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APPLICATION OF EXTRACTION CHROMATOGRAPHY TO THE RECOVERY OF NEPTUNIUM, PLUTONIUM AND AMERICIUM FROM AN INDUSTRIAL WASTE

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ABSTRACT

A pilot scale investigation was made to evaluate the possible application of the extraction chromatographic method (LLC) to the partitioning of alpha emitters from liquid wastes containing traces of transuranium elements. A secondary purpose was to obtain pure AmO_2, which is used to produce alpha, gamma, and neutron sources.

The process developed for "alpha partitioning" consists essentially of the extraction of macro amounts of uranium with 30% TBP in dodecane in mixer-settlers, then coextraction of Np-237, Pu-239, and Am-241 by LLC on a macro column filled with di-n-hexyl-octoxy-methyl-phosphine oxide (POX.11) adsorbed on an inert support. In each run about 200 liters of initial waste are decontaminated of alpha emitters. The loading step is followed by selective elution of americium, neptunium, and plutonium.

The americium eluate is then subjected to the following operations: (1) separation of Am from Fe and Cd by LLC on a TBP column and (2) separation of Am from lanthanide traces by LLC on an HD(DiBM)P column after oxidation of Am(III) to Am(VI). The Am in the eluate is subsequently reduced to Am(III) and precipitated as oxalate with oxalic acid. The oxalate is then filtered and calcined to yield pure AmO_2.

INTRODUCTION

The process which is described in this report is part of the Commissariat a l'Energie Atomique (CEA) research program on the elimination of alpha-emitting nuclides from nuclear fuel reprocessing plant wastes. The process has two objectives: (1) to produce an effluent which is free from alpha emitters, and (2) to recover valuable transuranium elements such as neptunium, plutonium, and americium.

The process which has been developed was applied to the treatment of a real "Masurca" liquid waste. This waste, 4 m^3 in volume, contains about 400 g of americium, 200 g of plutonium, and 600 g of neptunium in a matrix consisting primarily of cadmium, uranium, and iron. The composition of the Masurca solution is given in Table 1.

Column extraction chromatography appears to be an attractive method for the separation of trace quantities of transuranium elements. It provides a high concentration factor, and is compatible with hot cell operations. Furthermore, a chromato-

TABLE 1

Composition of "Masurca" Solution

Element	Concentration (g/L)	Activity (mCi/L)
U	12	-
Np	0.18	-
Pu	0.07	-
Am	0.108	-
Fe	11.1	-
Cd	35.4	-
Ni	1.01	-
Cr	1.6	-
Ce-144	-	0.28
Ru-106	-	1.34
Cs-137	-	9.1
All fission products		10.7
free HNO_3	1.1 N	

graphic column is a simple unit; it can be easily scaled from laboratory usage to industrial operation.

Because the Masurca solution has a high uranium concentration, the first step consisted of counter-current liquid-liquid extraction prior to treatment on a chromatographic column, in order to avoid uranium saturation of the extractant, which would decrease the capacity of the column relative to the other transuranium elements. Then the extraction cycle on the chromatographi column is carried out, on the solution free of uranium. The raffinate obtained exhibits alpha activity compatible with an acceptable release limit (1 mg/L ^{241}Am). The transuranium elements: neptunium, plutonium, and americium are recovered. The americium is purified by supplementary extraction chromatographic cycles. It is then converted to the dioxide, which can be used to produce alpha, gamma and neutron radiation-emitting sources after mixture, or compound preparation, with suitable target elements (e.g., Li and Be).

