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Gregory R. Choppin[a]
[a] DEPARTMENT OF CHEMISTRY, FLORIDA STATE UNIVERSITY TALLAHASSEE, FLORIDA

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Separation Processes for Actinide Elements

GREGORY R. CHOPPIN

DEPARTMENT OF CHEMISTRY
FLORIDA STATE UNIVERSITY
TALLAHASSEE, FLORIDA 32306

Abstract

Separation processes for the actinide elements are reviewed. The difference in oxidation states for the elements Th through Am provide the basis of their separation techniques. The transplutonium elements require multiplate chromatographic or extraction processes to separate them due to the small chemical differences of the common trivalent states. Ion-exchange and solvent extraction systems useful in laboratory tracer level separations and in multigram plant separations are described.

INTRODUCTION

It is convenient to divide the separation processes for actinide elements into those concerned with the elements from atomic number 90 through 95 and those involving elements of atomic number 95 through 103. The first group of actinides exhibit different oxidation states in similar chemical systems, thereby providing a major basis for separation methods. Moreover, these elements include those actinides which are produced in gram to kilogram amounts in nuclear reactors, with the resulting requirement of large-scale technology in their separations. Except for nobelium ($Z = 102$), the elements beyond plutonium have a common trivalency and their separation methods are based on relatively small differences in properties within this trivalent state. For a few elements (e.g., $Z = 95, 97, 102$), other oxidation states are accessible in aqueous solutions and some separations have been developed around these states. Except for americium, the amounts of the elements which must be separated range from a few milligrams to a few

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atoms, so the most used methods are based on tracer level techniques. This paper reviews the classical methods of actinide separations for both groups of actinides and discusses several new developments.

SUBCURIUM ACTINIDES ($Z = 90–95$)

Pa is so rarely of interest that its separation and isolation is not discussed in this paper. The separation methods of the elements Th, U, Np, Pu, and Am use the differences in the chemistry of the oxidation states III, IV, V, and VI. Th(IV), U(VI), and Am(III) are the common states for these three elements. The IV, V, and VI states of neptunium must be considered although the V is the more commonly encountered state. Plutonium is unusual since it can, in certain systems, coexist in equilibrium in four

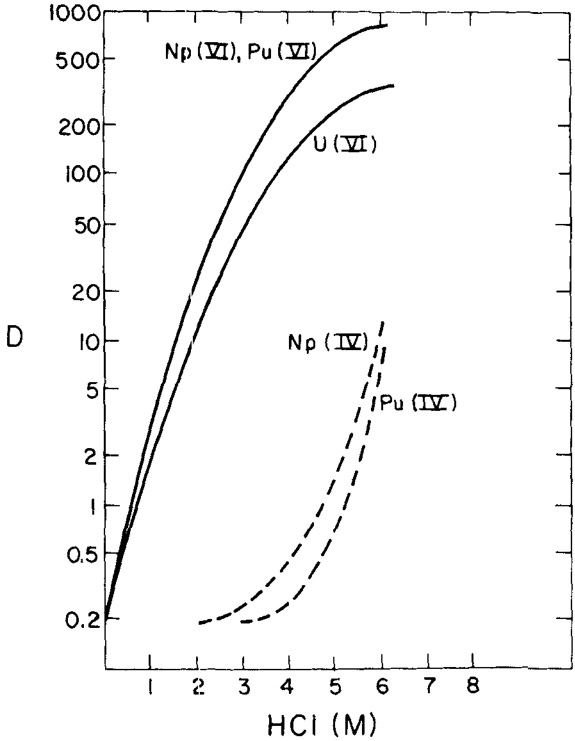

FIG. 1. Distribution coefficient, *D*, of several actinides from Dowex-1 anion exchange resin as a function of hydrochloric acid concentration.

