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THE SEPARATION OF SOME OF THE RADIOACTIVE
FISSION PRODUCTS BY ELECTRODIALYSIS

by

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INTRODUCTION

The processing of aqueous solutions of irradiated reactor fuel elements for the recovery of fissionable materials by solvent extraction and precipitation methods leaves a radioactive waste solution containing the fission products. This solution also contains various acids (HNO_3 , HF, etc.) depending on the method of dissolution of the fuel elements. The acid is recovered, leaving a waste solution containing the fission products. The nuclei formed by fission have mass numbers from 72 to 158 (18).

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 these waste solutions is less well-developed.

There have been many suggestions for the disposal of this fission product waste solution, some include recovery techniques for certain fission elements. The volume is usually reduced and the concentrate stored until the radiological hazard is reduced. The presence of cesium 137 and strontium 90 prolong this storage. Many of these radioactive isotopes are very useful in scientific research, medicine, industrial tools, and power generators for space technology.

Electrodialysis has been proposed by several investigators as a means of volume reduction and acid or electrolyte

recovery (9, 14, 16). The electrodialysis process is accompanied by electroendosmosis, water transport. Zirconium can be sorbed on silica gel and recovered with oxalic acid (4). Cesium and strontium can be fixed on siliceous materials (1). Other fission elements can be recovered by ion exchange or solvent extraction (1, 4). The colloidal nature of zirconium in nitric acid enables one to remove this isotope by means of silica gel, but this characteristic presents problems in other chemical processing.

Blumenthal considers the zirconium species to be almost non-ionic in nitric acid and proposes $\text{ZrO}(\text{OH})\text{NO}_3$ as the formula (3). Lister and McDonald consider the zirconium to be present as highly polymerized ions, possibly the tetramer, $\text{Zr}_4\text{O}_7^{+2}$, at low acid concentrations (12). They believe that this species dissociates to the dimer, $[(\text{OH})_2\text{-Zr-O-Zr-(OH)}]_2^{+2}$ and then to $[\text{Zr}(\text{OH})_2\text{NO}_3]^{+1}$ as the acid concentration is increased. They proposed $[\text{Zr}(\text{NO}_3)_2]^{+2}$ as the predominate species in 4N acid and $[\text{Zr}(\text{OH})_2(\text{NO}_3)_4]^{-2}$ or possibly $[\text{Zr}(\text{NO}_3)_6]$ at higher acid concentrations.

A review of the literature indicated that electrodialysis, using ion exchange (permselective) membranes, can be employed for the fractionation and purification of some of the radioactive fission elements. Ion exchange membranes are thin sheets of either cation or anion exchange resins bound to an inert matrix or they may be prepared by rolling colloidal ion exchange material into a foil under pressure. Helfferich presents an excellent description and preparation of these membranes (11).

EXPERIMENTAL

Electrodialysis experiments were performed using various types of electrodialyzers and ion exchange membranes. A five-cell electrodialyzer was purchased from Brosites Machine Co., Inc., 50 Church Street, New York 7, N. Y. Several units were constructed in this laboratory from acrylic plastic and polyvinyl chloride (6,7,19). Radioisotopes were purchased from Union Carbide Nuclear Company, Oak Ridge, Tennessee.

CHEMICAL BEHAVIOR OF ZIRCONIUM

The chemical behavior of Zirconium in aqueous solutions was investigated by means of electrodialysis and solvent extraction.

Electrodialysis experiments were performed using a three-cell electrodialyzer and permittit 3142 and 3148 cation and anion membranes. Acid solutions of zirconium (total activity 11,250 cps) were electrodialyzed for a period of one hour with a current density of 114 milliamperes per cm^2 . The results shown in Table I indicate that zirconium remained in the feed cell during electrodialysis in all acids except hydrofluoric. In this acid the zirconium was present as ZrF_6^{-2} and transferred to the anode cell. Most of the zirconium was deposited on the exchange membrane when the other acids were used. The same trend was observed when fritted glass partitions were used instead of ion exchange membranes. The fractions in each cell of the electrodialyzer were analyzed by a radioactive

counting technique. Aluminum absorbers were used to differentiate the zirconium and niobium activities.

Nitric acid solutions of radioactive (150 cps per ml) and natural zirconium were prepared and extracted with an equal volume of 0.05 M theonyl trifluoroacetone in xylene. After 30 minutes shaking with a mechanical shaker, the two phases were separated and analyzed.

The radioactive zirconium was analyzed by the radioactive counting technique and the natural zirconium was analyzed by a colorimetric method using the pyrocatechol violet method. The data in Table II shows that at a given acid concentration, natural zirconium is more easily extracted than zirconium-95.

Table I
ELECTRODIALYSIS OF ZIRCONIUM-95 (a)

<u>Acid Soln.</u>	<u>Normality</u>	% dialyzed (c)	
		<u>Anode</u>	<u>Cathode</u>
HNO ₃	3.28 ^b	0.13	0.12
	2.22	0.12	0.15
	1.04	0.13	0.17
	0.66	0.14	0.15
	0.39	0.17	0.19
H ₂ C ₂ O ₄	1.98	40.00	3.90
	1.19	61.00	2.20
	0.69	59.20	1.80
HF	1.72	72.00	2.90
	0.94	90.50	2.10
H ₂ SO ₄	3.00	14.40	1.30
	2.14	15.80	0.80
	1.00	11.30	0.40
	0.50	5.10	0.80
HCl	3.30	0.14	0.15
	2.11	0.12	0.14
	1.06	0.11	0.16
	0.68	0.13	0.19
	0.41	0.16	0.20
HClO ₄ (b)	6.27	0.2	0.3
	3.97	0.30	0.30
	2.07	0.11	0.13
	1.12	0.12	0.11
	0.43	0.08	0.07

(a) Electrodialyzed for one hour unless otherwise indicated.

(b) Electrodialyzed for two hours.

(c) Recoveries ranged from about 89 to 102%.

Table II
TTA EXTRACTION OF ZIRCONIUM IN ACID^(c)

<u>Acid Normality</u>	<u>Solution of Isotope</u>	<u>% Extracted</u>
0.98	Zr-95	90.1(a)
0.97(b)	Zr-95 & Zr-nat	90.1(a)
0.97(b)	Zr-95 & Zr-nat	99.6
1.00	Zr-nat	99.1
1.40	Zr-95	93.8(a)
1.45(b)	Zr-95 & Zr-nat	92.4(a)
1.45(b)	Zr-95 & Zr-nat	99.1
1.48	Zr-nat(b)	99.1
1.86	Zr-95	97.9(a)
1.97(b)	Zr-95 & Zr-nat	96.2(a)
1.97(b)	Zr-95 & Zr-nat	99.3
1.96	Zr-nat(b)	99.7
2.45	Zr-95	98.3(a)
2.37(b)	Zr-95 & Zr-nat	98.4(a)
2.37(b)	Zr-95 & Zr-nat	100.0
2.41	Zr-nat(b)	99.9
2.94	Zr-95	99.2(a)
2.76(b)	Zr-95 & Zr-nat	98.8(a)
2.76(b)	Zr-95 & Zr-nat	99.8
2.94	Zr-nat	99.8

(a) The % extraction of zirconium-95.