EXPERIMENTAL

Apparatus

The operations were conducted remotely in a hot cell (10 cm of lead) housing the apparatus. The apparatus for the counter-current liquid-liquid extraction cycle consisted of two batteries of Plexiglas mixer-settlers, one with ten stages (total flow 10 L/h), and the second with eight stages (total flow 5 L/h); three diaphragm-type proportioning pumps; and solution receiving tanks. The apparatus for the chromatographic separation cycles consisted of Plexiglas columns filled with sized silica gel, diaphragm-type proportioning pumps, and an on-line gamma counting system which was designed to monitor the activity of americium-241 in the column effluent. The counting system included a miniature Geiger-Muller detector which was placed in contact with the column effluent outlet tube and protected from ambient

TABLE 2

Characteristics of the Chromatography Columns

Stationary Phase		Diameter	Effective height	Interstitial volume	Total weight
Material	Weight (g)	(mm)	(mm)	(L)	(kg)
*POX 30%/ silica gel	9090	150	680	4.	29
TBP 27%/ silica gel	1500	60	680	0.8	5
HD(DiBM)P 30%/ silica gel	1500	60	680	0.8	5

*The "Hercules" column is of a special type. The 5-mm thick Plexiglas tube is fitted with a 2-mm thick steel jacket to accommodate the mechanical stresses resulting from the service pressure and partial pressure of the radiolysis gases (see Fig. 1).

irradiation by lead shielding, and the associated electronics. While operating on the POX.11 cycle (see below), the detector is used to actuate automatic shutoff of the column feed pump.

The main characteristics of the chromatographic columns which were used in the second cycle and the americium purification cycles are presented in Table 2. The inert support consisted of 60 to 230 mesh silanized silica gel supplied by Merck (West Germany). This support was placed in contact with the extractant, which was diluted in acetone or hexane; the diluent was subsequently expelled by evaporation at reduced pressure. The extent of impregnation was 30% with POX.11*, 27% with TBP**, and 30% with HD(DiBM)P***.

Reagents

Technical grade HNO_3; $Al(NO_3)_3 \cdot 9H_2O$; $LiNO_3$; and $LiOH \cdot H_2O$ were used in this study. These were all supplied by Prolabo.

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*Di-n-hexyl-octoxy-methyl-phosphine oxide.

**Tri-n-butyl phosphate.

***Bis 2-6 dimethyl-4-heptyl-phosphoric acid.

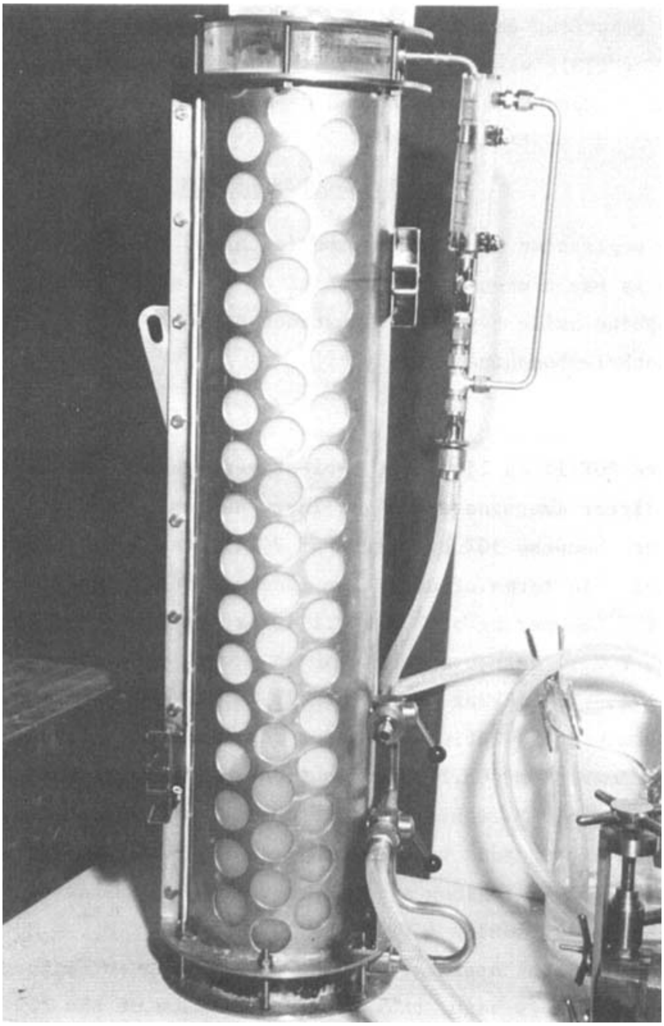

FIGURE 1. Photograph of the "Hercules" column.