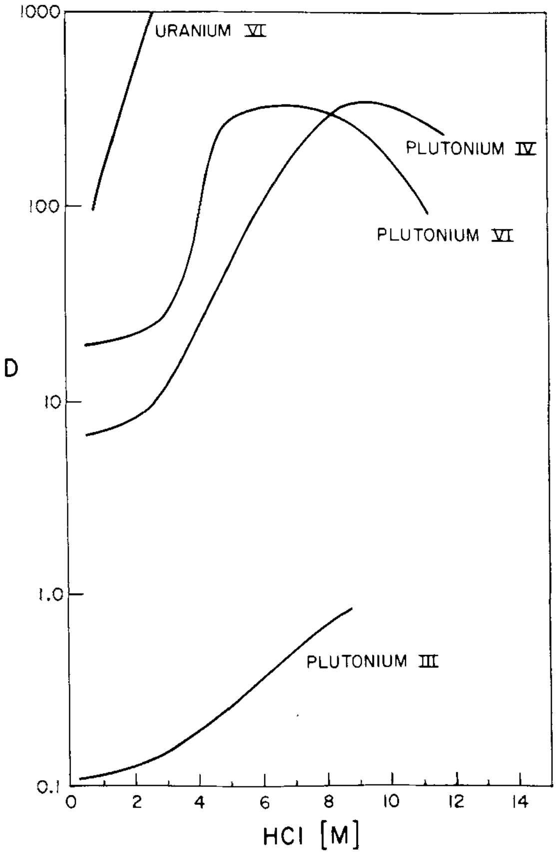

FIG. 2. Variation of D with hydrochloric acid concentration for extraction by 0.1 M TOPO in cyclohexane.

oxidation states, III through VI. For plutonium, the higher oxidation states gain in relative stability with increasing pH. The ease of achieving redox reactions with plutonium is a major feature of the chemistry of its separation methodology.

At the laboratory level, ion-exchange chromatography and solvent extraction partition techniques are used to achieve separations of these actinide elements. The different oxidation states of the actinides form complexes whose strength varies (usually) in the sequence IV > VI > III ≫ V. By adjustment of the proper concentrations of different ligands, it is possible to form complexes of the general formula MX_n where n varies from 0 to 6 and is largest for An(IV) and smallest for An(V) species.

The use of differential complexation is illustrated in Fig. 1 which shows the distribution of actinide elements between anion-exchange resin and hydrochloric acid (*1*). Anionic chloro complexes such as $An^{VI}O_2Cl_3^-$ and $An^{IV}Cl_5^-$ sorb to the resin and are separated from noncomplexed and cationic complexed species. The data in Fig. 1 reflects that the $An^{VI}O_2Cl_3^-$ species is sorbed strongly already in 1 *M* HCl solution whereas the An(IV) species, requiring formation of the pentachloro complex to be anionic, is sorbed only above 2 *M* HCl. The formation of chloro complexes by the An(III) and An(V) cations is too weak to allow appreciable sorption of anionic species even in 12 *M* HCl. The nitrate complexing is stronger, and both An(IV) and An(VI) species are sorbed strongly by anion-exchange resin even in 1 *M* HNO_3 (*2*).

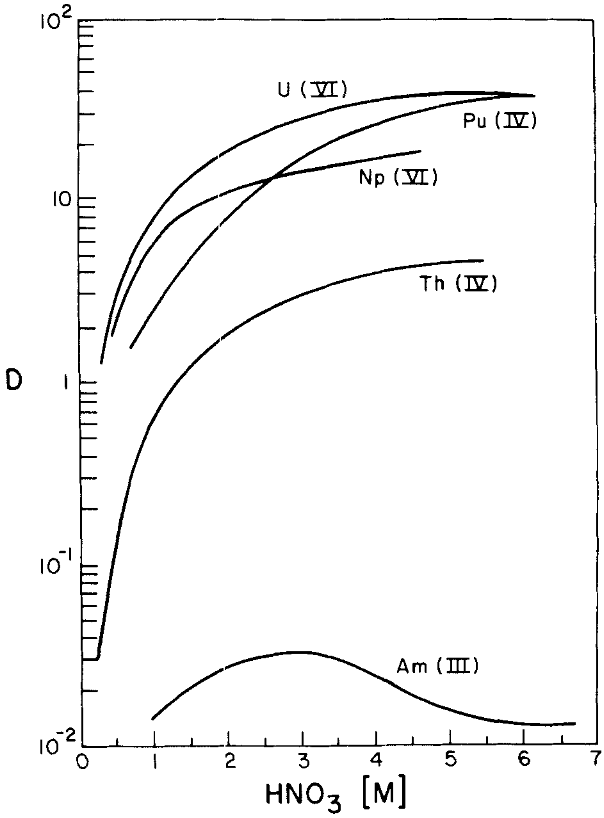

FIG. 3. Variation of *D* for actinides between 30 vol% TBP and nitric acid.