(b) Indicates the solution containing Zr-95 & Zr-nat, which was analyzed both for natural - Zirconium and Zr-95 content

(c) The amount extracted given in table is an average of ten runs.

FRACTIONATION OF CERIUM, CESIUM, PROMETHIUM,
STRONTIUM, AND ZIRCONIUM

Electrodialysis methods were used for the fractionation of Cs-Ba¹³⁷, Ce-Pr¹⁴⁴, Sr-Y⁹⁰, Pm¹⁴⁷, and Zr-Nb⁹⁵.

Experiments were performed with both three-cell and seven-cell electrodialyzers. The operating conditions and description of electrodialyzers were reported by Bub and Webb (6) and Bub, Vie, and Webb (7). Figure 1 shows the flow diagram for the seven-cell electrodialyzer. This electrodialyzer provided a flow system for anion and cation wash solutions for cooling and also reduced the sorption of Zr-Nb⁹⁵ and Ce-Pr¹⁴⁴.

The results presented in Tables III, IV, V, and VI show that these elements were separated into three fractions when HF, NH₄HF₂ or a mixture of NH₄HF₂ and HNO₃ were used. The Sr⁹⁰ and Cs-Ba¹³⁷ were transferred to the cathode cell as simple positively charged ions, the Zr⁹⁰ was transferred to the anode cell as ZrF₆⁼ and the Ce¹⁴⁴ and Pm¹⁴⁷ remained in the feed cell as radiocolloidal fluorides.

Separations were unsatisfactory when HNO₃ alone was used because most of the zirconium was present in colloidal form. When H₂C₂O₄ was used, zirconium did not transfer as well as with HF; and the Ce¹⁴⁴ was distributed in all cells of the dialyzer.

Figure 1. Flow Sheet for Seven Cell Electrodialyzer

F. - Feed solution containing radioactive isotope.
C. - Cation wash solution. A. - Anion wash solution.

Table III. Separation of Cs-Ba¹³⁷, Zr-Nb⁹⁵, and Ce-Pr¹⁴⁴

	Initial Isotope Acitivity in Feed Cell, D.P.S. ^a	Isotope Activity after 2-Hr., <u>Electrodialysis, D.P.S.^a</u> Anode Cell Feed Cell Cathode Cell		
Isotope		<u>Experiment I</u>		
		In 1.23 <u>N</u> Hydrofluoric Acid		
Cs-Ba ¹³⁷	46,125	0.0	585	45,000
Zr-Nb ⁹⁵	21,550	19,920	465	0.0
Ce-Pr ¹⁴⁴	37,500	0.0	19,100	0.0
Total, D.P.S. ^a	105,175	19,920	20,150	45,000
Recovery ^b	80.9%			
Final Acidity, <u>N</u>		1.36	0.21	0.95
		In 1.20 <u>F</u> Ammonium Acid Fluoride ^c		
Cs-Ba ¹³⁷	38,050	0.0	905	36,550
Zr-Nb ⁹⁵	11,475	10,050	510	0.0
Ce-Pr ¹⁴⁴	39,350	0.0	32,300	0.0
Total, D.P.S. ^a	88,875	10,050	33,715	36,550
Recovery ^b	90.4%			
Final Acidity, <u>N</u>		1.93	0.33	0.72

Table III. Separation of Cs-Ba¹³⁷, Zr-Nb⁹⁵, and Ce-Pr¹⁴⁴ (cont.)

Isotope	Initial Isotope Activity in Feed Cell, D.P.S. ^a	Isotope Activity after 2-Hr., Electrodialysis, D.P.S. ^a		
		Anode Cell	Feed Cell	Cathode Cell
<hr/>				
		Experiment 2		
<hr/>				
		In 1.23 N Hydrofluoric Acid		
Cs-Ba ¹³⁷	46,900	0.0	650	46,100
Zr-Nb ⁹⁵	21,900	17,200	475	0.0
Ce-Pr ¹⁴⁴	35,300	0.0	21,800	0.0
Total, D.P.S. ^a	104,100	17,200	22,925	46,100
Recovery ^b	82.8%			
Final Acidity, N		1.37	0.21	0.97
		In 1.20 F Ammonium Acid Fluoride ^c		
Cs-Ba ¹³⁷	48,000	0.0	1,050	44,700
Zr-Nb ⁹⁵	14,600	11,420	985	0.0
Ce-Pr ¹⁴⁴	39,400	0.0	31,700	0.0
Total, D.P.S. ^a	102,000	11,420	33,735	44,700
Recovery ^b	88.1%			
Final Acidity, N		1.92	0.30	0.79

a. Disintegrations per second.

b. Losses due to sorption on ion exchange membranes.

c. Formula weights per liter of solution.

Table IV.

Electrodialysis of Cs-Ba¹³⁷, Zr-Nb⁹⁵ and Ce-Pr¹⁴⁴
in Ammonium Acid Fluoride Solution
using the Seven Cell Unit.

Per cent of Initial Isotope
Activity in Solutions After
2 Hours Electrodialysis, %.

Initial Isotope				
<u>Isotope</u>	<u>Activity, D.P.S.^a x 10⁶</u>	<u>Anion</u>	<u>Feed</u>	<u>Cation</u>
Initial Acidity,	<u>N</u>	0.69	1.15	0.62
Cs-Ba ¹³⁷	17.38	0.0	26.0	73.7
Final Acidity,	<u>N</u>	1.49	0.50	0.14
Initial Acidity,	<u>N</u>	0.53	1.03	0.54
Zr-Nb ⁹⁵	8.35	55.3	40.5	0.0
Final Acidity,	<u>N</u>	1.62	0.40	0.08
Initial Acidity,	<u>N</u>	0.65	0.48	0.48
Ce-Pr ¹⁴⁴	3.31	0.0	99.5	0.0
	3.24	0.0	98.1	0.0
Final Acidity,	<u>N</u>	1.10	0.19	0.26
Flow Rate, ml/min.		150	109	200

^a Disintegrations Per Second.

Table V.

Separation of Cs-Ba¹³⁷ and Zr-Nb⁹⁵
in 0.5 Formal Ammonium Acid Fluoride
using the Seven Cell Unit.

Per cent of Initial Isotope
Activity in Solutions After
1 1/2 Hours Electrodialysis, %.

