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ION EXCHANGE PROCESS FOR SEPARATING AMERICIUM AND CURIUM FROM IRRADIATED PLUTONIUM

J. A. KELLEY

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ION EXCHANGE PROCESS FOR SEPARATING AMERICIUM AND CURIUM FROM IRRADIATED PLUTONIUM

by

J. A. Kelley

Approved by

J. A. Porter, Research Manager
Separations Chemistry Division

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E. I. DU PONT DE NEMOURS & COMPANY
SAVANNAH RIVER LABORATORY
AIKEN, S. C. 29801

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ABSTRACT

An ion exchange process was developed for separating americium and curium from each other and from fission products in a lanthanide (Ln) - actinide (An) concentrate containing a high Ln/An ratio and a significant amount of ^{242}Cm . The Ln-An mixture was produced by irradiating ^{239}Pu in the program to prepare higher actinide precursors of ^{252}Cf .

CONTENTS

	<u>Page</u>
Introduction	6
Summary	8
Description of Plutonium Burner Concentrate	9
Lanthanide-Actinide Loading Curve	10
Nonradioactive Tests	10
Tracer Test	12
Semiworks Tests	13
Displacement Development Chromatography	14
Band Length Requirements	14
Nonradioactive Scouting Tests	15
Curium-Americium Test	19
Semiworks Tests	20
Removal of Residual Fission Products from Resin	22
Proposed Process	24
Acknowledgment	25
Appendices	
A. Equilibrium Treatment for Column Loading	26
B. Band Length Requirements for Curium-Americium Separation	30
References	39

LIST OF TABLES

<u>Table</u>	<u>Page</u>
I Actinides and Fission Products in Solvent Extraction Concentrate (About 1 year cooling) . .	9
II Decay Heats of Actinides and Fission Products in Solvent Extraction Concentrate (About 1 year cooling)	10
III Sorption of Pr^{3+} , H^+ , and Na^+ from Nitrate Solutions by "Dowex" 50W-X8 Resin at 70°C	11
IV Band Length Requirements for Plutonium Burner Concentrate with DTPA as Elutriant	15

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Fit of Sorption Data Assuming Constant Ratios of Activity Coefficients in Resin and Aqueous Phases	13
2	Theoretical Plate Height as a Function of pH at 16 and 32 ml/(min-cm ²)	16
3	Variation of Neodymium Peak Concentration with pH of DTPA	17
4	Separation of Samarium, Neodymium, and Praseodymium with 0.05M DTPA at pH 3.0 and 50 ml/(min-cm ²)	18
5	Separation of ²⁴⁴ Cm and ²⁴³ Am with 0.05M DTPA at pH 3.0 as Elutriant	19
6	Semiworks Test of Ion Exchange Process with 8-, 6-, 4-, and 2-inch Columns	21
7	Removal of Neodymium from a 1/3-Loaded Column with DTPA	23

INTRODUCTION

^{239}Pu is irradiated, or burned, in a Savannah River nuclear reactor in the program to produce higher actinide precursors of ^{252}Cf . After cooling, the targets are dissolved and processed by solvent extraction to isolate residual plutonium and a transplutonium fraction also containing lanthanide fission products. The americium and curium in the transplutonium fraction are separated and purified by ion exchange in the Multipurpose Processing Facility (MPPF), a series of manipulator-operated cells in the 221-F canyon building.

Ion exchange process development was required because of the large quantities of lanthanides, entrained sodium, and ^{242}Cm .

Pressurized cation exchange chromatography was used at the Savannah River Laboratory to separate 100 g batches of ^{244}Cm and ^{243}Am in a curium production campaign (Cm-II).^{1,2} Cm-II ion exchange feed had a Ln/An ratio of $\sim 5:1$ and contained no ^{242}Cm . ^{252}Cf , produced at the Savannah River Plant by irradiating ^{242}Pu in a californium campaign (Cf-I), can also be separated by pressurized cation exchange chromatography with the Cm-II process. Cf-I material has a Ln/An ratio of $\sim 2:1$ and contains no ^{242}Cm . By contrast plutonium burner concentrate has a Ln/An ratio of $\sim 17:1$. The high Ln/An ratio lowers the quantity of americium and curium that can be processed per ion exchange batch. A batch of plutonium burner targets processed through solvent extraction contained 177 moles of lanthanides and actinides. If this material were processed in MPPF at the maximum rate specified by Cf-I process, 2.4 moles/batch, 74 ion exchange batches would be required to complete the campaign.

The solvent extraction concentrate also contained a large amount of entrained NaNO_3 , expected to be ~ 300 moles after recycle through solvent extraction. Before this work, no suitable method was available for determining the number of moles of Ln+An that could be sorbed on an ion exchange bed from solutions containing monovalent cations at various concentrations.

After about one year cooling, the solvent extraction concentrate contained ~ 20 g of ^{242}Cm and ~ 700 g of ^{244}Cm , which produce ~ 4400 watts from alpha decay. The Cm-II or Cf-I process could not be used for purifying the concentrate because the small size ion exchange columns would overheat during elution.

This report describes a method for determining the efficiency of Ln-An sorption from solutions containing monovalent cations, a process for purification of $^{242},^{244}\text{Cm}$ and americium from large quantities of lanthanides, and a method for removing residual fission products from an ion exchange column.

SUMMARY

A process was developed for separating americium and curium from each other and fission products in the Ln-An concentrate from plutonium burner targets. A method for determining the number of moles of Ln+An that can be loaded on an ion exchange bed from solutions containing various concentrations of NaNO_3 , HNO_3 , and $\text{Ln-An}(\text{NO}_3)_3$ was developed. A chromatographic ion exchange process was developed for separating curium and americium with 0.05M diethylenetriaminepentaacetic acid (DTPA), at pH 3.0 and a flow of 32 ml/(min-cm²); this high flow minimizes column heatup and resin degradation. The most efficient agent for removing residual fission products from ion exchange resin was 0.3M DTPA at pH 8.0.

DESCRIPTION OF PLUTONIUM BURNER CONCENTRATE

The plutonium burner concentrate is primarily a mixture of curium, americium, and lanthanide fission products obtained after plutonium is removed by solvent extraction. Table I shows the quantities of actinides and lanthanides in a batch of solvent extraction concentrate after about 1 year cooling. After recycle through solvent extraction, the concentrate will also contain ~300 moles of entrained NaNO_3 and 13 moles of PO_4^{3-} from de-graded TBP. A feed batch is adjusted to ~1M HNO_3 by formic acid denitration before the ion exchange column is loaded. At lower acidity, Ln-An phosphates could precipitate.