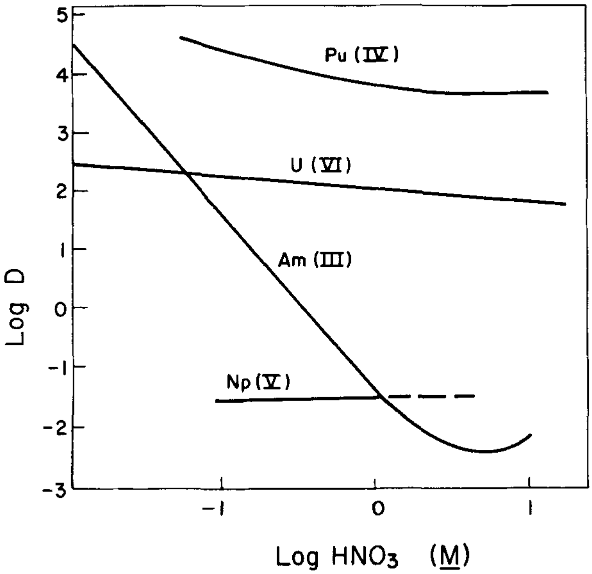

FIG. 4. Dependency of log D for the extraction between 0.5 M HDEHP in isooctane and nitric acid.

In solvent extraction, complexation can be used to enhance or to retard extraction of cations. Trioctylphosphine oxide (TOPO) is a neutral extractant and forms extracted species with the general formula $An^{(n+)}X_n(TOPO)_i$ (where $i = 1$–3). In such a system, formation of the neutral species, AnX_n, in the aqueous phase can be considered as a prerequisite to extraction. Figure 2 shows the extraction dependence of different oxidation states of plutonium on HCl concentration and 0.1 M TOPO in cyclohexane. These data agree with the elution patterns in 6 M HCl from anion resin in which the elution sequence of oxidation states is $V \gg III \gg IV > VI$. In the TOPO extraction, $An^{IV}Cl_4$ and $An^{VI}O_2Cl_2$ are the chloro complexes extracted whereas $An^{IV}Cl_5^-$ and $An^{VI}O_2Cl_3^-$ are the anionic complexes initially sorbed to anion-exchange resin.

Amines—both tertiary and quaternary—which are soluble in organic phases and extract anionic complexes can be used in actinide separations. Such "anionic" extractants provide separations which are very similar to those (in terms of complexing ligand dependence, pH, etc.) obtained with anion-exchange resins.

A widely used neutral extractant is tributylphosphate, TBP. The variation of the extraction coefficient for actinides in the III, IV, and VI oxidation states with nitric acid concentration (*4*) is shown in Fig. 3 ($D = [An]_{org}/$

$[An]_{aq}$). In 4–8 M HNO_3, uranium exists as U(VI), plutonium as Pu(IV), and americium as Am(III), with large differences in D between each element. This difference is the basis of the Purex process for the separation of uranium and plutonium for irradiated nuclear fuel. Following dissolution of the fuel elements, the nitric acid solution (6 M HNO_3) is contacted with a solution of TBP in kerosene into which $UO_2(NO_3)_2(TBP)_2$ and $Pu(NO_3)_4(TBP)_2$ are extracted. The organic solution is contacted with a reducing (Fe^{2+} or U^{4+}) nitric acid solution into which plutonium is stripped as Pu(III). Subsequently, the uranium is stripped (without redox) into a dilute HNO_3 aqueous solution. This Purex process is in universal use for nuclear reprocessing and recovery plants.

Solvent extraction systems utilizing cationic extractants provide excellent separations. Figure 4 shows the variation in extraction coefficient with nitric acid concentration for one such extractant, diethylhexylphosphoric acid (*5*). In general, the value of D decreases with increasing HNO_3 concentration which is consistent with the reaction

$$An(NO_3)_{i(a)}^{+(n-i)} + n(HDEHP)_{2(o)} = An(DEHP)_{2n(o)} + 2nH^+_{(a)} + iNO^-_{3(a)}$$

HDEHP exists as a dimeric species, $(HDEHP)_2$. The possibility of excellent separations is obvious in Fig. 4. Another useful cationic extractant which was developed almost 40 years ago is the beta-diketone, thenoyltrifluoroacetone (TTA). At pH 0, TTA solutions extract Pu(IV) but not Am(III), Np(V), or U(VI). However, at pH 3–4, the III, IV, and VI species are extracted strongly. Figure 5 presents the relation of log D and pH for TTA solutions in xylene (*6*). It was also shown in Ref. *6* that the extraction rate at pH 3–4 differs, with ~100% extraction of U(VI) in 1 min while Th(IV) requires 5 min. Other beta-diketonates, such as dibenzoylmethane (DBM) and 1-phenyl-3-methylpyrazolone-5 (PMBP), are useful extractants. DBM is useful at $pH > 4$ as it is less soluble in water than TTA at neutral and basic pH's. Alternately, PMBP provides better extraction from strongly acidic solutions than does TTA.