Initial Isotope				
Isotope	Activity, D.P.S. ^a x 10 ⁶	Anion	Feed	Cation
<u>Exp. 1.</u>				
Cs-Ba ¹³⁷	2.21	0.0	18.0	81.6
Zr-Nb ⁹⁵	1.68	63.5	34.0	0.0
Final Acidity,	<u>N</u>	1.29	0.24	0.49
<u>Exp. 2.</u>				
Cs-Ba ¹³⁷	2.07	0.0	9.9	89.6
Zr-Nb ⁹⁵	1.74	69.7	29.2	0.0
Final Acidity,	<u>N</u>	1.09	0.21	0.31
Flow Rate, ml/min.		150	109	200

^a Disintegrations Per Second.

Table VI.

Summary of Results from the Seven Cell Unit
in a Mixture of 0.5 Normal Nitric Acid and
0.5 Formal Ammonium Acid Fluoride.

Per cent of Initial Isotope
Activity in Solutions After
2 Hours Electrodialysis, %.

<u>Isotope</u>	<u>Initial Isotope Activity, D.P.S^a x 10⁶</u>	<u>Anion</u>	<u>Feed</u>	<u>Cation</u>
<u>Exp. 1.</u>				
Cs-Ba ¹³⁷	1.92	0.0	9.5	90.5
Zr-Nb ⁹⁵	1.61	34.9	62.1	0.0
Ce-Pr ¹⁴⁴	2.11	0.0	98.0	0.0
Sr-Y ⁹⁰	4.43	0.0	70.0	30.0
Pm ¹⁴⁷	3.95	0.0	98.0	0.0
Flow Rate, ml/min.		150	109	250
<u>Exp. 2.</u>				
Cs-Ba ¹³⁷	2.37	0.0	8.2	91.8
Zr-Nb ⁹⁵	1.64	30.7	63.7	0.0
Ce-Pr ¹⁴⁴	3.24	0.0	99.0	0.0
Sr-Y ⁹⁰	4.75	0.0	60.0	39.7
Pm ¹⁴⁷	4.02	0.0	99.0	0.0
Flow Rate, ml/min.		150	109	200

^a Disintegrations Per Second.

SEPARATION OF CESIUM AND STRONTIUM

Separation by Electrodialysis

Since both cesium and strontium migrated as positively charged ions to the cathode cell during the fractionation of the fission elements a method had to be devised for the separation of these ions. Quantitative electrodialytic separation of two species is practical only when their ionic charges in solution are opposite or when one species is neutral.

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 (10) 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 (pK_{sc}) 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 (2). 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.

Electrodialysis studies in this laboratory were performed with two and three cell electrodialyzers as described by Bub and Webb (6), and Bub, Vie, and Webb (7). 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 VII and VIII.

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.

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

Table VII

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.

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 VII 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 mem-

Table VIII

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.

brane 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.

Separation by Liquid-Liquid Extraction

A study of the separation of strontium from cesium by means of liquid-liquid extraction was made using Di-2 ethyl

hexyl phosphoric acid (D2EHPA). The application of this extractant was also reported by Schulz and Richardson (17).

McHenry and Posey (13) have shown that in low concentrations D2EHPA, dissolved in an inert solvent, reacts with a metallic ion as follows:

where M^{++} is the extracted ion. They reported that the value of the K_d for a particular ion varies inversely with the square of the hydrogen ion concentration. It was also shown that K_d for strontium extracted by 0.5 M D2EHPA is higher at low strontium concentrations than at higher concentrations, because excess D2EHPA forces the reaction of complexation to completion.

Butler and Ketchen (8) studied the effect of radiation on 1 M D2EHPA dissolved in an organic solvent in contact with 1.0 N nitric acid. Cobalt-60 was the source of gamma radiation. An exposure dose of 85 watt-hrs per liter had little effect on the K_d .

The D2EHPA was obtained from the Union Carbide Corporation, New York, New York. Purity was 91.5% which was satisfactory for this investigation. The xylene was obtained from the Mallinckrodt Chemical Company, St. Louis, Missouri. The EDTA was purchased from the Eastman Kodak Company, Rochester, New York. Carrier-free radioisotopes were obtained from the Oak Ridge National Laboratory. They are in equilibrium with their daughter products as cesium-barium-137 and strontium-yttrium-90.

The feed solutions were prepared by using either radioactive strontium or radioactive cesium in nitric acid solution. Sodium hydroxide was used to adjust the solution pH to the desired values. The EDTA feed solutions were 0.002 M. The organic phase consisted of 40% by volume of D2EHPA in xylene (1.21 M D2EHPA). Twenty-five ml of feed and twenty-five ml of organic solution were shaken for one hour with a mechanical shaker.

The feed solutions for the final test runs contained natural strontium and natural cesium, with concentrations of 3 mg per ml each, and were made 0.002 M with EDTA. The feed solutions also contained a radioactive tracer of either radioactive strontium or radioactive cesium. The tracers were used to determine the fraction of the solute extracted. Sodium hydroxide was used to adjust the pH of these solutions. The extractions were performed by the same method as described for the preliminary studies. Additional runs were then made under the identical conditions with the other tracer to determine the behavior of the other solute.

Analyses for the activity of radiocesium and radiostrontium were performed using a shielded Geiger-Muller counter.

EDTA was used as a suppressant for other extraceable ions, especially traces of the rare earth elements. These elements form non-extractable ions with the rare earths at a pH of 4-5 while a pH of 11 is required for the complexation of strontium with EDTA.

The data in Tables IX and X show that unless the feed solution is buffered, a high degree of extraction is not

obtained. Best results were obtained by extracting from a buffered aqueous solution at a pH of 4-5.

The data in Tables XI and XII show that in the presence of EDTA a high degree of extraction can be obtained if the feed solution is buffered at a pH of 3.5-4. Very little cesium is extracted by the D2EHPA, as shown in Table XIII. Table XIV shows that at a pH of 5 approximately 74 per cent of the strontium can be separated from the mixture by a single extraction. This extract contains 1.5 per cent cesium.

Table IX

Extraction of Strontium-90
from Nitrate Solutions⁽¹⁾

pH of Feed Solution	Distribution Ratio	Per Cent Extraction into Organic Phase
1.0	0.43	30.2
2.0	0.51	34.0
3.0	0.69	41.0
4.0	0.84	45.6
5.0	1.05	51.1
6.0	1.06	51.5
8.0	0.74	42.5

(1) Activity of feed solution for each run was 80,000 cps.

Table X

Extraction of Strontium-90
in Buffered Solution⁽¹⁾

pH of Feed Solution	Distribution Ratio	Per Cent Extraction into Organic Phase
3.0	3.82	79.5
3.5	15.85	94.1
4.0	44.70	97.9
4.3	72.40	98.6
5.0	68.20	98.5

(1) Activity of feed solution for each run was 330,000 cps.

