experiment performed. This experiment was then repeated using radiocesium as tracer. The carrier-free radioisotopes of Cs-Ba-137 and Sr-Y-90 were obtained from the Oak Ridge National Laboratory.

The concentration of strontium or cesium in each solution was determined with an accuracy of $\pm 5\%$. However, radio-counting techniques are extremely accurate in determining the

absence of a radioelement. The limit of detection is less than 0.1%. Thus, the concentration is less than 0.1% for the values reported as 0.0% in Tables I and II.

EDTA and DTPA, manufactured by Geigy Chemical Company, were added in large excess to the feed solutions. The initial feed solution pH was adjusted to 11 by adding sodium hydroxide. Design and operation of the experiments precluded the use of buffering agents since the buffering agent rather than the chelate would transfer through the membrane. All other cells were filled initially with 0.5 molar sodium hydroxide.

The approximate activities used in the initial feed solutions for the two cell electrodialyzer were 140,000 cps for the strontium tracer and 100,000 cps for the cesium tracer in a volume of 150 ml. For the three cell electrodialyzer, the activities were 35,000 cps for the strontium tracer and 22,000 cps for the cesium tracer in a volume of 33 ml. The concentrations of carrier strontium and cesium were 1.1×10^{-5} moles per liter and 7.3×10^{-6} moles per liter, respectively, in the two cell electrodialyzer experiments while in the three cell electrodialyzer the concentrations were 3.4×10^{-7} moles per liter and 2.2×10^{-7} moles per liter, respectively.

DISCUSSION OF RESULTS AND CONCLUSIONS

The results of the investigation are summarized in Tables I and II. The two cell electrodialyzer was used to determine the optimum feed solution pH. It was found that in

strongly basic solutions the mobile hydroxide ions transferred through the membrane instead of the less mobile strontium chelate ion. An initial pH of 11 was found to give the highest transfer of strontium. Below a pH of 11, the concentration of free strontium ions becomes significant. During these experiments, the feed solution pH increased because every negatively-charged species passing through the anion exchange membranes was replaced by a number of hydroxide ions (which were produced by the electrolysis of water at the cathode) equal to the charge of the species transferred. In the two cell experiments, no cesium at all was transferred to the anode cell whereas the strontium transfer was 74.9% in the EDTA solution and 46.7% in the DTPA solution. The strontium concentrations in the final feed solutions were 4.3% and 20.4%, respectively. The remainder of the strontium was sorbed in the membrane and on the walls of the electrodialyzer.

Table I shows that the pH of the feed solution increased more rapidly in the presence of DTPA than in the presence of EDTA in the two cell experiments because the greater negative charge of DTPA in basic solution results in the production of one more hydroxide ion per ion of DTPA transferred, than per ion of EDTA. Thus, the more rapid increase in basicity and the subsequent competing transfer of hydroxide ion account for the less efficient transfer of strontium DTPA in these experiments. However, under conditions of absolutely constant feed solution pH the difference in transfer rates might be negligible.

It was also attempted to separate strontium from cesium in a two cell electrodialyzer employing a cation exchange membrane and using the anode compartment as the feed cell. However, after about 20 minutes of electrodialysis the feed solution pH dropped to less than 7.0 where both cesium and strontium exist primarily as uncomplexed cations. The feed solution pH had dropped rapidly because the sodium cations in the feed solution (added with the disodium DTPA or EDTA and with the sodium hydroxide used to adjust the pH), which were present in large excess compared with cesium, transferred freely to the cathode cell and were replaced in the feed cell by hydrogen ions formed at the anode. Thus, this method was completely unsatisfactory.

The three cell electrodialyzer was used to study the separation of strontium from cesium in 0.005 molar EDTA solutions at an initial pH of 11.0 employing either two cation or two anion exchange membranes separating the feed cell from the cathode and anode cells. The results obtained with anion exchange membranes show that 94% of the cesium was retained in the feed cell while 2.2% of it transferred to the anode cell with 85% of the strontium. When cation exchange membranes were used, 75% of the strontium was retained in the feed cell while 11% of it transferred to the cathode cell with 81% of the cesium. This transfer of the strontium might be due to the fact that the cation membrane was not completely permselective.

On the basis of these results, it was concluded that cation exchange membranes are unsatisfactory for this process. Use of the Permutit anion exchange membranes resulted in quantitative separation of strontium from cesium when used in the two cell electrodialyzer and in excellent separation when used in the three cell electrodialyzer. EDTA provided better separation than DTPA under the specific experimental conditions used in these experiments. This process is feasible for the separation and purification of strontium and cesium. Further development work should include a study of increased current density, better pH control and increased electrodialysis time.

TABLE I. Separation of Strontium and Cesium in the Two Cell Electrodialyzer

EXPERIMENT NUMBER	1	2	3	4
Chelating agent*	EDTA	EDTA	DTPA	DTPA
Tracer isotope	Sr-90	Cs-137	Sr-90	Cs-137
Current density, ma/cm ²	11.9	19.0	19.0	21.4
Electrodialysis time, min	120	120	120	120
Initial pH	10.8	11.0	11.0	11.0
Final pH	12.1	12.6	12.6	12.6
Final anode activity**	74.9	0.0	46.7	0.0
Final feed activity**	4.3	97.5	20.4	99.0

* Chelate concentration was 0.0033 molar in all experiments.

**Per cent of initial feed solution activity.

TABLE II. Separation of Strontium and Cesium in the Three Cell Electrodialyzer with EDTA* as the Chelating Agent

EXPERIMENT NUMBER	1	2	3	4
Membrane type	Anion	Anion	Cation	Cation
Tracer isotope	Sr-90	Cs-137	Sr-90	Cs-137
Current density ma/cm ²	14.8	19.7	27.1	41.1
Electrodialysis time, min	60	60	90	90
Initial pH	11.0	11.0	11.0	11.0
Final pH	11.4	11.8	12.1	12.1
Final anode activity**	85.5	2.2	0.0	1.7
Final feed activity**	2.7	94.4	75.1	1.7
Final cathode activity**	0.4	3.4	11.3	81.5

* Chelate concentration was 0.005 molar in all experiments.

**Per cent of initial feed solution activity.

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