Technical grade TBP and dodecane, from Progil-France, were also employed, whereas analytical grade ethylenediaminetetraacetic acid (EDTA)-Merck, was used. The POX.11 extractant was synthesized by IRCHA (Institut de Recherche et de Chimie Appliquee, Paris); and the HD(DiBM)P was prepared in our laboratory by the method described by Mason, Bollmeier, and Peppard (1).

RESULTS AND DISCUSSION

The separation process for americium and the other transuranium elements is based upon the properties of a neutral extractant of the phosphine oxide type. This extractant, POX.11, is di-n-hexyl-octoxy-methyl-phosphine oxide (2).

Properties of POX.11

Since POX.11 is liquid at ambient temperature, it is suitable for the direct impregnation of an inert support. A high capacity is attained because 30% by weight of POX.11 can be adsorbed on silica gel. In terms of americium loading, this corresponds to 66.9 g of ^{241}Am per kg of 30% POX.11-impregnated silica gel. In addition, POX.11 extracts americium in a weakly salted and slightly acid medium, thus making it preferable to TBP (3). This simplifies the adjustment of solutions intended for fixation on chromatographic columns. Americium-POX.11 distribution coefficients which were determined in a 3 M lithium nitrate medium are presented as a function of nitric acid concentration in Fig. 2. The affinity of cations for POX.11 follows a sequence which is similar to that of trioctyl-phosphine oxide (TOPO), viz., $M^{+} \sim M^{++} < M^{3+} < M^{4+} \sim MO_2^{2+}$.

In the present application, the uranium concentration in the initial solution is high, thus rapid saturation of the POX.11 with uranium would be expected to occur, and this would result in a decrease of the americium and neptunium/plutonium extraction capacity. We therefore made provision for an initial uranium extraction cycle in the process flowsheet. The high affinity of TBP for actinides of oxidation state VI led to its choice as the

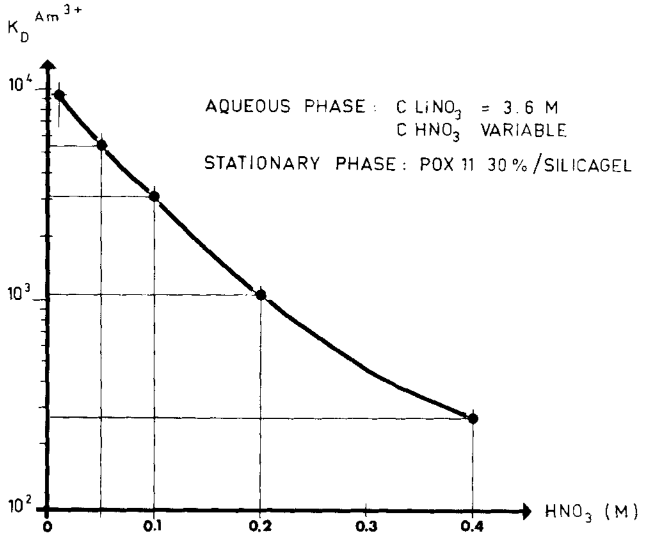

FIGURE 2. Am^{3+} extraction by POX.11 30%/silica gel. Variation of the distribution coefficient of Am^{3+} with HNO_3 concentration.

selective uranium extractant. The process thus consists of two steps: (1) selective extraction of uranium by TBP; and (2) coextraction of americium, plutonium and neptunium by POX.11.

Description of the Separation Process for Uranium and Transuranium Elements

The uranium extraction flowsheet is presented in Fig. 3. The Masurca solution, without adjustment, is fed into the extraction battery at the rate of 3 L/h. The uranium is extracted with a 30% TBP/dodecane flow rate of 1 L/h. The organic phase is subjected to a reducing scrub (at 0.25 L/h) to avoid plutonium(IV) losses, and the uranium is then stripped by water, at a flow rate of 0.7 L/h. The raffinate from the extraction battery contains americium, neptunium, plutonium, the inactive matrix, and the fission products. It is then sent to the second cycle.