Table XI

Extraction of Strontium-90
in the Presence of EDTA⁽¹⁾

pH of Feed Solution	Distribution Ratio	Per Cent Extraction into Organic Phase
2.0	0.82	45.0
3.0	1.74	63.5
4.0	2.24	69.1
5.0	1.93	65.9
6.0	3.39	77.2
7.0	5.80	85.2
11.0	9.87	90.8

(1) Activity of feed solution for each run was 124,000 cps.

Table XII

Extraction of Strontium-90 in the
Presence of EDTA and Buffered Solution⁽¹⁾

pH of Feed Solution	Distribution Ratio	Per Cent Extraction into Organic Phase
3.0	7.16	87.9
3.5	20.40	95.5
4.0	19.85	95.2
4.5	15.05	93.2
5.0	3.92	79.2
6.0	1.71	63.1

(1) Activity of the feed solution for each run was 80,000 cps.

Table XIII

Extraction of Strontium⁽¹⁾ and Cesium⁽¹⁾
in the Presence of EDTA

pH of Feed Solution	Per Cent Extraction of Strontium into Organic Phase	Per Cent Extraction of Cesium into Organic Phase
3.0	57.0	1.5
4.0	57.1	1.6
5.0	73.6	1.5
6.0	61.4	1.7
7.0	60.5	1.4
8.0	60.4	1.5

(1) Concentration was 3 mq/ml.

Table XIV

Extraction of Cesium-137
from Nitrate Solutions⁽¹⁾

pH of Feed Solution	Distribution Ratio	Per Cent Extraction into Organic Phase
4.0	0.0288	2.8
5.0	0.0309	3.0
3.0 *	0.0362	3.5
4.0 *	0.0309	3.0

(1) Activity of feed solution for each run was 123,500 cps.

* EDTA was used.

SEPARATION CERIUM AND PROMETHIUM

Electrodialysis methods were investigated for the separation of the rare earth elements especially cerium and promethium. The separation of these elements must depend upon the slight changes in their chemical properties induced by using various complex formers at varying pH and in a few cases differences in oxidation state. Both complex formers and precipitants were investigated in this study.

Aminopolycarboxylic Acids

These acids have been used for the separation of the rare earth elements by ion exchange methods. Brill, Brill, and Krumholz (5) reported the application of electrodialysis for the separation of some of the rare earths, although the efficiency was very low. Ethylenediaminetetraacetic acid (EDTA) and n-hydroxyethyl-ethylene diaminetriacetic acid (HEDTA) were investigated as possible reagents for the separation of the rare earth elements by electrodialysis.

No tabulations of metal ion concentration, pM , versus hydrogen ion concentration, pH , are available in the literature for solutions of rare earth ions and aminopolycarboxylic acids. However, the acid dissociation constants of the more important chelating agents and their stability constants with the rare earth ions are available (2). As a part of this project it was necessary to prepare tabulations of pM versus pH for lanthanum,

cerium, praseodymium, neodymium, and samarium ions in solutions of EDTA and HEDTA, in order to determine the proper operating conditions in electrodialysis experiments involving these chelate complexes. These tabulations were made from calculations with acid dissociation constants and stability constants available in the literature. The IBM 1620 digital computer located in the Computer Center, Department of Mathematics, Missouri School of Mines and Metallurgy, was used to solve the resulting equations. Following are a brief description of the computation and tables of pM versus pH.

The acid dissociation constants for EDTA (denoted as Y) are defined as minus the logarithms of the thermodynamic equilibrium constants (pK) for the following reactions:

where pK_1 is the acid dissociation constant for reaction (8), pK_2 for reaction (9), pK_3 for reaction (10), and pK_4 for reaction (11). The acid dissociation constants for HEDTA are defined by the following equations:

where pK_1 is the constant for reaction (12), pK_2 for reaction (13), and pK_3 for reaction (14). Table VXXVI presents the acid

dissociation constants for EDTA and for HEDTA.

The stability constants (pK_{sc}) for EDTA and HEDTA were defined for reactions (1) and (2), page 8, in the section on cesium and strontium. In addition, an acid chelate dissociation constant (pK_{HMY}) for EDTA must be defined for the following reaction because of its importance at low pH values:

Table XVI presents the stability constants for HEDTA and EDTA and some of the rare earth ions and the acid chelate dissociation constants for EDTA and some of the rare earth ions.

Table XV

ACID DISSOCIATION CONSTANTS OF EDTA AND HEDTA

<u>Acid</u>	<u>Temp. (°C)</u>	<u>pK_1</u>	<u>pK_2</u>	<u>pK_3</u>	<u>pK_4</u>
EDTA*	20	1.99	2.67	6.16	10.26
HEDTA**	20	2.90	5.41	9.89	---

*Bjerrum, J., Schwarzenbach, G., and Sillen, L.G., "Stability Constants, Part 1: Organic Ligands," p. 77. The Chemical Society, London, 1957.

**Mackey, J.L., and Powell, J.E., Determination of the Rare Earth-HEDTA Stability Constants by the Mercury Electrode Method. Inorg. Chem., 1, 418 (1962).

Table XVI

STABILITY CONSTANTS FOR RARE EARTH ION-HEDTA AND EDTA COMPLEXES

Acid	Temp. (°C)	Constant	La(III)	Ce(III)	Pr(III)	Nd(III)	Sm(III)
EDTA*	20	pK _{sc}	-15.13	-15.80	-16.16	-16.47	-16.90
EDTA**	20	Pk _{HMY}	----	----	----	----	----
HEDTA***	20	pK _{sc}	-13.82	-14.45	-14.96	-15.16	-15.64

*Bjerrum, J., Schwarzenback, G., and Sillen, L.G., "Stability Constants, Part 1: Organic Ligands," p. 77. The Chemical Society, London, 1957.

**Kolot, R.S., and Powell, J.E., The Solid Rare Earth Chelates of Ethylenediaminetetraacetic Acid. Inorg. Chem., 1, 485 (1962).

***Mackey, J.L., and Powell, J.E., Determination of the Rare Earth-HEDTA Stability Constants by the Mercury Electrode Method. Inorg. Chem., 1, 418 (1962).

A mass balance is used to solve the equations preceding for metal ion concentration as a function of hydrogen ion concentration. In EDTA solutions the total metal concentration equals the concentration of the free ions, (M^{+3}), plus the concentration of the metal chelate complex, (MY^-), plus the concentration of the acid metal chelate complex, (MHY). The total chelate concentration equals the summation of the concentrations of the metal chelate complex, (MY^-), of the acid metal chelate complex, (MHY), and of each of the remaining chelate species (H_4Y), (H_3Y^-), (H_2Y^{--}), ($HY^{=}$), and (Y^{-4}). Using the equilibrium constants for the reactions previously defined and a mass balance, it is possible to solve the resulting simultaneous equations for metal ion concentration as a function of the pH. Table XVII presents pM versus pH data for solutions of EDTA and the five lightest lanthanides that are found in nature. The EDTA concentration was 0.00333 moles per liter

while a concentration of 0.000001 moles per liter of lanthanide was used for the calculation. These are the concentrations used experimentally. Promethium is between neodymium and samarium in the periodic table, and the pM of solutions of promethium in EDTA for a given pH would be expected to be higher than that of neodymium but lower than that of samarium.