TABLE I
Actinides and Fission Products in
Solvent Extraction Concentrate
(About 1 year cooling)

<u>Actinide</u>	<u>kg</u>	<u>Moles</u>	<u>Lanthanide</u>	<u>Moles</u>
^{241}Am	0.05	0.21	La	20.5
			Ce	41.6
$^{242\text{m}}\text{Am}$	0.001	-	Pr	19.1
			Nd	59.9
^{243}Am	1.7	7.00	Pm	0.78
			Sm	16.6
^{242}Cm	0.02	0.08	Eu	2.87
			Gd	5.72
^{244}Cm	0.7	2.87	Tb	0.03
			Dy	0.01
^{245}Cm	0.004	$\frac{0.02}{10.2}$		$\frac{-}{167}$

Total An+Ln = 177 moles

After about 1 year cooling, the concentrate produces ~4400 watts from alpha decay of ^{242}Cm and ^{244}Cm and ~12 kilowatts from beta-gamma decay of fission products. Table II shows decay heats from actinides and fission products in the solvent extraction concentrate.

TABLE II

Decay Heats of Actinides and Fission Products in
Solvent Extraction Concentrate

(About 1 year cooling)

Actinide	α Heat, watts	Fission Product	β Heat, watts	γ Heat, watts
^{241}Am	5	^{91}Y	31	0
^{243}Am	10	^{95}Zr	3	19
^{242}Cm	2400	^{95}Nb	3	37
^{244}Cm	2000	^{103}Ru	0	3
		^{106}Ru	27	0
		^{106}Rh	2188	509
		^{141}Ce	1	1
		^{144}Ce	654	321
		^{144}Pr	7296	603
		^{147}Pm	51	0
		^{154}Eu	20	120
Total $\rightarrow$	4400		10,270	1610

Total heat from $\alpha+\beta+\gamma = 16,300$ watts

LANTHANIDE-ACTINIDE LOADING CURVE

Tests were made to develop a method for determining the number of moles of Ln+An that can be loaded on an ion exchange column from solutions of various HNO_3 , NaNO_3 , and $\text{Ln-An}(\text{NO}_3)_3$ concentrations. Some distribution data for sorption of cations from HNO_3 are available,³ but these data do not cover the concentration ranges of interest. A method applicable to plutonium burners was developed in small-scale nonradioactive tests, an intermediate scale tracer-level test, and full-scale semiworks tests. A general equilibrium treatment for sorption of an n-valent cation from a mixture of two monovalent cations, and specific equations for Pr^{3+} , Na^+ , and H^+ are given in Appendix A.

NONRADIOACTIVE TESTS

To develop a loading curve, sorption tests were made with standardized $\text{Pr}(\text{NO}_3)_3$ solution to simulate the behavior of all lanthanides and actinides. Pr^{3+} was sorbed onto "Dowex"* 50W-X8,

* Registered trademark of Dow Chemical Co.

200-400 mesh resin in a 2.0-cm-diameter by 76-cm-long steel column, which was maintained at 70°C. The capacity of the resin bed was determined by passing excess 0.1M $\text{Pr}(\text{NO}_3)_3$ through the column, rinsing the column with deionized water, stripping sorbed Pr^{3+} with 2M HNO_3 , and determining the amount of sorbed Pr^{3+} by EDTA titration. Before each test, resin was converted to the Zn^{2+} form by passing excess 0.5M $\text{Zn}(\text{NO}_3)_2$ through the column. A solution containing known concentrations of $\text{Pr}(\text{NO}_3)_3$, NaNO_3 , and HNO_3 was passed through the column at 8 ml/(min-cm²), and the column was rinsed with deionized water. The amount of non-sorbed Pr^{3+} was determined spectrophotometrically. Before the next test, Pr^{3+} was stripped from the column with 2M HNO_3 . Results of these tests are shown in Table III. Several of the tests were repeated at a flow of 4 ml/(min-cm²), but no significant differences were observed.

TABLE III

Sorption of Pr^{3+} , H^+ , and Na^+ from Nitrate Solutions
by "Dowex" 50W-X8 Resin at 70°C

<u>$[\text{Pr}(\text{NO}_3)_3]$, M</u>	<u>$[\text{HNO}_3]$, M</u>	<u>$[\text{NaNO}_3]$, M</u>	<u>Fraction of Resin in Pr^{3+} Form, f</u>
0.02	1.0	2.1	0.192
0.02	1.0	2.5	0.169
0.03	1.5	4.0	0.102
0.04	1.0	5.0	0.112
0.05	0.6	4.5	0.165
0.06	1.0	5.0	0.147
0.07	1.5	4.2	0.175
0.09	1.1	4.1	0.242
0.10	1.5	2.7	0.300
0.10	1.5	3.0	0.269
0.10	1.1	3.0	0.306
0.11	1.2	3.6	0.283
0.20	1.5	3.0	0.395
0.20	0.7	2.5	0.561
0.30	1.5	3.0	0.485
0.30	0.5	0.8	0.836
0.40	0.5	0.16	0.956
0.40	1.4	2.5	0.568
0.50	1.4	2.5	0.615
0.50	1.5	2.0	0.648
0.60	1.5	2.0	0.684
0.60	1.0	0.3	0.885
0.80	1.5	2.5	0.690
1.0	0.25	0.16	0.983
1.0	0.50	0.5	0.963

Figure 1 shows a plot of f versus σ , where f is the fraction of resin in the Pr^{3+} form and

$$\sigma = \frac{0.125 [\text{Na}^+] + 0.057 [\text{H}^+]}{[\text{Pr}^{3+}]^{1/3}}$$

The solid line in Figure 1 represents a theoretical curve derived from the equilibrium treatment (Appendix A), and the open circles are the data in Table III. Ratios of the activity coefficients in both phases (resin and aqueous) were treated as constants. Coefficients in the expression for σ were obtained by a least squares analysis of the data in Table III. Treatment of the sorption data with calculated activity coefficients⁴ gave only a slightly better fit to the theoretical curve than the treatment using molar concentrations.

