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### Separations Chemistry for Actinide Elements: Recent Developments and Historical Perspective

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**SEPARATIONS CHEMISTRY FOR ACTINIDE ELEMENTS:  
RECENT DEVELOPMENTS AND HISTORICAL PERSPECTIVE**

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**ABSTRACT**

With the end of the cold war, the principal mission in actinide separations has changed from production of plutonium to cleanup of the immense volume of moderately radioactive mixed wastes which resulted from fifty years of processing activities. In order to approach the cleanup task from a proper perspective, it is necessary to understand how the wastes were generated. Most of the key separations techniques central to actinide production were developed in the 40's and 50's for the identification and production of actinide elements. Total actinide recovery, lanthanide/actinide separations, and selective partitioning of actinides from inert constituents are currently of primary concern. To respond to the modern world of actinide separations, new techniques are being developed for separations ranging from analytical methods to detect ultra-trace concentrations (for bioassay and environmental monitoring) to large-scale waste treatment procedures. In this report, the history of actinide separations, both the basic science and production aspects, is examined and evaluated in terms of contemporary priorities.

## INTRODUCTION

The transuranium (5f) elements are not naturally occurring. They were produced in the last 50 years as a result of the research of nuclear scientists who predicted how they could be synthesized, and developed the methods to do so as well as to isolate and purify the few atoms made in the discovery experiments. Since their discovery, these elements have been made in amounts which range from tons (Pu) to micrograms (Es) as a part of nuclear power and weapons operations. Some small amounts have been introduced into the environment. Highly specific, rapid separations as well as remote automated procedures continue to be developed to meet the needs in 5f element science and technology.

In this review, we will present a historical background for the development of actinide separation science, summarize the current drivers for continued development of actinide separation processes, and suggest potential new frontiers for continued research in this field. We will not discuss lanthanide separations except as they impact the science and technology of actinide separations.

### Basic Actinide Solution Chemistry

To discuss the separation of actinides, a little consideration of basic actinide solution chemistry is needed. For the elements beyond plutonium, except for nobelium, the trivalent oxidation state is the most stable although Am(V) and Bk(IV) can be utilized in separations in basic systems. As a result, the solution chemistry of the transplutonium elements strongly resembles that of the trivalent lanthanides. For thorium, only the tetravalent oxidation state is important. For U, Np, and Pu, the redox chemistry is varied and different oxidation states are of use in separation schemes. The lower oxidation states (III and IV) exist as hydrated cations in aqueous solutions while the upper oxidation states (V and VI) are linear dioxocations having formal +1 and +2 charges. In general, acidic solutions favor lower oxidation states while basic media promote the stability of the higher states. In actinide processing the most important species are  $U^{4+}$ ,  $UO_2^{2+}$ ,  $Np^{4+}$ ,  $NpO_2^+$ ,  $NpO_2^{2+}$ ,  $Pu^{3+}$ ,  $Pu^{4+}$ , and  $PuO_2^{2+}$ , though the hexavalent oxidation states of Pu and Np are moderately strong oxidants. The middle oxidation states (IV and V) are prone to disproportionation at moderate concentrations in acidic solutions. The multiplicity of readily available oxidation states for these elements is of major significance in their process chemistry.

These ions form weak complexes with halides (except  $F^-$ ) and moderate to strong complexes with oxygen donor ligands like aminopolycarboxylates and polycarboxylic acids. The relative order of complex stability is typically  $An^{4+} > AnO_2^{2+} > An^{3+} > AnO_2^+$ . The relative strength of trivalent and hexavalent complexes is occasionally reversed for complexes of appropriate coordination geometry. The coordination numbers for these ions in solution are variable, reflecting the strongly ionic nature of the bonding: 9-12 for  $An^{4+}$ , 7-9 for  $An^{3+}$ , and 4-6 for  $AnO_2^{+/-2+}$  (axial coordination only). They are strongly hydrated in aqueous solutions and readily hydrolyzed (hydroxides precipitate at pH 1 for  $An^{4+}$ , pH 5 for  $AnO_2^{2+}$ , pH 7 for  $An^{3+}$ , pH 9 for  $AnO_2^+$ ). The actinides exhibit a slightly greater tendency to interact with soft donor atoms (sulfur, chloride, nitrogen) than analogous lanthanides. These chemical characteristics are important in the separation chemistry of these elements.

### The Beginnings of Actinide Separations

Actinide separations had its beginning with the discovery of radioactivity. Crookes and Becquerel found that addition of carbonate to a solution containing uranium caused the formation of a precipitate which contained the  $\beta$ ,  $\gamma$  radioactivity while the uranium remained in the solution phase. Rutherford and Soddy made a similar observation for thorium. Marie and Pierre Curie began a program to separate the components of pitchblende. In 1898 they announced the discovery of the new element polonium, 400 times more radioactive than uranium. The separation method used by these pioneers involved precipitation, which remained the predominant separation technique until the Manhattan Project of World War II.