Of great interest are the synergistic extraction systems in which a combination of two extracting agents provides greater extraction than predicted from the sum of the individual extraction coefficients. For example, the D for extraction of Am(III) by a 0.10-M solution of DBM in benzene is 0.007 while for a 0.01-M TOPO solution in benzene, D(Am) = 0.3. However, for a solution of 0.10 M DBM + 0.01 M TOPO, D(Am) = 1.0 (*7*). For the TTA + TBP systems, formation in benzene of the combined extraction species $An(TTA)_n(TBP)_m$ (compared to the extraction of $An(TTA)_n$ only) gave increased log D values of 4.7 for Th(IV) and U(VI) and 6.5 for Am(III) (*7*). In cyclohexane this synergistic effect of TTA

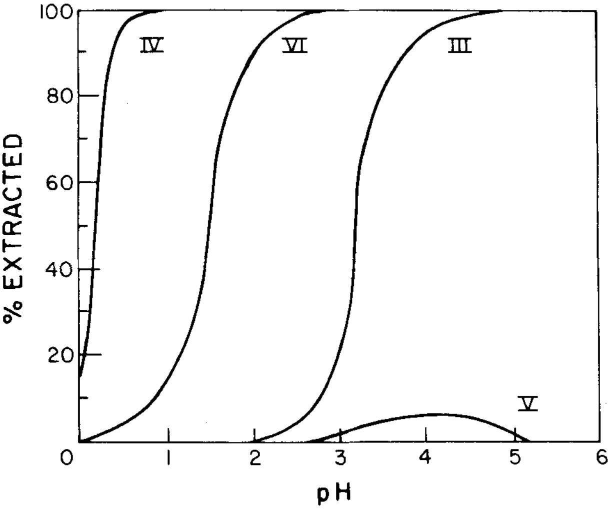

FIG. 5. The percent extracted by 0.5 *M* HTTA in xylene as a function of aqueous phase pH for different oxidation states of the actinides.

+ TBP is even larger; it is also greater for TTA + TOPO than for TTA + TBP. The synergistic enhancement in cyclohexane solutions of TTA + TOPO in log *D* units is 8.9 for Th(IV), 6.5 for U(VI), and 12.0 for Am(III) (*8*).

The synergistic effect is the result of the increased hydrophobic character of the AnT_nS_m species compared to AnT_m. Calorimetric studies (*9*) of the organic (water saturated and anhydrous) phase reaction

$$AnT_n + mS = AnT_nS_m$$

provided equilibrium constants for Nd(III), Th(IV), and U(VI) systems which did not differ greatly from those derived from two phase extraction systems. However, the enthalpies and entropies differed quite significantly between all three systems (extraction, calorimetric of water-saturated, and of anhydrous organic solutions). This was interpreted to reflect the results of the loss of the hydrated waters from the species AnT_n upon addition of the adduct S (TBP or TOPO). Although changes in coordination number, more complete dehydration of the cation, etc. are associated with the synergistic extraction of actinides, the synergistic effect is primarily the result of increased lyophilic character of the synergistic complex in the organic phase.

Interest in the behavior of these actinide elements and, in particular, of plutonium in a variety of natural systems has grown with the need to provide data which can be used in choosing the best method for ultimate disposal of nuclear wastes. A major question in such ecosystems is the speciation of plutonium within its four possible oxidation states. Such speciation depends on the pH, the E_h, the presence of various complexing agents, the concentration of plutonium, biological action, etc. Several procedures have been reported for separating plutonium into its different oxidation states without, hopefully, shifting the redox equilibria during the separation. In general, redox is rather fast between the III and IV states and the V and VI states as simple electron transfer may be involved. However, for reactions such as

$$\mathrm{Pu^{VI}O_2^{2+} + 4H^+ \xrightarrow{+2e} Pu^{4+} + 2H_2O}$$

or

$$\mathrm{Pu^{V}O_2^{+} + 4H^+ \xrightarrow{+e} Pu^{4+} + 2H_2O}$$

the Pu—O bonds of the VI and V species must be broken and the redox reaction rate is often much slower.