Figure 1 can be used to determine the number of moles of $\text{Ln}+\text{An}$ that can be loaded on an ion exchange column from solutions of various Na^+ , H^+ , and Ln^{3+} - An^{3+} concentrations. This method requires a feed analysis to determine the Na^+ , H^+ , and $\text{Ln}-\text{An}$ concentrations. Other monovalent cationic impurities can be treated as Na^+ . This method cannot be used to predict loading from solutions containing more than 0.15 equivalent/liter of divalent plus trivalent cations (excluding Ln^{3+} and An^{3+}). These cationic impurities are sorbed by the ion exchange resin and cause breakthrough of lanthanides and actinides.

TRACER TEST

An intermediate-scale test was made with tracer-level feed to determine whether Figure 1 could be used to predict loading of a larger column than that used in the initial tests. The test was made with a 4-inch-diameter by 4-ft-long steel column and on-line analysis system. Feed was sorbed on "Dowex" 50W-X8, 200-400 mesh, Zn^{2+} -form resin at 75°C. Column capacity was determined by titrating the acid displaced during resin conditioning with 0.5M $\text{Zn}(\text{NO}_3)_2$. The feed (4.3 moles $\text{Ce}(\text{NO}_3)_3$, 8.6 moles NaNO_3 , and $\sim 10^8$ dpm/ml ^{154}Eu) was loaded from a 5.3-l feed tank at 8 ml/(min-cm²). Cerium in the feed corresponded to 70% of the measured column capacity; maximum loading capacity for $\text{Ln}-\text{An}^{3+}$ determined from Figure 1 is 73%. Analysis of the column effluent for ^{154}Eu indicated a breakthrough of $\sim 0.03\%$, indicating that Figure 1 could be used to determine loading for larger columns.

FIGURE 1. Fit of Sorption Data Assuming Constant Ratios of Activity Coefficients in Resin and Aqueous Phases

SEMIWORKS TESTS

Tests were made with an 8-inch-diameter by 5-ft-long column to determine loading characteristics of a production-scale column. Test conditions were the same as those in the tracer test. In one test, 18 moles of nonradioactive rare earths were successfully loaded from 18 ℓ of 1M HNO_3 -2M NaNO_3 , approximating a production batch in size and composition. Figure 1 was used to determine that this quantity of feed could be loaded without breakthrough. As a result of these tests, Figure 1 will be used in MPPF to predict the quantity of Ln+An that can be loaded on cation exchange columns.

DISPLACEMENT DEVELOPMENT CHROMATOGRAPHY

Small-scale nonradioactive tests, a curium-ameridium test, and full-scale nonradioactive tests indicated that plutonium burner concentrate could be processed in MPPF at the rate of ~ 18 moles Ln+An per ion exchange batch.

After lanthanides and actinides are sorbed onto ion exchange resin, the mixture is separated with a suitable complexing agent, such as DTPA. In the Cm-II campaign, a 4-inch-diameter by 4-ft-long steel column was loaded to $\sim 1/3$ capacity with ~ 2 moles of Ln+An. ^{244}Cm and ^{243}Am were purified with 0.05M DTPA flowing through the 4-, 3-, 2-, and 1-inch columns at 16 ml/(min-cm²).^{1,2} A similar flowsheet is planned for ^{252}Cf separation in MPPF (Cf-I campaign).

With the Cf-I process, 74 ion exchange batches would be required to process plutonium burner concentrate. A larger loading column could be used, but the quantity of ^{242}Cm in each batch would overheat the 2- and 1-inch columns. However, when DTPA at pH 6 is the elutriant, both the 2-inch and 1-inch columns cannot be eliminated from the process. With a 3-inch collection column, the Cm-Am binary fraction would contain all of the curium; no pure curium would be obtained. The objective of this work was to design a plutonium burner process that would have 8- to 10-fold greater throughput than the Cf-I process, yet would permit separation of curium and ameridium and prevent overheating.

BAND LENGTH REQUIREMENTS

The first step in designing a displacement development ion exchange process is to determine the band lengths of unloaded resin required to separate the elements of interest. A band length can be defined as the number of liters of resin required to sorb the feed; band length can be determined with a feed analysis and Figure 1. Helfferich and James⁵ described a method for calculating the band lengths required to separate a multi-component mixture by displacement development chromatography. Data required for this calculation are separation factors of the components relative to the last element eluting from the column and mole fraction composition of the mixture to be separated. A more detailed discussion of this method and a computer code to perform the calculations are given in Appendix B. A list of band length requirements for resolution of the solvent extraction

concentrate is shown in Table IV. Curium is separated from lanthanides after <0.2 band length of resolution distance; separation of curium and americium requires ~0.5 band length. To account for uncertainties in separation factors and to ensure that equilibrium is reached under actual process conditions, approximately twice the calculated band length requirement is allowed for resolution of curium and americium.

TABLE IV
band Length Requirements for the
Plutonium Burner Concentrate with DTPA as Elutriant

<u>Element</u>	<u>Mole Fraction</u>	<u>Band Length Required to Separate from Curium</u>
La	0.114	0.126
Ce	0.250	0.127
Pr	0.108	0.129
Nd	0.323	0.134
Pm	0.005	0.135
Sm	0.093	0.163
Gd	0.016	0.179
Tb	0.032	0.181
Am	0.041	0.493
Cm	0.018	-

NONRADIOACTIVE SCOUTING TESTS

The studies of Wheelwright⁶ and Lowe⁷ were extended to determine the effects of flow and pH of DTPA on the separation of nonradioactive lanthanides. Equimolar mixtures of neodymium, praseodymium, and samarium were sorbed onto "Dowex" 50W-X8, 200-400 mesh, Zn²⁺-form resin in a 0.5-inch-diameter by 60-inch-long stainless steel column maintained at 70°C. In each test, the column was loaded to ~1/3 capacity. Neodymium, praseodymium, and samarium were used because results of an ion exchange test could be determined quickly and easily by spectrophotometric analysis of the effluent samples. The theoretical plate height (TPH) for each separation test was calculated by the method of Wheelwright⁶ and Lowe.⁷

Figure 2 shows results of separation efficiency tests made with 0.05M DTPA at flows of 16 and 32 ml/(min-cm²) and pH values of 3 to 6. The lower pH limit was set at 3 because DTPA crystallizes from a 0.05M solution at pH 2.8. The TPH for the test with DTPA at pH 3 and 32 ml/(min-cm²) is approximately equal to

FIGURE 2. Theoretical Plate Height as a Function of pH at 16 and 32 ml/(min-cm²)

that for the test with DTPA at pH 6 and 16 ml/(min-cm²). These tests indicate that excellent separation of curium and americium can be obtained with 0.05M DTPA at any pH from 3 to 6 with a flow of 16 ml/(min-cm²). With 0.05M DTPA at 32 ml/(min-cm²), pH 3 is required for a low TPH and good separation of curium and americium.