Between 1934 and 1939, about 50 research papers described the discovery and study of transuranium elements with  $Z=93, 94, 95, 96$ . In 1939, Hahn and Strassman conducted very careful separations on irradiated uranium samples and proved that these "transuranium elements" were, in fact, products of nuclear fission with atomic numbers below 60. This led to new experiments in 1940 in which neptunium ( $Z=93$ ) and plutonium ( $Z=94$ ) were synthesized and isolated. These new elements were isolated using an oxidation-reduction cycle (with  $BrO_3^-$  as the oxidizing agent) followed by precipitation of the reduced metal ions with crystalline  $LaF_3$ .

Within the context of world politics in the 1930's and 1940's, it was perhaps inevitable that the discovery of fission would be first valued for its potential military applications. Two approaches to the assembly of a critical mass were immediately

recognized, isotope enrichment to increase the atom percent of the fissionable uranium isotope  $^{235}\text{U}$ , and transmutation of  $^{238}\text{U}$  by neutron capture and  $\beta$  decay to produce  $^{239}\text{Pu}$ . The former option required a many theoretical plate isotope separation process where the stage-wise efficiency is limited by the small difference in mass of the two principal isotopes. Plutonium production relies on neutron capture (without fission) as the rate limiting step with the different chemistries of uranium and plutonium favoring more efficient separation processes. Both methods were pursued on a large scale as a part of the Manhattan Project.

Plutonium production was accomplished at the Hanford site on the Columbia River near Richland, Washington (1). Plutonium production began with B reactor in September, 1944 and continued through the lifetimes of eight single-pass reactors, N reactor (the only dual-use Hanford reactor which produced both usable steam and Pu), and the Fast Flux Test Facility ending in the early 1980's. The isolation of plutonium from uranium and fission products was initially accomplished by precipitation with  $\text{BiPO}_4$ . The process, pioneered by S. G. Thompson, involves coprecipitation of Pu(IV) by  $\text{BiPO}_4$  followed by oxidation to Pu(VI), which doesn't carry on  $\text{BiPO}_4$ . This batch process is inherently inefficient and has the additional disadvantage of losing uranium to the precipitate. It was soon replaced by solvent extraction processes based on the use of methyl(isobutyl)ketone (REDOX Process) and later tributyl phosphate (PUREX Process). PUREX remains the principal method for processing spent reactor fuel today.

### Isotope Separation

The natural abundances of these isotopes are 0.7%  $^{235}\text{U}$ /99.3%  $^{238}\text{U}$ . The heavy isotope,  $^{238}\text{U}$ , is a fertile material suitable for breeding fissile isotopes like  $^{239}\text{Pu}$  but does not fission with thermal neutrons. On the other hand,  $^{235}\text{U}$  is a fissile material. The concentration of  $^{235}\text{U}$  in natural uranium is too low to sustain a nuclear chain reaction moderated by  $\text{H}_2\text{O}$ . Separation of the isotopes is required to convert natural uranium to either low-enriched (about 3%  $^{235}\text{U}$ , suitable for a sustained chain reaction in a reactor) or high-enriched (>80%  $^{235}\text{U}$ , suitable either for energy generation or nuclear explosives) by several techniques often centered around uranium hexafluoride.  $\text{UF}_6$  is a volatile compound of U(VI), which sublimes at 64°C. It is highly corrosive and reacts with water to produce  $\text{UO}_2\text{F}_2$  (and four equivalents of HF). The most developed methods for isotope separation enrichment of uranium are:

**Gaseous Diffusion:** Gaseous  $\text{UF}_6$  flows through cells divided into two parts by a membrane (10-100 nm pore size) at elevated temperature. The theoretical separation factor for separation of the isotopes is  $1.0043 ((\text{mass}_{238\text{UF}_6}/\text{mass}_{235\text{UF}_6})^{1/2})$ . At this enrichment factor, 3000 stages are required for enrichment to 80%  $^{235}\text{U}$  (from natural abundance). This method is a very energy-consuming process requiring about 3 MWh/kg. As a result of the large number of stages required, gaseous diffusion plants are enormous (2).

**Electromagnetic Separation:** During the Manhattan Project, electromagnetic separation was used to obtain pure  $^{235}\text{U}$ . Operationally equivalent to a mass spectrometer,  $\text{UF}_6$  is isotopically separated in giant electromagnetic separators called *calutrons*. These calutrons have been used since the W.W.II for the preparation of pure isotopes of essentially all elements.