The extraction chromatography cycle on the POX.11 column is presented in Fig. 4. This cycle can be carried out in two ways.

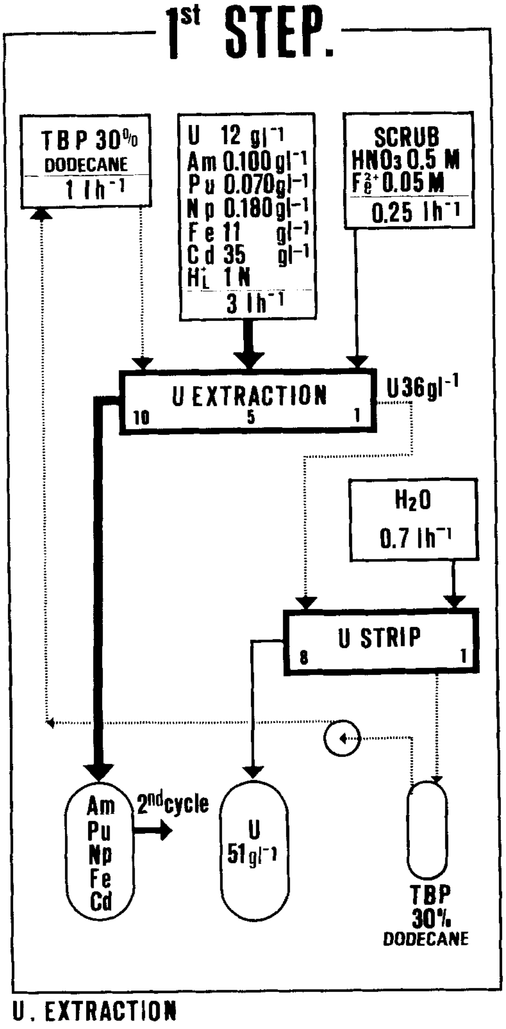

FIGURE 3. Uranium extraction flowsheet.

In the first method (Method I), the solution from the first cycle is treated with lithium nitrate to increase the salting out effect, and the acidity is adjusted with aluminum nitrate deficient in the nitrate ions $Al(NO_3)_{3-x}(OH)_x$. A strong base such as caustic soda cannot be added because this would rapidly cause hydrolysis

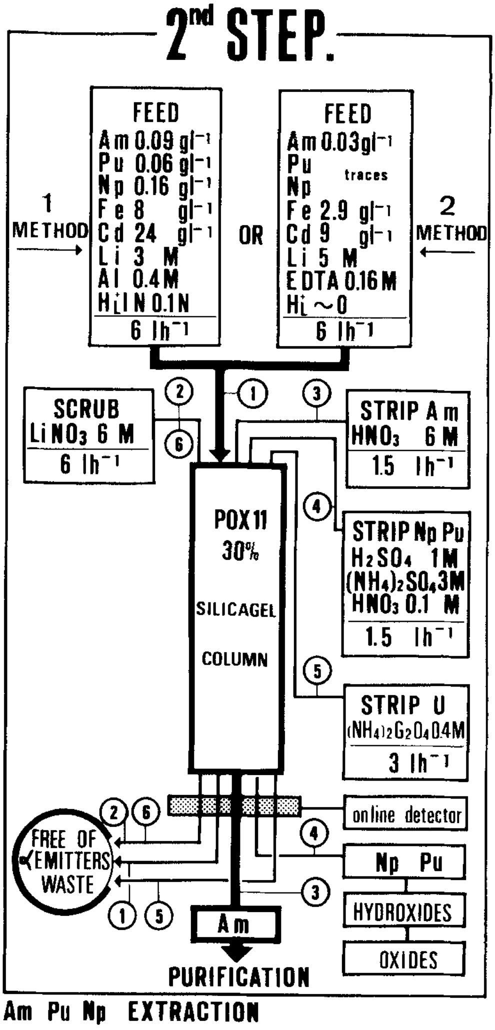

FIGURE 4. Americium, plutonium and neptunium extraction flowsheet.

of the iron. After these adjustments the composition of the solution is as given in Table 3.