Figure 3 shows the variation of neodymium peak concentration with pH at a flow of 32 ml/(min-cm²). Although neodymium concentration in the column effluent decreased with decreasing pH, the volume of elutriant required to attain breakthrough remained constant. With DTPA at pH 3, the concentrations of lanthanides in the aqueous and resin phases are ~2.6 times smaller than with DTPA at pH 6. This band spreading in the resin phase is beneficial because the decay heat of ²⁴²Cm and ²⁴⁴Cm will be distributed over a larger volume of resin, minimizing the chance of column overheating. With DTPA at pH 3, the product volume is ~2.6 times larger than with DTPA at pH 6, but this presents no problem since ample space is available in MPPF for product collection.

FIGURE 3. Variation of Neodymium Peak Concentration with pH of DTPA

A test was made at $50 \text{ ml}/(\text{min}\text{-cm}^2)$ to extend the range of usefulness of 0.05M DTPA, pH 3, as an elutriant. Figure 4 shows the results of a test made with samarium, neodymium, and praseodymium. The mixture was separated satisfactorily at a flow >3 times that used in the Cm-II campaign. Flows in this range will not be needed to process plutonium burner concentrate, but this test demonstrates the versatility of 0.05M DTPA at pH 3.0 as an elutriant.

FIGURE 4. Separation of Samarium, Neodymium, and Praseodymium with 0.05M DTPA at pH 3.0 and $50 \text{ ml}/(\text{min}\text{-cm}^2)$

CURIUM-AMERICIUM TEST

A test was made with the Cm-II column system to demonstrate that curium and americium could be separated from simulated plutonium burner concentrate with 0.05M DTPA at pH 3.0 and 32 ml/(min-cm²). The columns used were 4-, 3-, and 2-inch-diameter by 4-ft-long; filled with "Dowex" 50W-X8, 200-400 mesh, Zn²⁺-form resin; and maintained at 80°C. The 4-inch column was loaded to ~80% capacity with feed containing 81.2 g of ²⁴⁴Cm, 75.6 g of ²⁴³Am, 162 g of cerium, 60 g of praseodymium, 250 g of neodymium, 62 g of samarium, 9 g of europium, and 22 g of gadolinium. Elutriant was pumped at 16 ml/(min-cm²) through the 4- and 3-inch columns, and at ~36 ml/(min-cm²) through the 2-inch column. Figure 5 shows the elution diagram for this test. Approximately 59 g of pure ²⁴⁴Cm was obtained. Analysis of the data from the Ge(Li) detector indicated that ~31 g of pure ²⁴³Am was eluted from the 2-inch column.

FIGURE 5. Separation of ²⁴⁴Cm and ²⁴³Am with 0.05M DTPA at pH 3.0 as Elutriant

This test demonstrated that plutonium burner concentrate can be processed with 0.05M DTPA at pH 3 as elutriant. With a flow of ~ 32 ml/(min-cm²) through the 2-inch column, no over-heating problems will arise. With DTPA elutriant at pH 3, the quantity of curium in the curium-ameridium binary on the 2-inch column is lowered from ~ 60 g (based upon Cm-II experience) to ~ 25 g.

SEMIWORKS TESTS

Tests were made to demonstrate the plutonium burner process with a production-size batch of ion exchange feed. The first full-scale tests of the plutonium burner process were made with 10-ft-long columns, 6-, 4-, and 2-inch diameter. Although separation of curium and americium stand-ins (dysprosium and terbium) was excellent, DTPA flows of only 13, 16, and 20 ml/(min-cm²) were obtained through the 6-, 4-, and 2-inch columns, respectively, at the desired pressure limit of 1000 psig. A flow of 32 ml/(min-cm²) through the 2-inch column was not obtained even at 2250 psig. Accordingly, another column set was designed with decreased length, increased diameters, and equal volume.

Subsequent semiworks tests were made with these 8-, 6-, 4-, and 2-inch-diameter columns. The 8-inch column was 5-ft-long to provide a resin bed large enough to sorb ~ 20 moles of Ln+An; the other columns were 4 ft long.

Two tests were made to demonstrate the process with these columns, one at an effluent temperature of 70°C and another at 80°C. All columns were filled with ~ 80 μ m "Dowex" 50W-X8 resin in the Zn²⁺-form. Feed for both tests was 18 moles nonradioactive lanthanides, 20 moles HNO₃, and 40 moles NaNO₃. Dysprosium and terbium were used as stand-ins for curium and americium, respectively. The 8-inch column was loaded at 8 ml/(min-cm²) to $\sim 72\%$ capacity. In the first test, approximately 1.5% of the feed did not load because feed was loaded from an 18-l volume instead of the desired 20 l. Concentration of the feed resulted in breakthrough as predicted by Figure 1. (In MPPF, the feed will be ~ 1 M HNO₃, 2M NaNO₃, and ~ 1 M Ln-An(NO₃)₃, and will be loaded from an 18-l feed tank.) In the second test, HNO₃ and NaNO₃ were adjusted to 1M and 2M, respectively, and no breakthrough occurred.

Figure 6 shows the elution diagram for the separation test at 70°C; the test at 80°C gave essentially the same results. Elutriant (0.05M DTPA at pH 3.0) was pumped through the 8-, 6-, and 4-inch columns at 16 ml/(min-cm²) and through the 2-inch column at 32 ml/(min-cm²). The Dy-Tb binary in both tests contained ~ 20 g each of dysprosium and terbium, corresponding to

~30 g each of curium and americium. Approximately 40 g of the original 65 g of dysprosium were lost because of a valving error during elution. Approximately 5 g of pure dysprosium and the complete Dy-Tb binary were collected from the 2-inch column. Because the size of the Dy-Tb binary eluting from the 2-inch column is not a function of total dysprosium in the column system, the results of this test are valid. The elution diagram shows dysprosium collected from the 2-inch column as a solid line and the remainder, estimated from previous tests, as a dashed line.

These two tests successfully demonstrated the chromatography portion of the plutonium burner process. The solvent extraction concentrate can be processed in MPPF in ~10 batches. Approximately 18 moles of Ln+An can be loaded on the 8-inch column from feed solutions containing ~1M HNO₃ and ~2M NaNO₃. Elution with 0.05M DTPA at pH 3.0 will give excellent separation of curium and americium. A flow of 32 ml/(min-cm²) through the 2-inch column will prevent overheating from the alpha decay of ²⁴²Cm and ²⁴⁴Cm.