**Gas Centrifuge:**  $\text{UF}_6$  is separated in large centrifuges with a per-stage separation factor of 1.4-2.0 requiring 10 stages for enrichment from 0.7 to 3.0 mole %  $^{235}\text{U}$  (with a 0.2 % tail). This process is less energy intensive than gaseous diffusion, but many centrifuges are needed for large-scale production hence eliminating most of the cost advantage of this method.

**Photoionization Processes:**  $\text{UF}_6$  is irradiated by a laser beam producing selective vibrational excitation in the  $^{235}\text{UF}_6$  molecule. By irradiation with ultraviolet light, the photoexcited  $^{235}\text{UF}_6$  (but not  $^{238}\text{UF}_6$ ) is dissociated forming  $^{235}\text{UF}_{6-x}^{x-}$  which is collected by electromagnetic fields.

**Atomic Vapor Laser Induced Separation (AVLIS):** Electron vaporization of uranium metal accompanied by selective (multiple wavelength) laser excitation of uranium in the vapor phase can be used to selectively separate isotopes of uranium. The vapor phase metal atoms are ionized by the second (or third) laser pulse and attracted to a charged metallic surface. The per-stage efficiency of this process is very good, but the engineering obstacles related to the production and chemical processing of the deposited separated isotopes represent a considerable cost and technological barrier to successful development of a process based on this method.

### The PUREX Process

From the late 40's through the early 80's, plutonium production for nuclear weapons was the principal driver for technology development in actinide separations. The (Plutonium/Uranium Extraction) PUREX process became the standard method

for plutonium production and remains the predominant method in use today. The PUREX process solvent is 1.0-1.4 M tributylphosphate in a kerosene diluent and the aqueous medium is usually nitric acid. The PUREX process solvent extracts plutonium as the complex  $\text{Pu}(\text{NO}_3)_4(\text{TBP})_2$  and uranyl as  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  but does not extract trivalent (Am, Cm) or pentavalent (Np) actinides. Likewise, most fission products or non-radioactive components are not extracted by this solvent. Plutonium is removed from the extractant phase by contact with a nitric acid solution of  $\text{Fe}^{2+}$  or  $\text{U}^{4+}$ , which reduces  $\text{Pu}^{4+}$  to  $\text{Pu}^{3+}$ .  $\text{UO}_2^{2+}$  is subsequently stripped with dilute  $\text{HNO}_3$ . The relative extractability of actinide ions is shown in Figure 1.

### The Transplutonium Elements

Prior to 1940, the transuranium elements were unknown. Following the discovery of neptunium and plutonium in 1940, a major research effort was launched to synthesize and determine the properties of the transplutonium elements. It was not clear at this time whether these new elements represented the 6d-transition series or 5f series, analogous to the lanthanides. Seaborg proposed that these elements represented the 5f series and headed a team that synthesized and characterized the remaining 9 members of the series (which begins with actinium, hence the name actinide) over the period of 1944 - 1961 (Table 1).

The irradiation methods used to produce the new elements are always accompanied by some fission. Most important among fission products from a separations perspective are lanthanides, whose solution chemistry closely resemble that of transplutonium actinides. Identification of the new transplutonium elements therefore required efficient separations methods not only for actinides from actinides but also for actinides from lanthanides. Fortunately, there are two characteristics of the trivalent lanthanides and actinides which can be exploited to affect the necessary separations: 5f actinides interact more strongly with soft-donor ligands like  $\text{Cl}^-$  and  $\text{SCN}^-$ , and cation radii contract across the series. The former characteristic can be used to separate actinides from lanthanides and the latter to separate individual members of the series. Many of the chemical properties of the transplutonium elements were predicted based on those of the corresponding lanthanides.

The development of synthetic ion exchange resins provided the necessary phase-transfer "platform" for accomplishing these separations. Early work by Diamond et al (13) established that in concentrated  $\text{HCl}$  solutions (greater than 6 M),  $\text{Am}^{3+}$  and

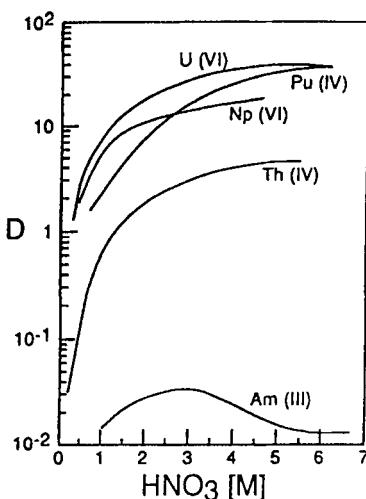


Figure 1. Dependence of the extraction of several actinides as a function of nitric acid concentration into 30% (v/v) tributylphosphate in kerosene ( $D = [An]_o/[An]_a$ ) (2).