The adjusted solution is fed to the column at the rate of 6 L/h. It is possible to fix volume fractions of 100 to 200 liters, corresponding to about 10 g of ^{241}Am. The effective

TABLE 3

Composition of Adjusted Solution

Li^+	Al^{3+} (M)	H^+	Am	Pu	Np (g/L)	Fe	Cd	Fission products (mCi/L)
3	0.4	∿0.1	0.08	0.06	0.16	8	24	9

americium capacity is low in comparison with theoretical capacity, because of the competitive fixation of iron, which can be seen by the rust color assumed by the support. The column exhibits successive fronts, from top to bottom, of americium (brown ring), neptunium (green ring), and uranium (yellow ring). The column is fed from the bottom in order to remove the radiolysis gases.

Scrubbing and loading operations are carried out by a salting out solution of 6 M $LiNO_3$, which is designed to eliminate the solution contained in the interstitial volume of the column.

Three selective elutions are carried out. The americium is eluted by a 6 M nitric acid solution at a flow of rate (V/3) L/h, where V is the fixation flow rate. The americium recovery yield is about 95%. The use of a solution strongly loaded with sulfates, 1 M H_2SO_4, 3.5 M $(NH_4)_2SO_4$, and 0.1 M HNO_3 allows recovery of the plutonium and neptunium, whereas the traces of uranium that are fixed on the column are eluted by a 0.4 M $(NH_4)_2C_2O_4$ solution.

Neptunium and plutonium are concentrated by precipitation as hydroxides. The hydroxides are calcined, and the resulting oxides are stored. The americium eluate, with an americium concentration of about 1 g/L, still contains iron, cadmium, and lanthanide traces, and must be purified.

The fixation effluent is decontaminated of alpha emitters. On-line detection of the gamma activity of the americium, together with spot checks of alpha activity, indicate the discharge of an effluent containing less than 1 mg/L of ^{241}Am, or 3.4 mCi/L. The ^{237}Np and ^{239}Pu concentrations cannot be detected by alpha spectrometry, in view of the mass activity ratios relative to the ^{241}Am.

The second method (Method 2) was developed because of problems caused by the iron present. The coextraction of iron and americium brings two unfavorable factors, a lowering of the americium capacity of the column and the presence of iron impurity in the americium eluate. However, the extraction of Am in the presence of high iron concentrations is possible: indeed, (a) the extraction kinetics of Am^{3+} on POX.11 is better than that of Fe^{3+}, as shown in Fig. 5; and (b) POX.11 shows greater affinity for Am^{3+} at equilibrium, as shown in Fig. 6.

Alternatively, to eliminate the extraction of iron, it is possible to form an iron complex in the fixation solution which is

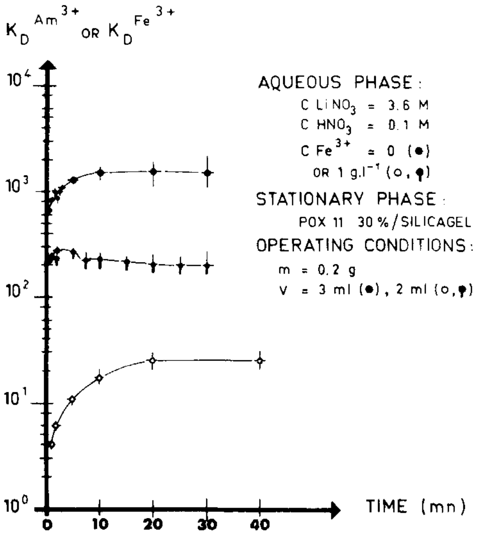

FIGURE 5. Extraction kinetics of Am^{3+}, Fe^{3+}, and Am^{3+}/Fe^{3+} mixtures.