FIGURE 6. Semiworks Test of Ion Exchange Process with 8-, 6-, 4-, and 2-inch Columns

REMOVAL OF RESIDUAL FISSION PRODUCTS FROM RESIN

Tests indicated that 0.3M DTPA, pH 8, is the most efficient agent for removing residual fission products from ion exchange resin. After curium and americium are collected from the 2-inch column, fission products must be stripped from the resin before the columns are discarded. Because the waste volume generated in the loading and eluting steps is large (~ 750 l), waste generated from column stripping must be minimized.

Figure 7 shows the results of stripping tests made with DTPA at various concentrations and pH values. In these tests, nonradioactive neodymium was loaded on the top 1/3 of a 0.5-inch-diameter by 2.5-ft-long steel column containing "Dowex" 50W-X8 resin, 200-400 mesh. Neodymium was stripped from the resin at 70°C and 16 ml/(min-cm²) with the test solution. The most efficient stripping solution from the standpoint of waste volume and DTPA economy was 0.3M DTPA at pH 8.0. Lanthanide removal was slightly faster with 0.5M DTPA at pH 8.0, but not enough to justify the 67% increase in DTPA consumption. Considerable neodymium trailing occurred at pH 10, indicating formation of small amounts of neodymium hydroxide in the column.

These lab-scale results were confirmed in semiworks tests. At the end of the chromatographic separation tests, residual lanthanides were completely removed from the resin with 2 column volumes of 0.3M DTPA at pH 8.0.

FIGURE 7. Removal of Neodymium from a 1/3-Loaded Column with DTPA

PROPOSED PROCESS

The ion exchange process for plutonium burner concentrate comprises three parts: 1) loading step, 2) separation of americium and curium by displacement development chromatography with 0.05M DTPA at pH 3.0 as elutriant, and 3) residual fission product stripping with 0.3M DTPA at pH 8.0.

The ion exchange columns to be used are 8, 6, 4, and 2 inches in diameter. All columns are 4 ft long except the 8-inch column, which is 5 ft long. With this process, ~ 18 moles of Ln+An can be separated from solution containing 1M HNO_3 and 2M NaNO_3 . Larger concentrations of NaNO_3 and HNO_3 decrease the batch size by decreasing column capacity for Ln+An. The maximum Ln+An batch size for any HNO_3 and NaNO_3 concentration can be determined from Figure 1.

Curium and americium can be separated from each other and from fission products with 0.05M DTPA at pH 3.0 as elutriant. A Cm-Am binary containing ~ 30 g of each component can be obtained with a flow of 16 ml/(min-cm²) through the 8-, 6-, and 4-inch columns and 32 ml/(min-cm²) through the 2-inch column. At these flows and a water jacket temperature of 70°C, ~ 1000 watts can be processed through the 2-inch column without overheating the resin bed. After curium and americium are collected, residual fission products can be stripped from the resin with ~ 2 column volumes of 0.3M DTPA at pH 8.0.

ACKNOWLEDGMENT

R. M. Wallace and R. L. Snow assisted in developing the equilibrium model for cation exchange sorption (Appendix A). The computer code for calculating band length requirements (Appendix B) was written by J. T. Lowe.

APPENDIX A

EQUILIBRIUM TREATMENT FOR COLUMN LOADING²

An equilibrium model describing the sorption by cation exchange resin of an n-valent and two monovalent cations from solution is characterized by the following equations:

$$M^{n+} + n\bar{M}_1^+ = \bar{M}^{n+} + nM_1^+ \quad (1)$$

$$M^{n+} + n\bar{M}_2^+ = \bar{M}^{n+} + nM_2^+ \quad (2)$$

$$K_1 = \frac{(\bar{M}^{n+})(M_1^+)^n}{(M^{n+})(\bar{M}_1^+)^n} \quad (3)$$

$$K_2 = \frac{(\bar{M}^{n+})(M_2^+)^n}{(M^{n+})(\bar{M}_2^+)^n} \quad (4)$$

Parentheses denote concentrations in the aqueous and resin phases, and the bar denotes concentration in the resin phase. M_1^+ and M_2^+ denote the monovalent cations, M^{n+} denotes the n-valent cations, and K_1 and K_2 are equilibrium constants for Equations 1 and 2. During column operations, the equilibrium concentration of the cation initially sorbed on the resin is negligible, and, therefore, it is not necessary to consider it in the equilibrium model.

The capacity of the resin is defined by Equation 5.

$$C = n[\bar{M}^{n+}] + [\bar{M}_1^+] + [\bar{M}_2^+] \quad (5)$$

where C is the resin capacity in meq/g. Square brackets denote concentrations in meq/g in the resin phase and molarity in the aqueous phase.

Combining Equations 3 through 5 gives

$$(\bar{M}_1^+) = [\bar{M}_1^+] \bar{\gamma}_{M_1^+} = \left(\frac{(\bar{M}^{n+})}{K_1 (M^{n+})} \right)^{1/n} (M_1^+) \quad (6)$$

$$(\bar{M}_2^+) = [\bar{M}_2^+] \bar{\gamma}_{M_2^+} = \left(\frac{(\bar{M}^{n+})}{K_2 (M^{n+})} \right)^{1/n} (M_2^+) \quad (7)$$

$$C = n[\bar{M}^{n+}] + \frac{[\bar{M}^{n+}]^{1/n} (\bar{\gamma}_M^{n+})^{1/n}}{(M^{n+})^{1/n}} \left(\frac{(M_1^+)}{\bar{\gamma}_{M_1^+} K_1^{1/n}} + \frac{(M_2^+)}{\bar{\gamma}_{M_2^+} K_2^{1/n}} \right) \quad (8)$$

where $\bar{\gamma}_1$ is the activity coefficient of species 1 in the resin phase. The fraction of the resin, f , in the M^{n+} form is given by Equation 9.

$$f = \frac{n[\bar{M}^{n+}]}{C} \quad (9)$$

Substitution of Equation 9 into Equation 8 gives Equation 10.

$$1 = f + \sigma f^{1/n} \quad (10)$$

where

$$\sigma = \left(\frac{\bar{\gamma}_M^{n+}}{n(M^{n+}) C^{n-1}} \right)^{1/n} \left(\frac{(M_1^+)}{\bar{\gamma}_{M_1^+} K_1^{1/n}} + \frac{(M_2^+)}{\bar{\gamma}_{M_2^+} K_2^{1/n}} \right) \quad (11)$$