Pm<sup>3+</sup> were effectively partitioned on cation exchange resin due to the greater interaction strength of Am with the soft-donor chloride ion (Figure 2). Similar separations were reported for anion exchange separations from 10 M LiCl and 2 M NH<sub>4</sub>SCN solutions. The LiCl anion exchange and solvent extraction processes (TRAMEX) are still in use at the REDC for the production of small quantities of transplutonium elements for research purposes (14).

The separation of individual members of the series was initially accomplished by cation exchange using citrate, lactate, or EDTA as the eluant. Individual lanthanides were also produced by this method. In 1954, a new reagent,  $\alpha$ -hydroxyisobutyric acid, was reported as a superior eluting agent for the cation-exchange-based separation of individual trivalent actinide ions (15, Figure 3). Separation factors for adjacent lanthanide or actinide cations average 1.4. This technique remains in use for separation of individual trivalent transplutonium actinides from each other.

Emphasis in f element separation science shifted in the late 1950's and 1960's to the development of separation processes based on solvent extraction. Among these investigations, arguably the most important was the development of acidic

TABLE 1. TRANSPLUTONIUM ELEMENTS: YEAR OF DISCOVERY,  
INVESTIGATORS, METHOD OF PRODUCTION.

| Element     | Year | Discoverers                                      | Method                                                      |
|-------------|------|--------------------------------------------------|-------------------------------------------------------------|
| Neptunium   | 1940 | Mc Millan, Abelson (3)                           | Cyclotron Bombardment of U with neutrons                    |
| Plutonium   | 1940 | Seaborg, Wahl, Kennedy (4)                       | Cyclotron bombardment of U with $^2\text{H}$                |
| Americium   | 1944 | Ghiorso James, Morgan, Seaborg (5)               | Neutron capture by $^{239}\text{Pu}$ in a reactor           |
| Curium      | 1944 | Seaborg, James, Ghiorso (6)                      | Cyclotron bombardment of $^{239}\text{Pu}$ with $\alpha$    |
| Californium | 1950 | Thompson, Street, Ghiorso, Seaborg (7)           | Cyclotron bombardment of $^{242}\text{Cm}$ with $\alpha$    |
| Berkelium   | 1949 | Thompson, Ghiorso, Seaborg (8)                   | Cyclotron bombardment of $^{241}\text{Am}$ with $\alpha$    |
| Einsteinium | 1952 | Ghiorso et. al. (9)                              | Thermonuclear explosion bomb debris                         |
| Fermium     | 1952 | Ghiorso et. al. (9)                              | Thermonuclear explosion bomb debris                         |
| Mendelevium | 1955 | Ghiorso, Harvey, Choppin, Thompson, Seaborg (10) | Cyclotron bombardment of $^{253}\text{Es}$ with $\alpha$    |
| Nobelium    | 1958 | Ghiorso, Sikkeland, Walton, Seaborg (11)         | HILAC bombardment of $^{244}\text{Cm}$ with $^{12}\text{C}$ |
| Lawrencium  | 1961 | Ghiorso, Sikkeland, Larsh, Latimer (12)          | HILAC bombardment of Cf with $^{10}\text{B}$                |

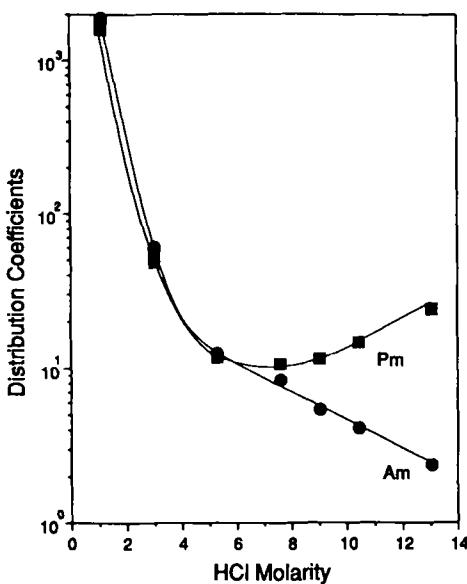
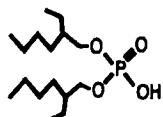


Figure 2. Lanthanide-actinide separation by cation exchange from HCl solutions (13).

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organophosphorus extractants. Phosphoric, phosphonic, and phosphinic acid esters containing at least one ionizable proton were extensively investigated as "liquid cation exchangers" for the separation of a variety of metals, but particularly for lanthanides and trivalent actinides. The premier example of these ligands is bis(2-ethylhexyl)phosphoric acid (HDEHP) (16). In Figure 4 is shown the extraction coefficients for trivalent actinide and lanthanide cations by HDEHP in toluene. The average separation factor for adjacent ions is greater than 2 for both the actinide and



lanthanide series. This reagent is perhaps the most important industrial reagent for lanthanide separations, and is extensively used for this purpose.