From Table XVII, it is evident that above pH of four, essentially all the rare earth ions in solution are complexed by EDTA. The extent of hydrolysis of the lanthanides in basic EDTA and HEDTA solutions is not sufficient to affect these results.

In HEDTA solutions the mass balances for lanthanide and chelate solutions are the same as for EDTA solutions, except that the (HMY) and (H₄Y) concentrations are zero since these species do not exist. The applicable equations were solved by modifying the input data to use the computer program written for H₄Y chelates (HEDTA is an H₃Y chelate, that is, it has three titratable hydrogens.). Table XVIII presents pM versus pH data for solutions of HEDTA and the five lightest lanthanides that are found in nature. For the calculation the total HEDTA concentration was 0.00333 moles per liter, and the lanthanide concentration 0.000001 moles per liter. As for EDTA, data for promethium would be expected to fall between that of neodymium and that of samarium.

From Table XVIII it is evident that above pH of four essentially all of the rare earth ions are complexed by HEDTA. Comparison of Tables X and XI indicate that above pH of four, EDTA is only slightly more effective than HEDTA as a chelating

agent. However, between pH of one and four, EDTA complexes are significantly more stable. This observed difference is directly attributable to the presence of the HMY species in EDTA solutions in this pH range.

The experiments performed to this date in this laboratory, using EDTA and HEDTA, have been unsuccessful as a practical method for the separation of the rare earth elements by electrodialysis. It has not been possible to control the pH of the solutions closely enough to effect adequate separations. The method which consists of oxidizing Ce(III) to Ce(IV) has failed because the Ce(IV) is reduced by the EDTA.

Table XVII

METAL ION CONCENTRATION(pM) VERSUS pH FOR
EDTA-LANTHANIDE SOLUTIONS AT 20°C

Total EDTA Concentration: 0.00333 moles per liter

Total Lanthanide Concentration: 0.000001 moles per liter

<u>Solution pH</u>	<u>La(III)pM</u>	<u>Ce(III)pM</u>	<u>Pr(III)pM</u>	<u>Nd(III)pM</u>	<u>Sm(III)pM</u>
1.000	6.000	6.002	6.005	6.010	6.027
2.000	6.228	6.628	6.926	7.209	7.621
3.000	8.174	8.842	9.202	9.512	9.941
4.000	10.223	10.893	11.253	11.563	11.993
5.000	12.203	12.873	13.233	13.543	13.973
6.000	14.004	14.674	15.034	15.334	15.774
7.000	15.333	16.003	16.363	16.673	17.103
8.000	16.384	17.054	17.414	17.724	18.154
9.000	17.368	18.038	18.398	18.708	19.138
10.000	18.202	18.872	19.232	19.542	19.972
11.000	18.580	19.250	19.610	19.920	20.350
12.000	18.644	19.314	19.674	19.984	20.414
13.000	18.651	19.321	19.681	19.991	20.421

Table XVIII

METAL ION CONCENTRATION (pM) VERSUS pH FOR
HEDTA-LANTHANIDE SOLUTIONS AT 20° C

Total HEDTA Concentration: 0.00333 moles per liter

Total Lanthanide Concentration: 0.000001 moles per liter

<u>Solution pH</u>	<u>La(III)pM</u>	<u>Ce(III)pM</u>	<u>Pr(III)pM</u>	<u>Nd(III)pM</u>	<u>Sm(III)pM</u>
1.000	6.000	6.000	6.000	6.000	6.000
2.000	6.013	6.054	6.156	6.227	6.488
3.000	7.341	7.955	8.462	8.662	9.141
4.000	9.673	10.303	10.813	11.013	11.493
5.000	11.627	12.257	12.767	12.967	13.447
6.000	13.133	13.763	14.273	14.473	14.953
7.000	14.238	14.868	15.378	15.578	16.058
8.000	15.247	15.877	16.387	16.587	17.067
9.000	16.218	16.848	17.358	17.558	18.038
10.000	16.994	17.624	18.134	18.334	18.814
11.000	17.292	17.922	18.432	18.632	19.112
12.000	17.337	17.967	18.477	18.677	19.157
13.000	17.342	17.972	18.482	18.682	19.162

Electrodialysis of Cerium and Promethium
in the Presence of Potassium Iodate

The insolubility of $\text{Ce}(\text{IO}_3)_4$ suggested a method for the separation of cerium from promethium. A feed solution was prepared by oxidizing $\text{Ce}(\text{III})$ to $\text{Ce}(\text{IV})$ with sodium bromate in strong nitric acid. Potassium iodate was added and the solution was diluted until it was 2.3 N with nitric acid and 0.07 M with iodate. The solution was electrodialyzed for one hour in a three-cell electrodialyzer, with a current density of 50 ma per cm^2 . The anode and cathode cells were filled with 0.25 M nitric acid.

The feed solution was placed in the middle cell with a cation membrane on the cathode end and an anion membrane on the anode end.

The same experiment was performed with promethium, except the oxidation step was omitted. The results shown in Table XIX indicate that this procedure was not successful as a possible method for the separation of these elements.

Table XIX
Electrodialysis of Cerium and Promethium
Using a Three-cell Electrodialyzer

<u>Isotope</u>	<u>Ce¹⁴⁴</u>	<u>Pm¹⁴⁷</u>
Total initial activity of feed, cps	25,800	1,200,000
Nitric acid concentration of feed, M	2.3	2.3
*Amount transferred to cathode cell, %	4.48	6.7
*Amount transferred to anode cell, %	1	0.5
*Amount remaining in feed cell, %	60.5	61.3

*Per cent of initial activity.

The same feed solutions described above were electro-dialyzed for 60 minutes with a current density of 300 ma per cm^2 using a two-cell electrodialyzer. The feed solution was added to the anode cell which was separated from the cathode cell with a cation membrane. The cathode cell was filled with 0.25 N HNO_3 . It was predicted that Pm(III) would be transferred to the cathode cell leaving the $\text{Ce}(\text{IO}_3)_4$ in the anode cell. The results as presented in Table XX show that after one hour most of the cerium remained in the feed cell whereas more of the promethium was transferred to the cathode cell. However the data obtained does not indicate that this system is suitable for the separation of cerium and promethium.