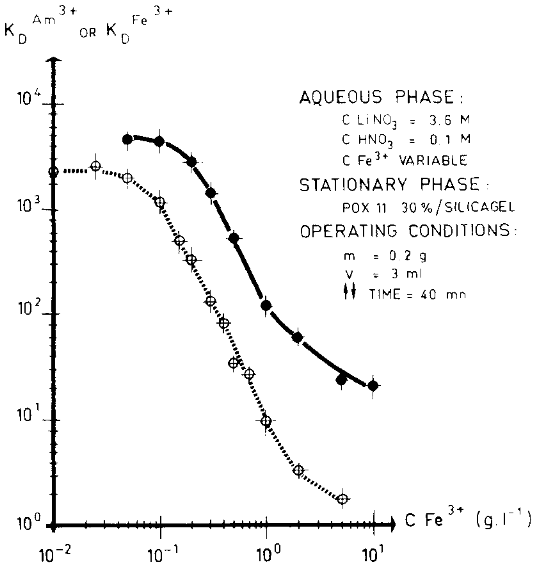

FIGURE 6. Extraction of Fe^{3+} and Am^{3+} by POX.11 30%/silica gel. Variation of the distribution coefficient of Am^{3+} and Fe^{3+} with Fe^{3+} concentration.

unextractable by POX.11. The addition of a solution of EDTA in lithium hydroxide (1 EDTA/3 LiOH) to the process solution, and neutralization of the free acidity H_L^+ to less than 0.1 N, gives rise to the desired complex, viz.,

$$Fe^{3+} + (EDTA)^{4-} \rightleftarrows Fe(EDTA)^- \quad (pK_c = 25.1).$$

The effect of EDTA addition on the distribution coefficients of Am^{3+} and Fe^{3+} is demonstrated in Fig. 7. On 30% POX.11/silica gel with 1/1 EDTA/iron stoichiometry, K_D Fe^{3+} tends towards zero, while K_D Am^{3+} rises to approach the values presented in Fig. 2.

The use of EDTA involved the elimination of the neptunium/plutonium couple by treatment on anionic exchange resin; after raising the nitric concentration to 5 M, the americium escapes in the effluent and its concentration is determined by counting its alpha activity. The concentration of hydrolyzed cations in

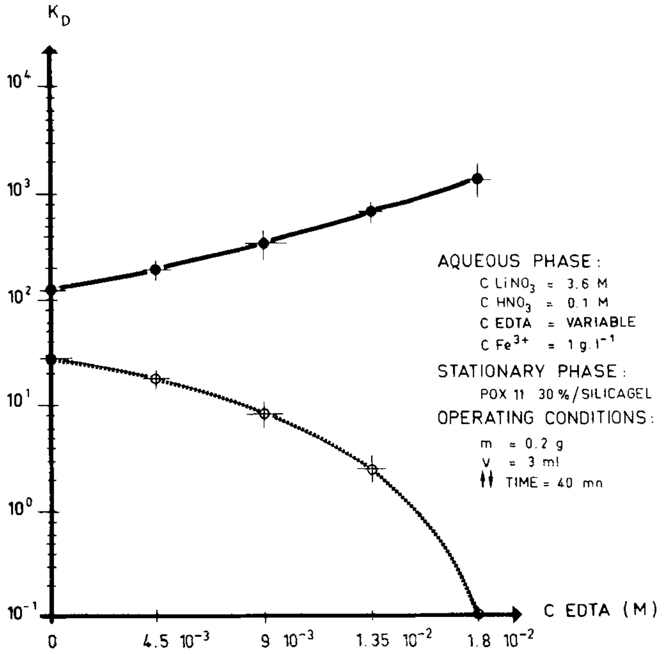

FIGURE 7. Extraction of Am^{3+} and Fe^{3+} by POX.11 30%/silica gel, in a complexing medium. Variation of the distribution coefficients of Am^{3+} and Fe^{3+} with EDTA concentration.

the solution is then determined by the difference between total acidity H_T^+ and free acidity H_L^+. The amount of EDTA added corresponds to the difference in concentration between hydrolyzed cations and americium.