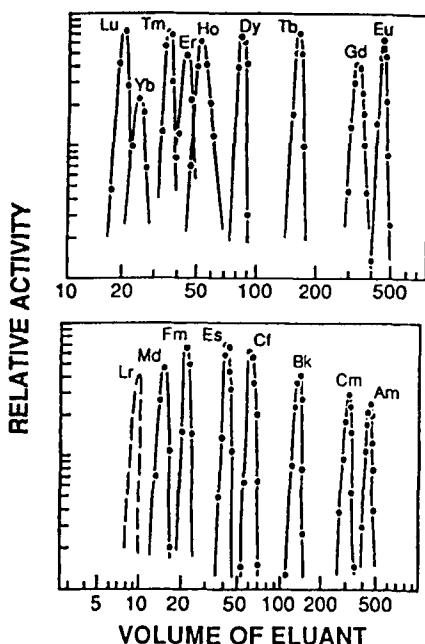


Figure 3. Elution of Ln(III) and An(III) from a column of cation exchange resin by a solution of ammonium  $\alpha$ -hydroxyisobutyrate at pH 4.0 (15).

It is clear from Figure 4 that this extraction system is not useful for the separation of lanthanides from trivalent actinides as the lanthanide and actinide cation radii and their extraction coefficients overlap. However, it does form the phases-transfer basis for a very effective separation of lanthanides from trivalent actinides, the Trivalent Actinide Lanthanide Separation by Phosphorus Extractants and Aqueous Komplexes process (18). In TALSPEAK, the aqueous medium is 1 M lactic acid/0.05 M diethylenetriaminepentaacetic acid (DTPA) at pH 3. The extractant is 0.3 M HDEHP in diisopropyl benzene. The lactic acid serves to promote dehydration of the metal ion, improve kinetics, and act as a coextractant. The DPTA preferentially complexes actinides so that they are retained in the aqueous phase while the lanthanides are extracted. Typical performance of this system is shown in Figure 5. The lanthanide/actinide separation factor is at least 10.

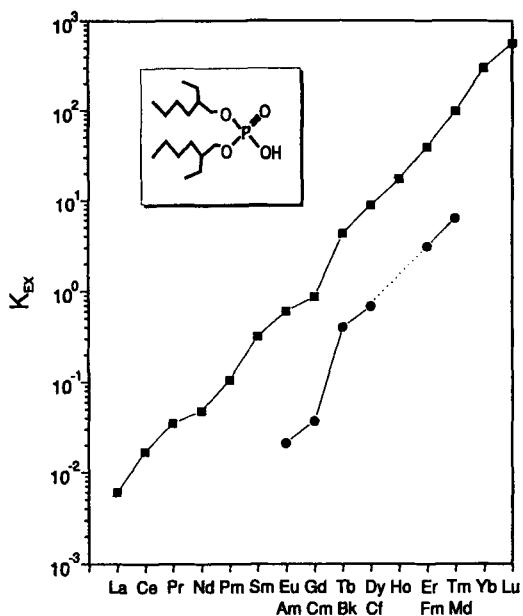


Figure 4. Separation efficiency for trivalent lanthanides and actinides by solvent extraction with bis(2-ethylhexyl)phosphoric acid (shown inset) (17).

#### Actinide Separations: Next Generation

With the end of the Cold War, the demand for actinide production for weapons has disappeared. Only those nations actively pursuing fuel reprocessing have active research programs investigating new methods for plutonium production. What remains to those nations not engaged in processing are the tasks of preventing actinide proliferation, waste stabilization and cleanup, environmental monitoring and restoration, and a continuing need for efficient bioassay techniques. The current generation of actinide separation processes address these new priorities.

With declining demand for plutonium production, actinide process chemistry has shifted focus to waste processing and minimization. The industry standard PUREX process suffers from the limitation (previously an advantage) that it is not an effective method for extraction of trivalent actinides (Am and Cm). However, PUREX is a

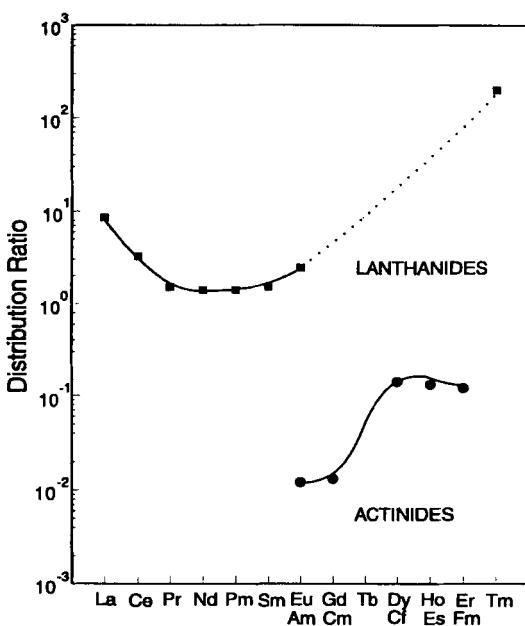


Figure 5. Trivalent Actinide Lanthanide Separation by Phosphorus Extractants and Aqueous Komplexes (TALSPEAK) process (18).

comfortable technology. The challenge of the early 80's was to devise a solvent extraction-based process for total actinide recovery which was fully compatible with PUREX technology.