This difference in redox rates is utilized in methods in which Pu(III + IV) is removed from solution by precipitation with LaF_3. The Pu(V + VI) is then reduced and removed by a second LaF_3 precipitation. The limitations of this method are overcome in more recent procedures in which Pu(IV + VI) are sorbed from basic solutions onto silicic acid with Pu(V) remaining in solution (*10*). Alternately, Pu(IV + V) can be sorbed on $CaCO_3$ from solutions of pH 9 (Pu(VI) remains in solution in this case). In either method the sorbed plutonium is removed in acid and the different oxidation states separated by LaF_3 precipitation. Another method uses sorption of Pu(V) onto TiO_2 solid at pH 9 following removal of Pu(III + IV) from the solution by precipitation with $BiPO_4$ (*11*).

Oxidation state separations can be achieved simply and rather cleanly with solvent extraction. Np(IV + V + VI) was separated by 40% (v/v) TBP in benzene. From 3 *M* HCl solution, in 5–10 min over 90% extraction of Np(VI) occurred with less than 5% of Np(IV) or Np(V). From 6 *M* HCl, after 5–10 min, 80% Np(IV) and 100% Np(VI) but no Np(V) is extracted (*12*). TTA solutions can be used equally (*6*) since a 0.5-*M* TTA solution in toluene extracts Pu(IV) 100% from a pH 0.6 solution in which Pu(V) and Pu(VI) are retained quantitatively. Adjustment of the pH to 4 with acetate allows extraction of the Pu(VI) completely from the Pu(V) (which remains totally in the aqueous phase). In order to minimize any redox change which might occur prior to separation by increased acidity, a separation scheme for neutral and basic aqueous phases using DBM organic phase solutions has been developed (*13*). Again, quite complete separation of actinides in the III, IV, V, and VI oxidation states is achieved.

TRANSPLUTONIUM ACTINIDES

Although a major characteristic of the chemistry of the transplutonium actinides is the stability in aqueous solution of the trivalent oxidation state, separations of some of the elements can be achieved by use of other states. Americium is recovered and purified in gram quantities by precipitation of $K_5AmO_2(CO_3)_3$ (*14*). It has also been shown that Am and Cm can be separated by oxidation of americium to Am(VI) followed by precipitation of curium as CmF_3 (*15*). Solvent extraction has also been used to separate Am(V) or Am(VI) from trivalent actinides and lanthanides. Methods of separation of berkelium as Bk(IV) have been reported. A recent review discusses the methods of separation of transplutonium elements using nontrivalent oxidation states (*16*).

The sequential elution of the trivalent actinides from a column of cation-exchange resin with a solution of a complexing agent was the major means of chemical identification of elements 97–101 in their discovery experiments. The ion-exchange reaction is

$$An^{3+}_{(a)} + 3NH_4^+R^- = AnR_3 + 3NH^+_{4(a)}$$

which is coupled with the complexing reaction

$$An^{3+}_{(a)} + 4X^-_{(a)} = AnX^-_{4(a)}$$

Although the differences for adjacent actinides (e.g., Cf(III) and Es(III)) are quite small for both reactions, they are sufficient to provide excellent separation since even small columns may have several thousand theoretical plates. The trivalent lanthanides elute in an analogous fashion and an unknown actinide elution position can be predicted from the relative lanthanide positions (Fig. 6). The separation factors of actinides from cation-exchange resin using solutions of ammonium α-hydroxyisobutyrate, of lactate, and of EDTA are compared with those by solvent extraction using HDEHP in Table 1. Improved separations with these cation-exchange systems have been achieved by use of rapid, high pressure elution through