Equation 10 can be solved easily for $n = 1, 2, 3$, and 4. For sorption of a trivalent ion ($n = 3$) from a solution containing two monovalent cations, the solution is

$$f = 1 - \sigma \left[\left[\frac{1}{2} + \left(\frac{1}{4} + \sigma^3/27 \right)^{1/2} \right]^{1/3} + \left[\frac{1}{2} - \left(\frac{1}{4} + \sigma^3/27 \right)^{1/2} \right]^{1/3} \right] \quad (12)$$

Figure 1 shows a plot of f versus σ , where σ was calculated from Equation 11 assuming that ratios of the activity coefficients in both phases (resin and aqueous) are constants, i.e.

$$\sigma = a_1 \left(\frac{[\text{Na}^+]}{[\text{Pr}^{3+}]^{1/3}} \right) + a_2 \left(\frac{[\text{H}^+]}{[\text{Pr}^{3+}]^{1/3}} \right) \quad (13)$$

where

$$a_1 = \left(\frac{1}{3 K_1 C^2} \right) \left(\frac{(\bar{\gamma}_{\text{Pr}^{3+}})^{1/3}}{\bar{\gamma}_{\text{Na}^+}} \right) \left(\frac{\gamma_{\text{Na}^+}}{(\gamma_{\text{Pr}^{3+}})^{1/3}} \right) \quad (14)$$

$$a_2 = \left(\frac{1}{3 K_2 C^2} \right) \left(\frac{(\bar{\gamma}_{\text{Pr}^{3+}})^{1/3}}{\bar{\gamma}_{\text{H}^+}} \right) \left(\frac{\gamma_{\text{H}^+}}{(\gamma_{\text{Pr}^{3+}})^{1/3}} \right) \quad (15)$$

The values for a_1 and a_2 , 0.125 and 0.057, respectively, were obtained by a least squares analysis of the data in Table III.

A slightly better fit of experimental data to the theoretical curve was obtained using calculated activity coefficients. The method of Reilly, *et al.*, was used to calculate activity coefficients in the aqueous phase.⁸ The parameters b_1 and b_2 for this fit are 0.145 and 0.024, respectively, where

$$b_1 = \left(\frac{1}{3 K_1 C^2} \right) \left(\frac{(\bar{\gamma}_{\text{Pr}^{3+}})^{1/3}}{\bar{\gamma}_{\text{Na}^+}} \right)$$

$$b_2 = \left(\frac{1}{3 K_2 C^2} \right) \left(\frac{(\bar{\gamma}_{\text{Pr}^{3+}})^{1/3}}{\bar{\gamma}_{\text{H}^+}} \right)$$

The ratio $\gamma_{\text{Na}^+}/(\gamma_{\text{Pr}^{3+}})^{1/3}$ is almost constant; the average value was 0.89 ± 0.03 . The ratio $\gamma_{\text{H}^+}/(\gamma_{\text{Pr}^{3+}})^{1/3}$, with an average value of 1.80 ± 0.22 (and $0.89 b_1 \approx a_1$ and $1.80 b_2 \approx a_2$), helps

to explain the small difference in the fits of the experimental data in Figures 1 and 2, and makes the initial assumptions regarding the activity coefficients more credible.

Since calculated activity coefficients for the aqueous phase only slightly improve the fit of experimental data to the theoretical curve, and the ratios of activity coefficients in the aqueous phase are almost constant, the more simple treatment using molar concentrations is preferred.

APPENDIX B

BAND LENGTH REQUIREMENTS FOR CURIUM-AMERICIUM SEPARATION

A mathematical treatment by Helfferich and James⁵ describes the method for calculating band length requirements for steady-state resolution of a multicomponent mixture by displacement development chromatography. The method uses the roots of the "h-function" to calculate resolution distances and times. The h-function is defined for an uncomplexed mixture by

$$\sum_{i=1}^n \frac{y_i}{\frac{1}{h} - \frac{1}{\alpha_{1i}}} = 0 \quad (1)$$

where

- n = the number of components
- y_i = the mole fraction of each component
- α_{1i} = the separation factor for component 1 and component i

The components are numbered so that the last element eluting from the column is component 1.

The roots of the h-function are bound by the separation factors. There are n-1 roots, then, satisfying the relations

$$\alpha_{11} \leq h_1 \leq \alpha_{12} \dots \leq \alpha_{1,n-1} \leq h_{n-1} \leq \alpha_{1n} \quad (2)$$

The roots are determined by assuming a trial value for h and calculating the sum in Equation 1. When values of h are determined, equations in Table I of Reference 5 are used to calculate $T_{j,k}$ and $Z_{j,k}$ for all pairs of components, where $T_{j,k}$ is the time in terms of initial band lengths required for components j and k to be resolved, and $Z_{j,k}$ is the distance the j,k boundary has moved when the components are resolved.

Table B-1 shows a computer code written to perform these calculations. Input data for the computer program are given in Table B-2 for the plutonium burner concentrate. Tables B-3, B-4, and B-5 show output from the computer program for the concentrate.