To extract trivalent actinides within a PUREX-style process, Horwitz et al (19) (based on earlier work by Siddall (20, 21)) developed the new extractant octyl(phenyl)-N,N-diisobutyl-carbamoylmethylphosphine oxide (CMPO) and a new process (TRUEX) which uses this extractant. The TRUEX process solvent consists of a standard PUREX process solvent with CMPO added for trivalent actinide extraction. A typical process solvent formulation would be 0.2 M CMPO, 1.2 M TBP in kerosene diluent. Extraction efficiency for actinides in the tri-, tetra-, and hexavalent oxidation states from nitric acid solutions is shown in Figure 6. All ions are more strongly extracted than they are by PUREX solvent (Figure 1). Extraction of  $\text{Am}^{3+}$  and  $\text{Pu}^{4+}$  is readily reversible by changes in  $[\text{HNO}_3]$  while  $\text{UO}_2^{2+}$  must be

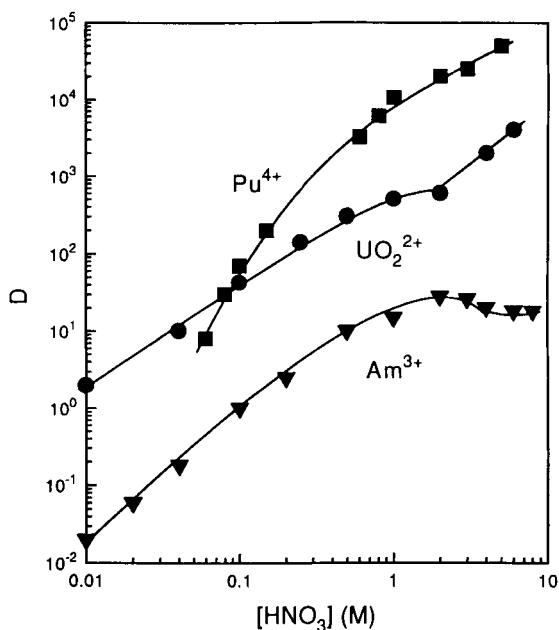


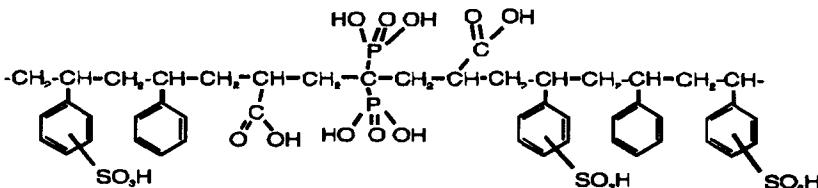
Figure 6. Dependence of the extraction of  $\text{Am}^{3+}$ ,  $\text{Pu}^{4+}$ , and  $\text{UO}_2^{2+}$  as a function of nitric acid concentration into TRUEX Process Solvent (0.2 M octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide (CMPO) and 1.2 M TBP in kerosene diluent (19).

stripped from the extractant phase using an aqueous complexant, typically oxalate or carbonate.

For certain applications, ion exchange methods are preferable to solvent extraction. Conventional cation and anion exchange resins have been extensively investigated for actinide sequestration, and many varieties of cationic, anionic and chelating resins are available. The development of pyridine-based anion exchange resins (Reilly Industries, Indianapolis) represents an important addition to the arsenal of ion exchange separations materials (22). Inorganic ion exchangers (zeolites) were used for some of the earliest ion exchange separations of f elements and are getting increasing scrutiny today. Recent work by Clearfield (23) has addressed the use of sodium titanate and pillared zirconium phosphate/phosphonate materials, but

interlanthanide separation factors are small for these ion exchangers. Actinide uptake has not been reported for these materials.