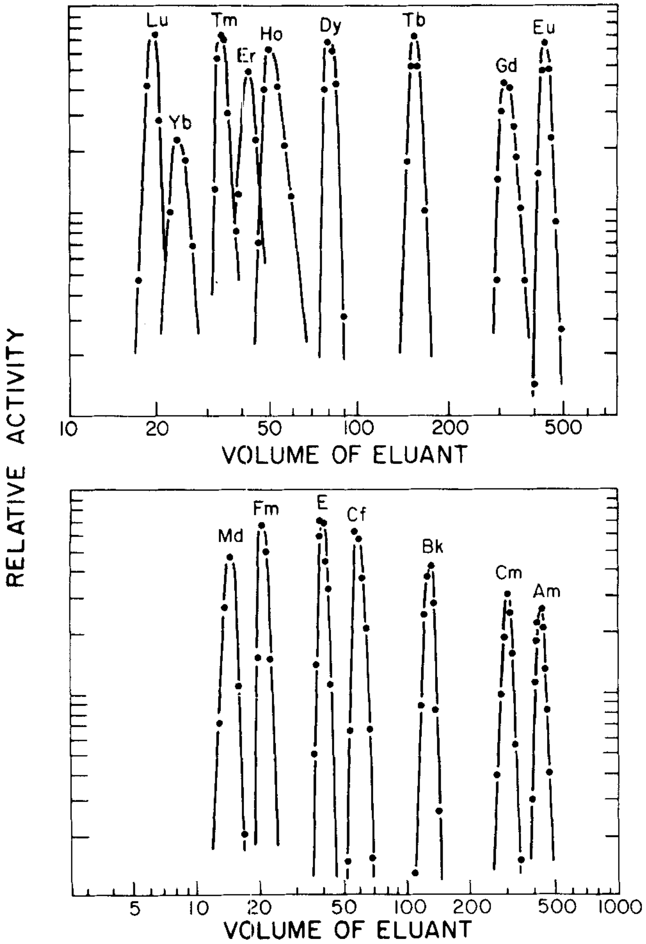

FIG. 6. Elution of tripositive lanthanides and actinides from a column of Dowex-50 cation exchange resin by a solution of ammonium α-hydroxyisobutyrate (*17*).

TABLE I
Separation Factors for Adjacent Trivalent Actinides

Element/ reagent	Lactic acid	α-Hydroxy-isobutyrate	EDTA	HDEHP (HNO_3)
Am/Cm	1.21	1.40	2.0	1.24
Cm/Bk	1.54	1.70	3.1	8.3
Bk/Cf	1.55	2.20	2.0	2.7
Cf/Es	1.25	1.50	—	1.02
Es/Fm	1.45	1.70	—	2.20
Fm/Md	—	1.4	—	4.4

beds of very finely divided resin (*18*). Nitrilotriacetic acid (NTA) and diethylenetriaminepentaacetic acid (DTPA) eluants have been used to purify kilogram amounts of Am(III) and gram amounts of Cm(III) from each other (*19*).

In tracer studies, trivalent lanthanides are often used as inactive carriers for the trivalent actinides (e.g., La(III) to precipitate and carry actinides on LaF_3). Also, in accelerator and reactor irradiations, fission product lanthanides are produced in actinide targets. Consequently, a number of techniques have been developed to separate the trivalent lanthanides and

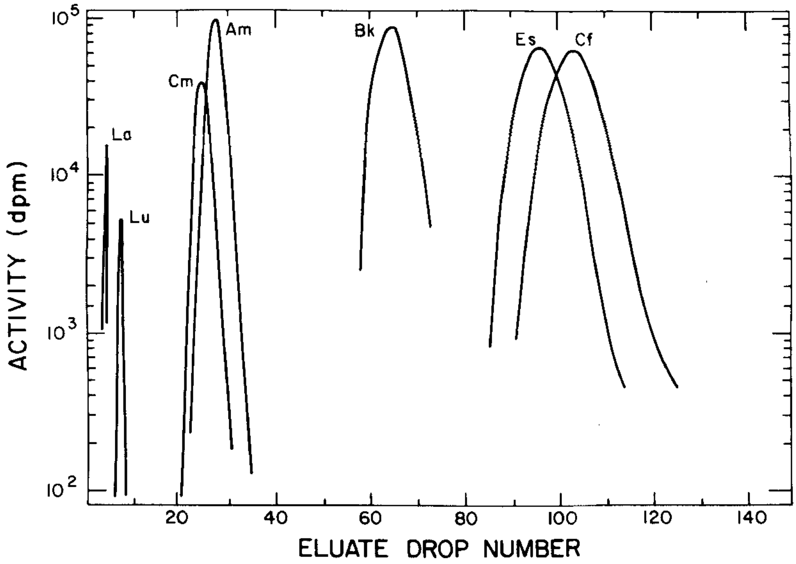

FIG. 7. Separation of lanthanides and tripositive actinides by elution from a column of Dowex-1 anion exchange resin (8% DYB) at 87°C with 9.9 *M* LiCl (0.11 *M* HCl).