Table XX
Electrodialysis of Cerium and Promethium
Using a Two-cell Electrodialyzer

<u>Isotope</u>	<u>Ce¹⁴⁴</u>	<u>Pm¹⁴⁷</u>
Total initial activity of feed, cps	9,000	35,000
Iodate Concentration, M	0.025	0.025
Nitric acid concentration of feed, M	2.46	2.46
*Amount transferred to cathode cell, %	29.3	54.4
*Amount remaining in anode (feed) cell, %	78.2	37.7

*Per cent of initial activity.

Electrodialysis of Cerium and Promethium in the Presence of Potassium Gluconate

Sawyer and Ambrose (20) reported that gluconic acid is a good complexing agent and stabilizing agent for Ce(IV). They reported that at a pH of 7.3 the complex ion, $[\text{Ce}_2(\text{GH}_4)_3(\text{OH})_9]^{-4}$, was present. This reagent was investigated to determine if it could be used for the separation of Ce(IV) from the tri-positive rare earth ions. A solubility test was performed to determine the pH at which Ce(IV) and La(III) will form a precipitate with potassium gluconate. The pH of Ce(IV) and La(III) solutions that were 0.1 M with potassium gluconate were adjusted by adding NaOH. A Beckman Model GS pH meter was used to determine the pH for the initial precipitation of Ce(IV) and La(III). The preliminary data indicate that Ce(IV) is in solution at a pH of 8.14, and La(III) begins to precipitate.

Electrodialysis experiments with cerium and promethium in the presence of gluconate revealed that promethium was transferred through an anion membrane at a greater rate than cerium. This indicates that promethium also exists as a negatively charged complex ion in the presence of gluconate. This system should be studied more thoroughly with respect to pH control and other operating conditions. Gluconate may be a reagent for possible separations.

SEPARATION OF TECHNETIUM AND ZIRCONIUM

The chemistry of technetium indicates that it should migrate as TcO_4^- through anion exchange membranes into the anode cell of an electrodialyzer. Since zirconium may be fractionated as $\text{ZrF}_6^{=}$ from solutions of HNO_3 and NH_4HF_2 the electrodialysis of technetium was studied under the same conditions. The presence of moderate concentrations of NaOH should prevent the transfer of zirconium and permit the transfer of technetium through anion exchange membranes. These facts suggested electrodialysis studies of these two elements in a number of electrolyte solutions.

Feed solutions were prepared by adding stock solutions of NH_4TcO_4 to various solutions of electrolytes. Technetium-99 as NH_4TcO_4 was obtained from Oak Ridge National Laboratory. Acid concentrations were determined by standard titration methods and radioactivities were measured by standard radioactive counting techniques. The feed solution was transferred to the cathode cell of a two-cell electrodialyzer with a Permutit 3148 anion exchange membrane separating the cells. The same electrolyte was placed in the anode cell.

The data presented in Table XXI shows that technetium can be transferred under these conditions.

Feed solutions of zirconium-95 were prepared by adding stock solutions of $\text{ZrO}(\text{NO}_3)_2$ to various solutions of electrolytes. The data in Table XXII indicate that the presence of NaOH prevents the transfer of zirconium. These data indicate that technetium can be separated from zirconium by the

electrodialysis of mixtures of these elements in 0.6 N NaOH and NH_4HF_2 . At this date experiments with mixtures of these elements have not been performed.

Table XXI

The Electrodialysis of Technetium-99 as Per technate Ion

Composition of Feed Soln in Addition to TcO_4^-	Initial Activity, cps	Electrodialysis Time, Hrs.	Current Density, ma/cm ²	Per Cent of Activity Trfd to Anode Cell
0.5 N HNO_3	416,610	0.67	185	63.2
0.98 N HNO_3	72,103	1.0	185	45.5
1.53 N HNO_3	70,941	1.0	185	22.9
2.0 N HNO_3	58,987	1.0	185	13.9
0.3 F NH_4HF_2	109,445	1.0	123	45.1
0.54 F NH_4HF_2	55,166	0.5	185	26
0.54 F NH_4HF_2	163,243	1.5	123	30.8
1.0 F NH_4HF_2	27,164	2.0	123	30
0.25 N HNO_3 and 0.25 F NH_4HF_2	17,665	1.0	123	53
0.5 N HNO_3 and 0.5 F NH_4HF_2	33,361	1	123	44
0.5 N HNO_3 and 0.5 F NH_4HF_2	69,141	2	123	47.3
0.3 N NaOH	60,950	2	123	1.8*
1.4 N NaOH	52,378	2	123	0.5*
2.0 N NaOH	29,000	2	123	29.7
0.6 N NaOH, 0.25 N NaF, 0.25 N NaNO_3 and 0.25 F NH_4HF_2	15,021	2	123	45.94

*91%-97% of activity was sorbed onto the anion exchange membrane.

Table XXII

The Electrodialysis of Zirconium

Composition of Feed Soln in Addition to Zr-95	Initial Activity, n cps	Per cent of Activity Trfd to Anode Cell
0.6 N NaOH	25,043	12.2
1.4 N NaOH	81,046	0.8
0.01 N NaOH, a. 0.25 N NaF, b. 0.25 F NH ₄ HF ₂ , c. 0.25 N NaNO ₃	17,359	25.3
0.1 N NaOH and a, b, and c	20,650	28
0.6 N NaOH and a, b, and c	26,531	1.58*
0.6 NaOH and a, b, and c	26,556	1.49*

Electrodialysis time was 2 hours for all experiments and current density was 123 ma/cm².

*Approximately 30% of the activity was sorbed onto the anion exchange membrane.

A STUDY OF THE EFFECTS OF IONIZING RADIATION ON ION EXCHANGE MEMBRANES

Ion exchange membranes are exposed to large amounts of ionizing radiation when used in the separation of radioactive materials. Since it has been established that radiation affects polymers, a study of the effects of ionizing radiation on ion exchange membranes was made. The effects of radiation on membranes manufactured by Ionics Incorporated have been reported by Mason and Parsi (15).

For this study membranes were obtained from the Permutit Company (Division of Pfaudler), New York, New York, Ionics Incorporated, Cambridge, Massachusetts, and the American Machine and Foundry Corporation, Springdale, Connecticut. Membranes purchased from the Permutit Company were MC3142 (cation) and MA3148 (anion). Membranes purchased from Ionics Inc. were Nepton Cr-61(cation) and Nepton AR-111-A (anion). Membranes donated by A.M.F. were C-60 (cation) and A-60 (anion).

Experimental Procedure

Samples of membranes were exposed to gamma radiation doses of approximately 1×10^6 , 1×10^7 , and 1×10^8 roentgens. The doses of 10^6 and 10^7 roentgens were obtained by use of the nuclear training reactor located at the University of Missouri, School of Mines and Metallurgy, Rolla, Missouri. The 10^8 dosage

was obtained by use of the High Gamma Irradiation Facility located at the Argonne National Laboratory, Lemont, Illinois. All dosages were determined by the use of the Fricke Ferrous Sulfate Dosimeter. The measured dosages received by the membrane samples are listed in Table XXIII.