This procedure was tested on a batch of 685 liters of solution, which was obtained after elimination of the uranium and the neptunium/plutonium couple. The composition of the solution after EDTA addition is presented in Table 4. Note, however, that the original solution is not the same as that presented in Table 1, but rather a Masurca solution which had been diluted by tank rinsing. Also, acidity adjustment was performed with LiOH (iron hydrolysis is inhibited by EDTA).

TABLE 4

Composition of Adjusted Solution
POX.11 Cycle. Method 2

Element	EDTA (M)	Li (M)	Am (g/L)	Pu	Np	Fission products (mCi/L)	Fe (g/L)	Cd (g/L)	H^+
Concentration	0.1	5	0.25				2.9	9	~ 0
Activity						2.7			

Decontamination factors F_D of the iron and cadmium from the americium are presented in Table 5. Performance of this separation cycle is probably somewhat better than that indicated in Table 5, as a colorimetric test indicated an iron content in the eluate that is considerably lower than the estimated value of 0.75 g/L.

The performance levels attained by the two methods relative to americium extraction are summarized in Table 6.

TABLE 5

Estimation of Iron and Cadmium Decontamination Factors

Solution type	Volume (L)	Fe (g/L)	Cd (g/L)	Eluate F_D (Am/Fe)	Eluate F_D (Am/Cd)
Feed	685	2.9	9		
Eluate	20	0.75	2.2	132	140

N.B. Assumption C_{Fe}

C_{Cd} = Σ concentration of hydrolyzable cations

TABLE 6

Americium Extraction
Comparison of Methods 1 and 2

Method 1	Feed	Effluents + scrub	Am eluate	Yield	Effluents F_D Am
K_D	89				
Volume (L)	96	105	5		
				0.95	19
Am (g/L)	0.073	0.0004	1.35		
Am (g)	7	0.042	6.75		
Method 2					
K_D	4381				
Volume (L)	685	696	20		
				0.89	34
Am (g/L)	0.025	0.0001	0.76		
Am (g)	17.1	0.069	15.2		

Americium Purification

The americium obtained from the POX.11 cycle contains impurities such as cadmium, traces of iron, and lanthanides. It is subjected to a two-stage purification cycle. The first stage involves the treatment by extraction chromatography with TBP to eliminate cadmium and iron. The second involves the separation of americium as Am(VI) from the lanthanides by extraction chromatography with HD(DiBM)P. This procedure uses a method described by Bourges, Madic and Koehly (4) for $^{243}Am/^{244}Cm$ separation by extraction chromatography, which is an adaptation of the liquid-liquid extraction process developed by Mason, Bollmeier, and Peppard (1). The purified americium is then converted to the oxide. The process flowsheet is presented in Fig. 8.

The americium eluate from the second cycle must be adjusted before fixation. Adjustment includes addition of $LiNO_3$, which