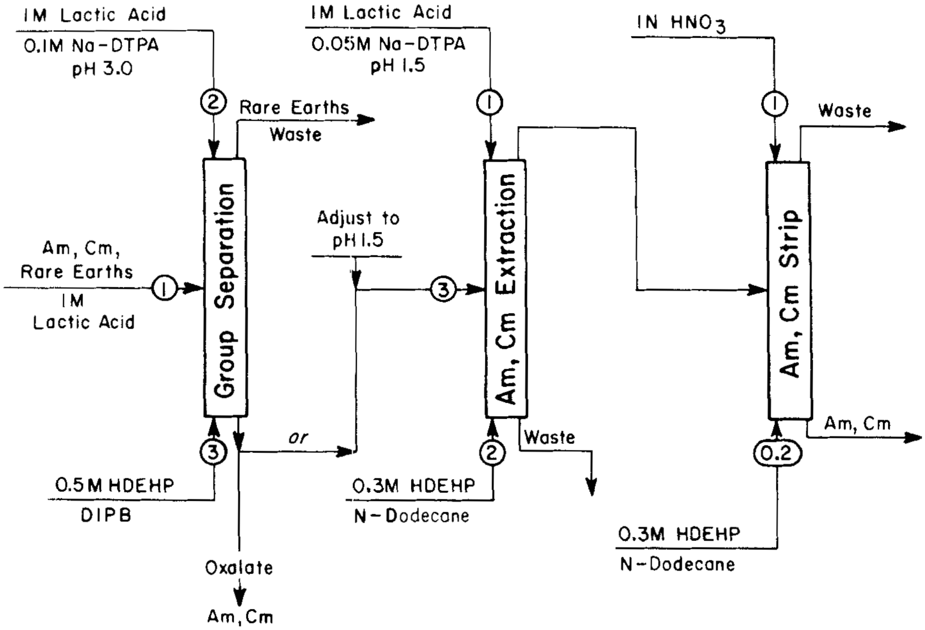

FIG. 8. The Talspeak process for separation of trivalent actinides and lanthanides.

actinides. Separation on a cation-exchange resin column using a 20% ethanol solution saturated with HCl (~12.5 *M* HCl) results in elution of the transplutonium elements within a few column volumes while the lanthanides require more than twice this volume to elute (*20*). This method is convenient for separation of trace level actinides from milligram concentrations of La(III) carrier. Separation on a column of anion-exchange resin using LiCl(HCl) eluant solution also provides excellent Ln-Am separation, as well as some interactinide separation (*21*) as shown in Fig. 7. The separation depends on the differences in the extent of chloride complexation of the actinides and lanthanides, a difference appearing only at high activities of chloride in which MCl_m^{3-m} ($m > 3$) complexes are formed.

Solvent extraction separations of transplutonium elements have been developed for anionic, neutral, and cationic extractants. The differences in complexation between trivalent lanthanides and actinides in concentrated LiCl solution is the basis of the Tramex process for plant-scale separation of the actinides from fission product lanthanides (*22*). A tertiary amine, such as Alamine 336 in kerosene, extracts the actinides from 11 *M* LiCl feed solution. In turn, the actinides are stripped from the organic phase into 8 *M* HCl solution.