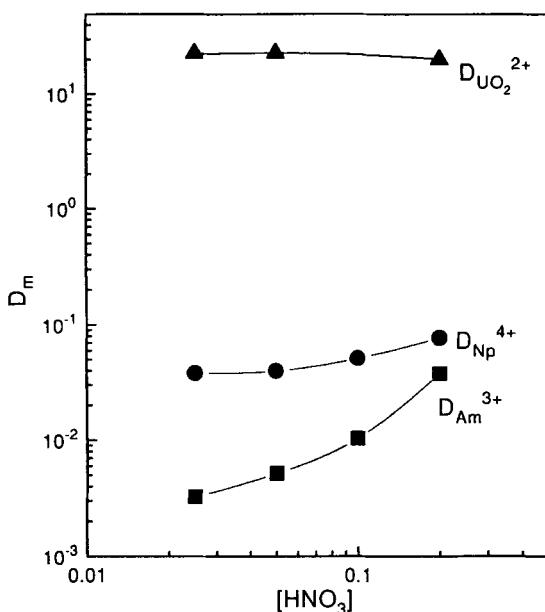
A new chelating ion exchange resin which combines good kinetics with the increased power of diphosphonate chelating groups provides additional options for actinide sequestration by cation exchange. Diphonix resin, which combines methylenediphosphonate, carboxylate, and sulfonate binding groups in a cross-linked



polystyrene resin base displays strong affinity for f-elements in all oxidation states (24), even in the presence of moderate concentrations of complexing anions and in concentrated acid. A representative monomer unit of Diphonix is shown below. This resin offers the possibility of total actinide removal from acidic, aqueous media. Diphonix has been demonstrated for this purpose in a mixed-waste treatment facility at ANL.

While extractants and solid resins are clearly necessary for effective separations, aqueous complexants are often critical to successful schemes, as illustrated by the LiCl anion exchange separation of Ln/An(III) and TALSPEAK. Besides these specific examples, aqueous complexants are typically used in actinide processing as hold-back or stripping reagents or for the decontamination of process equipment. A series of complexants based on methane diphosphonic acid ( $\text{CH}_2(\text{PO}_3\text{H}_2)_2$ ) have been prepared and characterized as complexants for f elements (at Argonne National Laboratory). Numerous applications have been suggested for their use in processing of actinides, including one oxidation state-specific separation based on TRUEX chemistry (25).

The polycarboxylic acid ligand tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) has been demonstrated as a highly specific stripping agent for trivalent and tetravalent actinides when used in a TRUEX-like process (26). Uranyl ion is selectively extracted by CMPO from this aqueous medium while  $\text{Am}^{3+}$  and  $\text{Pu}^{4+}$  preferentially distribute to the aqueous phase (Figure 7). This behavior is partially explained by the uncharacteristically weak interaction of uranyl with THFTCA in the aqueous phase (complexes are 100 times weaker than the corresponding europium



**Figure 7.** Extraction of Am<sup>3+</sup>, Np<sup>4+</sup>, and UO<sub>2</sub><sup>2+</sup> as a function of nitric acid concentration from an aqueous solution containing 0.5 M tetrahydrofuran-2,3,4,5-tetracarboxylic acid (THFTCA) into a Combined Process Solvent (0.2 M CMPO, 0.2 M 4,4'-(5')di(t-butylcyclohexano)-18-crown-6 (DtBCH18C6), and 1.2 M diamyl(amyI)-phosphonate DA(A)P in Isopar L) (26).

complexes). On the other hand, NMR spectroscopic data suggest a strong interaction between uranyl and THFTCA in the TRUEX phase, perhaps taking the form of an extensively organized polymeric complex. The segregation of U from TRU's has important implications for the reduction of the volume of wastes in a high-level repository.

Development and validation of thermodynamic models for actinide behavior in nature require accurate information on oxidation state distribution of the actinides in natural samples. A major difficulty in the determination of (for example) plutonium oxidation states in groundwater samples is the relative ease of interconversion among the oxidation states. Because of the typically very low concentrations involved (often less than 10<sup>-8</sup> M), conventional spectrophotometric techniques are not generally

applicable. Separations chemistry and radiometric analysis are the most appropriate techniques. The key objective is to determine the oxidation state using procedures which do not alter the oxidation state of the metal during the measurement. Several complementary separations methods can (and should) be applied to insure accuracy. Some examples of actinide oxidation state speciation methods based on sorption or solvent extraction are:

$\text{LaF}_3$  coprecipitation in which a lanthanide fluoride carries An(III) and An(IV) without An(V) or An(VI). Care must be used in application of this technique, as excess fluoride can promote reduction during the precipitation process (27).

Silica gel ( $\text{SiO}_2$ ) selectively sorbs An(IV) and An(VI) from basic media leaving An(V) in solution (28).

$\text{CaCO}_3$  selective sorbs An(V) and An(IV) leaving An(VI) in solution as the tris carbonato complex (29).

Thenoyltrifluoroacetone (TTA, 0.5 M in xylene) selectively extracts An(IV) from 0.25 M acid. The same extractant can then be used to extract An(VI) from acetate buffer at pH 4 (30).

Dibenzoylmethane (DBM, 0.2 M in xylene) selectively extracts An(IV) at pH < 2.5, An(VI) at pH 5, An(III) at pH 7. An(V) is not extracted (31).