Table XXIII

Gamma Dosages Received By Ion Exchange Membranes

Membrane	Dose (Roentgens)		
Permutit MC3142 (cation)	1.2×10^6	1.0×10^7	1.2×10^8
Permutit MA3148 (anion)	1.2×10^6	1.0×10^7	1.2×10^8
Ionic Nepton CR-61 (cation)	1.2×10^6	1.0×10^7	1.3×10^8
Ionic Nepton AR-111-A (anion)	1.2×10^6	1.0×10^7	1.3×10^8
A.M.F. C-60 (cation)	1.5×10^6	1.0×10^7	1.1×10^8
A.M.F. A-60 (anion)	1.5×10^6	1.0×10^7	1.1×10^8

The capacities of the cation and anion membranes were determined using the standard "total Capacity" procedure for ion exchangers ⁽¹¹⁾. The cation exchangers were converted to the H^+ form. They were then allowed to remain overnight in a measured amount of standard 0.1 N NaOH. Aliquots of the supernatant solutions were back titrated to a phenolphthalein end point. The capacity (meq per gram) was then calculated by division of the difference in milliequivalents before and after treatment by the appropriate weight term. The anion

exchangers were treated in a similar manner using standard 0.1 N HCl after their conversion to the OH⁻ form.

The electrical resistance measurements were determined by use of a conductivity cell (11). Measurement of the resistance of the cell with the membrane and 0.15 N KCl solution between the electrodes yielded the total resistance of the cell. The solution resistance was determined by a blank measurement without a membrane. The electrical resistance of the membrane was calculated by multiplying the cell area by the difference between the total resistance and the solution resistance.

The water content of the membrane was calculated by dividing the difference between the wet weight and the dry weight of a sample by the wet weight. The membrane samples were dried over phosphorus pentoxide at an absolute pressure of 0.0003 millimeters of mercury.

The bursting strength measurements were determined by use of a Mullen tester manufactured by B. F. Perkins and Sons, Inc., Style B, No. 543, Range 5-200 p.s.i.

The tensile strength measurements were made on samples one inch in width using a tensile tester manufactured by AMTHOR Testing Instrument Co., Brooklyn, New York. The ranges of the tensile tester were 0-90 and 0-200 pounds.

Results and Conclusions

Table XXIV presents the capacity based upon the dry weight prior to irradiation of the six membrane samples for exposure dosages of 0, 10^6 , 10^7 , and 10^8 roentgens. The capacity of the

anion membranes is affected to a lesser degree by increasing radiation than that of cation membranes. Appreciable effect on membrane capacity does not occur until a dose of 10^7 roentgens or greater has been reached.

Table XXV presents the capacity based upon the irradiated dry weight of the six membrane samples for the various exposure dosages. If the capacity loss as shown in Table XXIV were due entirely to uniform erosion of membrane material, the capacities of Table XXV for a given membrane would not vary. Each membrane of Table XXV showed a loss of capacity indicating that capacity loss is not due entirely to erosion of membrane material.

Table XXIX presents the water content of each membrane for the various exposure dosages. The water content of the Ionics membranes was relatively unaffected by the radiation exposures, while the water content of the Permutit membranes and the A.M.F. cation membrane increased with increased exposure. The A.M.F. anion membrane water content decreased with increased exposure.

Table XXVI presents the electrical resistance of the six membranes for the various measured exposure dosages. Exposure to radiation caused an increase in the membrane electrical resistance in all cases.

Table XXVII and Table XXVIII present the bursting strength and tensile strength of the six membranes for the measured exposure dosages. All membranes became more brittle upon exposure to radiation of 10^7 roentgens or above.

Table XXIV

Effect of Radiation on Capacity

Approximate Dose* (Roentgens)	Membrane Capacity (Meq/gram) based on the non-irradiated dry weight					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	A-60
0	2.23	1.19	1.49	0.50	1.80	1.56
	2.32	1.28	1.49	0.49	1.83	1.77
10 ⁶						1.70
	2.28	1.19	1.45	0.40	1.87	1.74
10 ⁷	2.28	1.26	1.45	0.54	1.87	1.71
	1.52	1.22	1.12	0.53	1.66	1.74
10 ⁸	1.43	1.28	1.08	0.46	1.62	1.60
	1.49	1.13	1.18	0.52	0.85	1.25
	1.50	1.09	1.18	0.49	0.95	1.20

Table XXV

Effect of Radiation on Capacity

Approximate Dose* (Roentgens)	Membrane Capacity (Meq/gram) based on the irradiated dry weight					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	A-60
0	2.23	1.19	1.49	0.50	1.80	1.56
	2.32	1.28	1.49	0.49	1.83	1.77
10 ⁶						1.70
	2.30	1.19	1.48	0.41	1.96	1.69
10 ⁷	2.29	1.26	1.48	0.55	1.96	1.66
	1.82	1.17	1.22	0.53	1.73	1.74
10 ⁸	1.71	1.23	1.13	0.46	1.69	1.60
	1.86	1.15	1.22	0.56	1.09	1.34
	1.87	1.11	1.23	0.53	1.22	1.29

*Measured dose see Table XXIII

Table XXVI
Effect of Radiation on Electrical Resistance

Approximate Dose* (Roentgens)	Membrane Resistance (ohm cm ²)					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	A-60
0	4.4	5.6	9.0	37.2	2.0	5.8
	3.8	6.0	9.4	37.4	2.2	6.4
	4.4	5.4	8.8	37.0	2.2	7.0
	3.6	5.8	9.4	37.4	2.0	
			9.4	35.8 36.8		
10 ⁶	3.8	5.4	9.2	37.0	2.0	5.8
	7.0	5.4	9.4	36.8	2.2	6.0
	3.6	5.4	9.4	36.6	2.4	6.0
	6.4		9.2	37.2	2.0	6.2
	7.0					
	3.4					
10 ⁷	10.6	10.6	11.0	58.0	5.9	15.0
	8.6	9.6	10.6	57.6	5.7	15.0
	9.4	10.0	10.8	58.6	6.1	15.4
	10.0	9.8			6.3	
10 ⁸	9.4	15.8	11.2	63.6	6.8	24.0
	9.4	14.8	9.8	62.8	7.4	22.6
	9.8	15.4	10.4	60.8	7.0	24.2
		15.6		61.8	6.0	
				54.8		
				53.8		

*Measured dose see Table XXIII

Table XXVII

Effect of Radiation on Bursting Strength

Approximate Dose (Roentgens)	Membrane Bursting Strength (psi)					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	A-60
0	143	121	182	196	x	x
	147	120	190	196	x	x
	147	116	188	195	x	x
		122	190	194	x	x
10 ⁶	143	120	184	1.90	x	x
	146	130	190	1.80	x	x
	145	118	182	1.80	x	x
	145		195	1.86	x	x
10 ⁷	140	120	169	120	x	x
	134	121	163	120	x	x
	136	131	176	124		
	142	135	163			
10 ⁸	107	90	140	127	36	89
	108	92	135	131	46	77
	113	90	124	133	36	81
	111	96	125	130		86

x-Membrane too flexible to be broken within limit of testing equipment

Table XXVIII

Effect of Radiation on Tensile Strength

Approximate Dose* (Roentgens)	Membrane Tensile Strength (pounds per inch width)					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	A-60
0	67	48	110	112	x ⁶	x
	62	50	110	110	x	x
10 ⁶	62	52	112	104	x	x
	58	56	118	106	x	x
10 ⁷	58	37	70	96	x	x
	60	38	75	95	x	x
10 ⁸	51	28	79	73	23	12
	49	29	77	74	28	11

x-Sample broke in vise grip at limit of jaw separation, resulting in an unacceptable test.