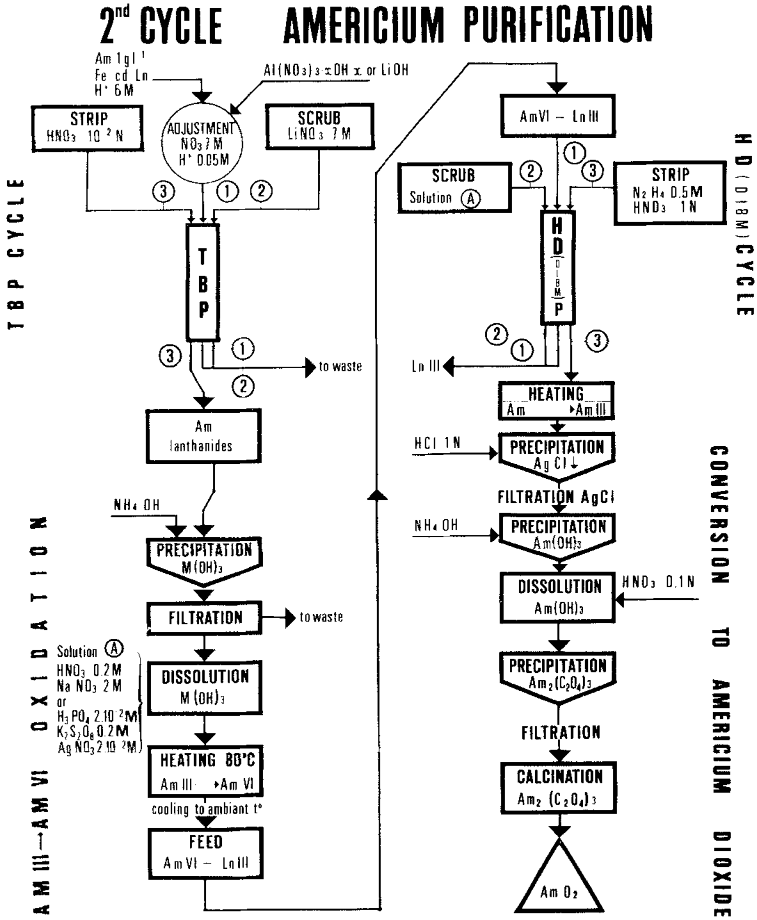

FIGURE 8. Americium purification cycle flowsheet.

raises the nitrate concentration of the solution to 7 $\underline{M}$, and acidity neutralization from 6 $\underline{M}$ to 0.05 $\underline{M}$ by $Al(NO_3)_{3-x}OH_x$, or by LiOH if a complexing medium is used. These adjustments are necessary for americium extraction by TBP. After fixation of the adjusted solution, the column is scrubbed by 7 $\underline{M}$ $LiNO_3$, and then eluted by 0.01 $\underline{M}$ HNO_3 (see Fig. 8, TBP cycle).

The eluate from the TBP cycle is reduced in volume by precipitation of the hydroxides. The fresh hydroxides are taken up by a solution (Solution A, Fig. 8) of the following composition:

HNO_3 = 0.2 M, $NaNO_3$ = 2 M or $H_3PO_4 = 2 \times 10^{-2}$ M,
$K_2S_2O_8$ = 0.2 M, $AgNO_3 = 2 \times 10^{-2}$ M.

The resultant solution is heated to 80°C for 30 min. After cooling, the solution is injected into a column packed with silica gel/ HD(DiBM)P 30% by weight. Am(VI) is fixed, whereas the lanthanides escape with the effluent. The column is then washed with the oxidizing solution. Elution of americium of oxidation states V and III is achieved by a 0.5 M $N_2H_5NO_3$, 1 M HNO_3 solution (4).

In the HD(DiBM)P eluate, the silver is separated by precipitation and filtration of the chloride. The filtrate is precipitated with ammonia, and the hydroxide is dissolved in nitric acid solution.

Then, americium oxalate is precipitated in a pH 1, C $H_2C_2O_4$ 0.2 M medium (5). It is then calcined for three hours at 800°C to obtain AmO_2. The resultant americium product is 99.3% pure.

CONCLUSIONS

Masurca waste was used to demonstrate the effectiveness and simplicity of use of extraction chromatography to eliminate alpha emitters from a solution rich in various metallic elements.

The column extraction chromatography process has the drawback of being a batch method. In the POX.11 cycle, the fixation operation occurs without direct monitoring, since feed control to the POX.11 column is monitored by detection of the activity of the americium in the effluent. (A planned improvement is the complete automation of the different operations in the chromatography cycle.) Furthermore, the properties of POX.11 relative to the separation of americium and transuranium elements resulted in an effluent which was satisfactorily decontaminated of alpha emitters (release limit < 1 mg/L ^{241}Am). Problems related to the coextraction of trivalent elements, chiefly iron, were solved by the introduction of a complexing agent (EDTA).

Americium purification by extraction of Am(VI) on a HD(DiBM)P column results in a product of high purity.

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