TABLE B-1

Computer Code for Calculating Band Length Requirements

```

      DIMENSIONAL(20),H(20),NAME(20),Y(20),Z(20,20),TAU(20,20)
      DIMENSION INDX(50),INDY(50),ZORDR(50)
      DIMENSION TITLE(18)
C     PROGRAM FOR CALCULATING MINIMUM ELUTION DISTANCES FOR BAND
C     RESOLUTION BY DISPLACEMENT DEVELOPMENT CHROMATOGRAPHY
      100 FORMAT(18A4)
      105 FORMAT (8F10.3)
      110 FORMAT (10I5)
      REAL*8 XTME,YTME
      10 READ (5,110) N
      IF(N)50,50,120
      50 STOP
      120 READ(5,100) (NAME(I),I=1,N)
      READ (5,100) TITLE
      READ(5,105) (AL(I),I=1,N)
      WRITE(6,1000)
      1000 FORMAT (1H1,T10,'CALCULATION OF ION EXCHANGE PARAMETERS'/T10,'BY T
      HE HELFFERICH-JAMES EQUATIONS'//)
      WRITE (6,100) TITLE
      READ (5,105) (Y(I),I=1,N)
      CALL TIME('A',XTME,YTME)
      WRITE(6,115) YTME,XTME
      115 FORMAT(15X,'YEAR:DAY=',A8,3X,'HOUR:MIN:SEC=',A8//)
C     INPUT DATA INCLUDES NAME OF EACH COMPONENT,THE SEPARATION FACTOR FOR
C     COMPONENT I AND COMPONENT I (AL(1)=1.0),AND THE MOLE FRACTION Y(I)
C     OF EACH COMPONENT.
C
C     BEGIN CALCULATION OF EACH H(I)
C
      I=0
      180 I=I+1
      ILCCP=C
      HUP=AL(I+1)
      HLCW=AL(I)
      HTRIAL= (AL(I+1) +AL(I))/2.0
      190 SM=SUM
      SUM=0.0
      ILOOP=ILOOP+1
      IF(ILOOP.LT.40) GO TO 195
      H(I)= HTRIAL
      WRITE (6,332) I,HTRIAL
      332 FORMAT ( 20X,'H(',I1,')=',F10.3,' AFTER 40 ITERATIONS')
      GO TO 380
      195 DO 200 J=1,N
      200 SUM= SUM+ Y(J)/(1.0/HTRIAL-1.0/AL(J))
      IF (ABS(SUM)-.001) 300,300,210
      210 IF (SUM) 220,220,240
C     FIRST CHECK IF SUM IS WITHIN 0.001 OF 0.0,AND SET H(I)=HTRIAL IF
C     IT IS. IF NOT,AND SUM IS POSITIVE, DECREASE HTRIAL AND REPEAT---IF
C     SUM IS NEGATIVE,INCREASE HTRIAL AND REPEAT.
      220 HLOW=HTRIAL
      HTRIAL=(HUP+HLOW)/2.0
      GO TO 190
      240 HUP=HTRIAL
      HTRIAL=(HUP+HLOW)/2.0
      GO TO 190

```

TABLE B-1 (Cont'd)

Computer Code for Calculating Band Length Requirements

```

300 H(I)=HTRIAL
    WRITE (6,333) I,H(I)
333 FORMAT( 20X,'H(',I1,')= ',F10.3)
380 IF(I.LT.(N-1)) GO TO 180
C
C    ALL N-1 VALUES OF H HAVE NOW BEEN CALCULATED
C    PROCEED WITH Z AND TAU CALCULATIONS
    DO 400 K=1,N
        TAU(K,K)=1.0
400  Z(K,K)=1.0
        DO 455 K=2,N
            FACTOR=1.0
            IF (K.GT.(N-1))GO TO 450
            L=N-1
            DO 410 I=K,L
210  FACTOR=FACTOR*AL(I)*(H(I)-1.0)/(H(I)*(AL(I)-1.0))
450  Z(1,K)=FACTOR*AL(N)/(AL(N)-1.0)
455  Z(K,1)= Z(1,K)
            F1=1.0
            DO 470 I=2,N
470  F1=F1*AL(I)/H(I-1)
            DO 497 K=2,N
                F2=1.0
                IF(K.GT.(N-1)) GO TO 495
                L=N-1
                DO 490 I=K,L
490  F2=F2*(H(I)-1.0)/(AL(I)-1.0)
495  TAU(1,K)=(1.0/(AL(N)-1.0))*F1*F2
497  TAU(K,1)=TAU(1,K)
C
C    ALL Z(1,K) AND TAU(1,K) NOW CALCULATED---
C    NEXT CALCULATE Z(K,N) AND TAU(K,N)
C
    DO 600 J=1,L
        F3=1.0
        F4=1.0
        F5=1.0
        DO 510 I=2,N
510  F3=F3* AL(I)/H(I-1)
            IF(J.EQ.1) GO TO 570
            M=J-1
            DO 520 I=1,M
                F4=F4* (AL(N)-H(I))/(AL(N)-AL(I))
520  F5=F5*AL(I)*(AL(N)-H(I))/(H(I)*(AL(N)-AL(I)))
570  Z(J,N)=1.0 + F5*AL(J)/(AL(N)-AL(J))
            TAU(J,N)= (1.0/(AL(N)-AL(J))) *F3*F4
            Z(N,J)= Z(J,N)
            TAU(N,J)= TAU(J,N)
600  CONTINUE
C
C    WITH THE TOP ROW AND LAST COLUMN OF THE MATRIX CALCULATED,
C    USE THE ITERATION FORMULAS TO CALCULATE THE REMAINING Z AND
C    TAU VALUES
C
    L=N-2
    IF(L.LT.2) GO TO 890

```

TABLE B-1 (Cont'd)

Computer Code for Calculating Band Length Requirements

```

      DO 800 KP=2,L
      K=N-KP+1
      KK=K-1
      DO 800 J=2,KK
C
C      K GOES FROM N-1 TO 3
C      J GOES FROM 2 TO K-1 FOR EACH K
C
      T1=(1.0/AL(J)-1.0/H(K))*Z(J,K+1)
      T2=(1.0/H(J-1)-1.0/AL(K))*Z(J-1,K)
      T3=(1.0/H(J-1)-1.0/H(K))*Z(J-1,K+1)
      T4=AL(J)*AL(K)/(AL(K)-AL(J))
      Z(J,K)=T4*(T1+T2-T3)
      T5=(H(K)-AL(J))*TAU(J,K+1)+(AL(K)-H(J-1))*TAU(J-1,K)
      T6=(H(K)-H(J-1))*TAU(J-1,K+1)
      TAU(J,K)=(T5-T6)/(AL(K)-AL(J))
      Z(K,J)=Z(J,K)
800  TAU(K,J)=TAU(J,K)
C      END OF CALCULATION--NOW PRINT OUT DATA
C
890  WRITE(6,900)
900  FORMAT(T10,'INDEX',T22,'ELEMENT',T35,'MOLE',T45,'SEPARATION'/T10,
1    'NUMBER',T33,'FRACTION',T44,'FACTOR ALPHA'//)
      DO 920 J=1,N
920  WRITE(6,930) J,NAME(J),Y(J),AL(J)
930  FORMAT(T12,I2,T23,A4,T35,F5.3,T44,F10.3)
      WRITE(6,940)
940  FORMAT(//T10,'MATRIX OF RESOLUTION DISTANCES')
      WRITE(6,950)(NAME(J),J=1,N)
950  FORMAT(T5,12(4X,A4))
      DO 980 J=1,N
980  WRITE(6,1005) NAME(J),(Z(J,K),K=1,N)
1005  FORMAT(T2,A4,12(F6.3,2X))
      WRITE(6,1010)
1010  FORMAT(///,T10,'MATRIX OF RESOLUTION TIMES')
      WRITE(6,950)(NAME(J),J=1,N)
      DO 1020 J=1,N
1020  WRITE(6,1005) NAME(J),(TAU(J,K),K=1,N)
      NMAX=(N*(N-1))/2
      ZMIN=Z(1,2)
      I1=0
1099  I1=I1+1
      M=N-1
      DO 1100 J=1,M
      L=J+1
      DO 1100 K=L,N
      IF (Z(J,K).GT.ZMIN) GO TO 1100
      ZMIN=Z(J,K)
      INDX(I1)=J
      INDY(I1)=K
1100  CONTINUE
      L=INDX(I1)
      M=INDY(I1)
      Z(L,M)=1000000.
      ZMIN=10000.
      IF(I1.GE.NMAX) GO TO 1120