Table XXIX

Effect of Radiation on Water Content

Approximate Dose* (Roentgens)	Membrane Water Content (Per Cent)					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	AA-60
0	39.5	37.3	10.2	14.0	37.5	31.1
	38.4	36.9	11.3	14.4	38.7	31.4
	39.3	36.8	9.5	14.1	38.3	31.2
10 ⁶	37.8	36.2	13.3	14.9	43.3	26.6
	37.1	35.7	13.6	15.0	46.1	27.1
		37.5	14.5			26.6
10 ⁷	35.2	35.4	13.9	15.3	45.9	24.7
	35.2	35.5	13.5	15.6	45.4	25.7
	35.0	35.0	14.3	16.1	44.4	24.7
10 ⁸	37.6	37.8	17.4	15.8	51.0	22.7
	37.5	36.9	18.1	19.2	51.2	22.9
	37.5	37.6	18.5	19.2	50.3	22.5

*Measured dose see Table XXIII.

Table XXX

Effect of Radiation on Wet Surface Density

Approximate Dose* (Roentgens)	Membrane Wet Surface Density (Grams/cm ² wet membrane)					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	A-60
0	0.6121	0.4210	0.1351	0.1454	0.2104	0.2039
	0.5484	0.4175	0.1349	0.1474	0.2088	0.2048
	0.5986	0.4237	0.1381	0.1457	0.2099	0.2007
10 ⁶	0.6125	0.4084	0.1381	0.1447	0.2144	0.2001
	0.5217	0.4124	0.1373	0.1467	0.2197	0.1960
	0.5671	0.4291	0.1413	0.1431	0.2160	0.1943
10 ⁷	0.4567	0.4240	0.1343	0.1488	0.2235	0.1859
	0.4639	0.4252	0.1375	0.1489	0.2276	0.1884
	0.4599	0.4293	0.1338	0.1508	0.2260	0.1856
10 ⁸	0.4557	0.4152	0.1462	0.1366	0.2017	0.1651
	0.4574	0.4107	0.1455	0.1484	0.2084	0.1699
	0.4625	0.4122	0.1382	0.1439	0.2020	0.1729

Table XXXI

Effect of Radiation on Dry Surface Density

Approximate Dose* (Roentgens)	Membrane Dry Surface Density (Grams/cm ² dry membrane)					
	CR-61	AR-111-A	MC 3142	MA 3148	C-60	A-60
0	0.3941	0.2821	0.1209	0.1310	0.1818	0.1762
	0.3579	0.2814	0.1193	0.1321	0.1769	0.1762
	0.3866	0.2861	0.1246	0.1311	0.1792	0.1732
10 ⁶	0.4029	0.2740	0.1211	0.1265	0.1832	0.1770
	0.3468	0.2788	0.1194	0.1273	0.1816	0.1724
		0.2819	0.1251		0.1817	0.1721
10 ⁷	0.3107	0.2966	0.1147	0.1300	0.1859	0.1763
	0.3155	0.2970	0.1181	0.1304	0.1792	0.1763
	0.3142	0.3025	0.1137	0.1304	0.1802	0.1763
10 ⁸	0.3053	0.3006	0.1178	0.1191	0.1538	0.1610
	0.3069	0.2979	0.1162	0.1233	0.1584	0.1685
	0.3102	0.2976	0.1079	0.1202	0.1562	0.1724

*Measured does see Table XXIII

DISCUSSION

Research conducted in this laboratory demonstrated that several of the radioactive elements can be separated by the electrodialysis process. The methods employing cation and anion exchange membranes were successful for the fractionation of some of the fission elements. The ZrF_6^- and TcO_4^- ions were transferred into an anion cell, Cs^+ and Sr^{++} into a cathode cell and the rare earth elements remained in the feed cell as radiocolloids.

Zirconium was found to be quite troublesome. The results indicated that in most acids it exists both as positive and negative species and as charged polymerized species. In fact electrodialysis is an excellent method for the purification of radiocolloidal zirconium. It was also observed that the radioactive isotopes of zirconium are more difficult to extract from aqueous solutions with theonyl trifluoroacetone. This may be attributed to the fact that the emitted radiation from Zr-95 enhanced the formation of polymerized ions and the colloidal nature of the zirconium compounds.

Ethylenediaminetetraacetic acid proved to be a selective complex former with strontium at a pH of 11. This provided an excellent medium for the separation of strontium from cesium. Either a two-cell or three-cell electrodialyzer may be used for this separation. The anion exchange membrane proved to be superior to the cation exchange membrane for this process.

The separation of zirconium from technetium should be feasible by this process. The removal of fluoride can be

accomplished by boric acid treatment and heating to distill off the BF_3 . However this operation may be more expensive than the addition of NaOH to the $\text{ZrF}_6^{=}\text{--TcO}_4^-$ fraction during the preparation for electrodialysis.

The methods employed in this study were not successful for the separation of the rare earth elements. A satisfactory method of pH control was not found. At this time the ion exchange techniques seem to be the best method for the separation of the rare earths. Liquid extraction methods show some promise, but has not been satisfactory for all the rare earth elements.

Radiation studies on the effect of radiation on ion exchange membranes indicate that a reasonable estimate of useful membrane life would be the time required for a total dosage of 10^8 to 10^9 roentgens. This varies slightly with different types of membranes, their age and types of solutions with which they are used. After this dosage, they become brittle and lose some of their exchange capacity.

The final conclusion that can be made from this investigation is that electrodialysis methods with ion exchange membranes can be used for the fractionation of the fission products. The process can also be used for the separation of cesium from strontium and zirconium from technetium. Although electrodialysis units have been developed for handling thousands of gallons of brackish water per day, the process has not been given as much attention as liquid extraction for the processing of radioactive materials. Development studies and an economic evaluation should be the next consideration for this investigation.

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