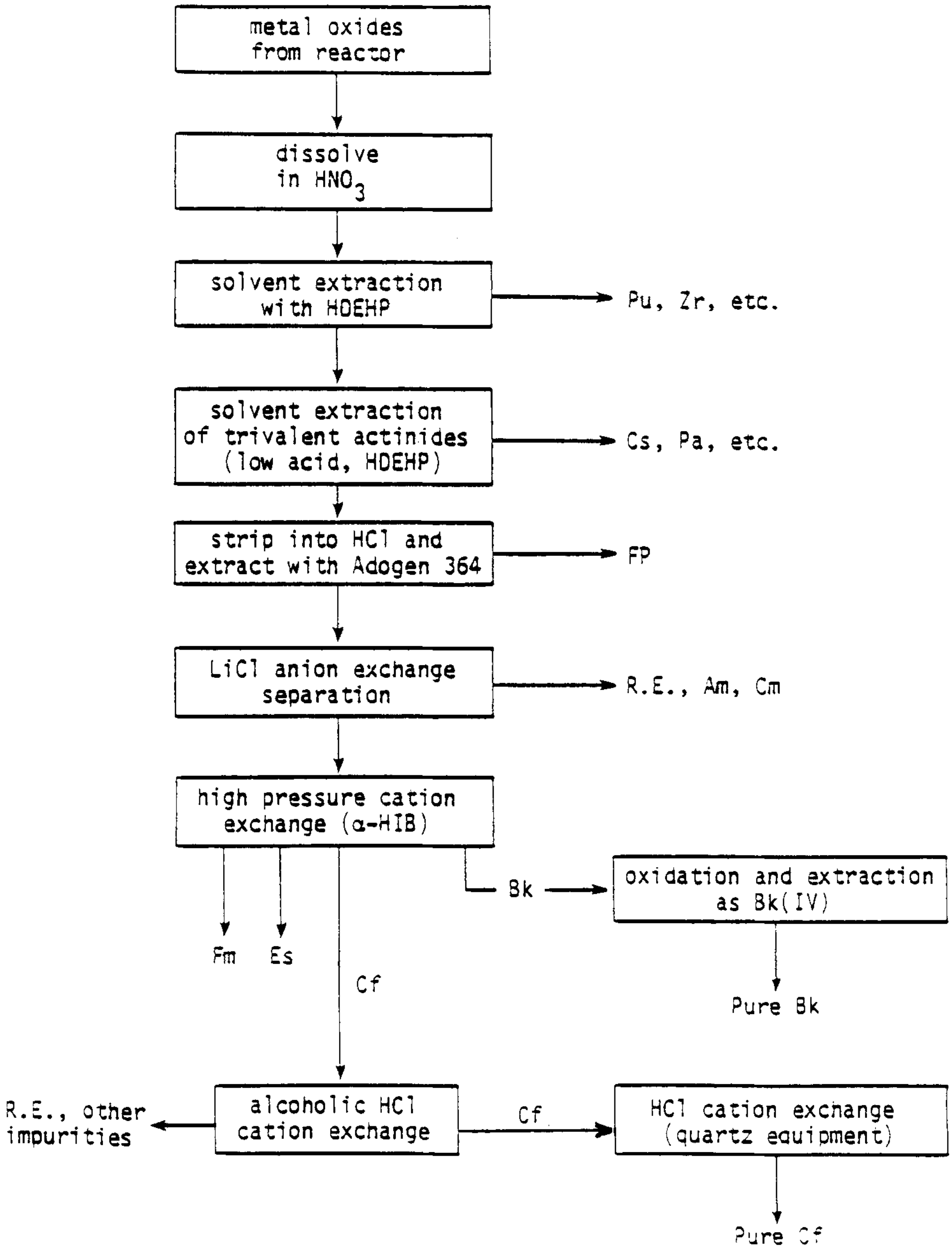

FIG. 9. Flow sheet for separation of the transplutonium actinides following reactor production.

TBP extracts trivalent actinides only weakly from strongly acidic solutions but more strongly from low acid, highly salted nitrate solutions such as 7 *M* $Al(NO_3)_3 + 0.2$ *M* HNO_3. The lanthanides are also strongly extracted from such solutions. However, addition of aminocarboxylic acids (such as DTPA) results in greater complexation of the actinides and the resulting preferential extraction of lanthanides provides a satisfactory separation from the actinides.

Cationic extractants and, in particular, HDEHP have been used in tracer and plant-scale separations of the transplutonium elements. A separation known as the Talspeak process (*23*) for purifying actinides from lanthanides is shown in Fig. 8. Talspeak uses the differential complexation of lanthanides and actinides by DTPA. A solution of lactic acid at pH 3 prevents precipitation of lanthanides (with coprecipitation of actinides) at higher concentrations by formation of lactate complexes. The actinide and lanthanide lactate complexation is not strong enough to prevent extraction of these cations into an HDEHP solution in an organic solvent. The actinides are then stripped from the organic phase by an aqueous solution containing DTPA, with which they form strong complexes.

To illustrate the use in practice of many of the separation techniques discussed in this article, a flow sheet for the separation of Am through Fm is presented in Fig. 9.

A very promising group of reagents for actinide separations by solvent extraction are the carbamoylmethylphosphonates first studied by Siddal (*24*). Since their application is the subject of a separate paper (*25*) in this symposium, they have not been included in the review.

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