```

TABLE B-1 (Cont'd)

Computer Code for Calculating Band Length Requirements

```
      GO TO 1099
1120 DO 1130 J=1,N
      L=J+1
      DO 1130 K=L,N
1130  Z(J,K)=Z(K,J)
      WRITE (6,1140)
1140  FORMAT (///,10X,'COMPONENTS ARE RESOLVED IN THE FOLLOWING ORDER',/
110X,'COMP.1  COMP.2  DISTANCE  TIME')
1150  FORMAT (10X,A4,3X,A4,3X,F10.3,2X,F10.3)
      DO 1200 I1=1,NMAX
      L=INDX(I1)
      M=INDY(I1)
1200  WRITE (6,1150) NAME(L),NAME(M),Z(L,M),TAU(L,M)
      GO TO 10
      END
```

TABLE B-2

Computer Code Input:
Composition of Mixture and Separation Factors

<u>Index Number</u>	<u>Element</u>	<u>Mole Fraction</u>	<u>Separation Factor, Alpha</u>
1	La	0.114	1.000
2	Ce	0.250	7.410
3	Pr	0.108	29.520
4	Nd	0.323	87.100
5	Pm	0.005	186.200
6	Sm	0.093	398.000
7	Gd	0.016	589.000
8	Eu	0.032	602.500
9	Am	0.041	1202.000
10	Cm	0.018	1380.000

TABLE B-3

Computer Code Output:
Matrix of Resolution Times, $T_{j,k}$

	LA	CE	PR	ND	PM	SM	GD	EU	AM	CM
LA	1.000	0.940	0.672	0.577	0.290	0.267	0.209	0.208	0.140	0.126
CE	0.940	1.000	0.737	0.608	0.295	0.271	0.211	0.210	0.140	0.127
PR	0.672	0.737	1.000	0.751	0.309	0.281	0.217	0.215	0.143	0.129
ND	0.577	0.608	0.751	1.000	0.365	0.317	0.235	0.233	0.149	0.134
PM	0.290	0.295	0.309	0.365	1.000	0.332	0.242	0.239	0.151	0.135
SM	0.267	0.271	0.281	0.317	0.332	1.000	0.418	0.410	0.186	0.163
GD	0.209	0.211	0.217	0.235	0.242	0.418	1.000	2.288	0.210	0.179
EU	0.208	0.210	0.215	0.233	0.239	0.410	2.288	1.000	0.213	0.181
AM	0.140	0.140	0.143	0.149	0.151	0.186	0.210	0.213	1.000	0.493
CM	0.126	0.127	0.129	0.134	0.135	0.163	0.179	0.181	0.493	1.000

TABLE B-4

Computer Code Output:
Matrix of Resolution Distances, $Z_{j,k}$

	LA	CE	PR	ND	PM	SM	GD	EU	AM	CM
LA	1.000	1.053	1.013	1.008	1.002	1.002	1.001	1.001	1.001	1.001
CE	1.053	1.000	1.101	1.057	1.016	1.013	1.009	1.009	1.005	1.005
PR	1.013	1.101	1.000	1.223	1.050	1.039	1.028	1.027	1.016	1.014
ND	1.008	1.057	1.223	1.000	1.160	1.115	1.077	1.076	1.043	1.038
PM	1.002	1.016	1.050	1.160	1.000	1.131	1.086	1.085	1.047	1.042
SM	1.002	1.013	1.039	1.115	1.131	1.000	1.310	1.303	1.114	1.099
GD	1.001	1.009	1.028	1.077	1.086	1.310	1.000	3.192	1.149	1.127
EU	1.001	1.009	1.027	1.076	1.085	1.303	3.192	1.000	1.154	1.130
AM	1.001	1.005	1.016	1.043	1.047	1.114	1.149	1.154	1.000	1.475
CM	1.001	1.005	1.014	1.038	1.042	1.099	1.127	1.130	1.475	1.000

TABLE B-5

Computer Code Output:
Order of Resolution

COMPONENTS ARE RESOLVED IN THE FOLLOWING ORDER

COMP.1	COMP.2	DISTANCE	TIME
LA	CM	1.001	0.126
LA	AM	1.001	0.140
LA	EU	1.001	0.208
LA	GD	1.001	0.209
LA	SM	1.002	0.267
LA	PM	1.002	0.290
CE	CM	1.005	0.127
CE	AM	1.005	0.140
LA	ND	1.008	0.577
CE	EU	1.009	0.210
CE	GD	1.009	0.211
CE	SM	1.013	0.271
LA	PR	1.013	0.672
PR	CM	1.014	0.129
CE	PM	1.016	0.295
PR	AM	1.016	0.143
PR	EU	1.027	0.215
PR	GD	1.028	0.217
ND	CM	1.038	0.134
PR	SM	1.039	0.281
PM	CM	1.042	0.135
ND	AM	1.043	0.149
PM	AM	1.047	0.151
PR	PM	1.050	0.309
LA	CE	1.053	0.940
CE	ND	1.057	0.608
ND	EU	1.076	0.233
ND	GD	1.077	0.235
PM	EU	1.085	0.239
PM	GD	1.086	0.242
SM	CM	1.099	0.163
CE	PR	1.101	0.737
SM	AM	1.114	0.186
ND	SM	1.115	0.317
GD	CM	1.127	0.179
EU	CM	1.130	0.181
PM	SM	1.131	0.332
GD	AM	1.149	0.210
EU	AM	1.154	0.213
ND	PM	1.160	0.365
PR	ND	1.223	0.751
SM	EU	1.303	0.410
SM	GD	1.310	0.418
AM	CM	1.475	0.493
GD	EU	3.192	2.288

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