Quantitative analysis of actinide concentrations in environmental or bioassay samples by standard methods require extensive treatment to promote the release of the radionuclides from the complex matrix. Analyses of such samples have required up to 24 hours processing time. Standard ion exchange and solvent extraction analytical methods have been used for these analyses. The recent development of more selective extraction chromatographic materials and the development of procedures for their use have greatly shortened the time required for these analyses (32). These extraction chromatographic materials are based on well-known solvent extraction methods, as follows:

TRU<sup>TM</sup> resin for selective sorption of An(III), An(IV), An(VI), Ln(III). The extractant is 0.75 CMPO in TBP

TEVA<sup>TM</sup> resin for sorption of An(IV). The extractant is  $(\text{C}_{10}\text{H}_{21})_2(\text{C}_8\text{H}_{17})(\text{CH}_3)\text{N}^+$  (Aliquat 336, neat).

U/Teva<sup>TM</sup> resin for sorption of U(VI), An(IV). The extractant is  $(\text{C}_5\text{H}_{11}\text{O})_2(\text{C}_5\text{H}_{11})\text{P}=\text{O}$  (DP[PP], neat).

An example of an element-specific separation scheme of actinides using TRU<sup>TM</sup> resin is as follows:

load sample from 2 M HNO<sub>3</sub>, rinse off non-TRU's with 1.0 M HNO<sub>3</sub> then 9 M HCl,

elute Am<sup>3+</sup> with 4 M HCl,  
elute Pu<sup>4+</sup> with 4 M HCl/0.1 M Hydroquinone,  
elute Th<sup>4+</sup> with 2 M HCl,  
elute Np<sup>4+</sup> with 1 M HCl/0.03 M oxalate,  
elute UO<sub>2</sub><sup>2+</sup> with 0.1 M NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub>,  
analyze fractions radiometrically.

### Future Directions in Actinide Separations

Actinide separations for plutonium processing (in connection with either weapons production or as a part of a breeder reactor program) involves primarily solvent extraction processes operating on acidic aqueous solutions. As a consequence of 50 years of both research and process experience, this technology must be considered mature, and has proven to be reliable though its application has generated complex wastes. Partly as a result of this maturity, but also due to changes in world politics, acid processing to recover actinides is no longer the principal driving force for development in actinide separations. The challenges attendant to the present status of actinide separations are determined by the current emphasis on waste cleanup and environment restoration. The current issues in actinide separations are defined by the physical and chemical state of actinides in the terrestrial environment:

1) Alkaline wastes in underground storage tanks;

The legacy of 50 years of plutonium production is a large volume of mixed wastes (containing TRU's, long-lived fission products, and non-radioactive but chemically hazardous materials) (33). These wastes take the form of sludges, solids, alkaline or acidic solutions, and slurry phases in which actinides coexist with long-lived fission products and non-radioactive constituents. In the face of this complexity, how can the volume of waste going to a repository be minimized? Two potentially important areas for development are: sludge washing procedures which selectively remove actinides from the solids or sludges (solid-liquid separation), and separation procedures suitable for plant-scale development which can operate in alkaline media.

2) Actinide burnup strategies;

A "permanent" remedy to the long-term hazard of actinides is to "incinerate" them in advanced reactors or accelerators and thus transform them into short-lived fission products. An added advantage of this approach is the potential for recovery of the

heat value of the actinides. Because lanthanides have high cross sections for neutron capture and thus interfere with the neutron physics of actinide burnup, robust Ln/An separation methods are demanded, in particular, processes resistant to radiolysis effects. Two areas of actinide separations research relevant to this problem are the continued development of the Integral Fast Reactor concept which includes a pyro-electrochemical separation process, and the development of new soft-donor extractants and aqueous complexants for actinide/lanthanide separations.

### 3) Actinides in the environment:

Minor concentrations of actinides are present in the terrestrial environment as a result of atmospheric weapons testing, the Chernobyl accident, and actinide production activities (including both planned and accidental releases). Accurate speciation techniques, environment decontamination methods, and in-situ immobilization techniques are needed. Three generic areas for research, all of which involve some form of separation science, are pertinent to this subject: the development of reliable speciation techniques and thermodynamic models, solid-solution separation methods for removal of actinides from soils, contaminated process equipment, etc., and solution-mineral conversion techniques to fix residual actinides in-situ and prohibit their entry into the hydrosphere/biosphere..

Outside of those countries pursuing a closed-loop fuel cycle (based on plutonium recycle), the principal drivers for continued development of actinide separations are the need to secure those supplies of plutonium susceptible to diversion, and environment cleanup/restoration/waste disposal. The major change in emphasis does not mean the end of the need for actinide separations, it indicates a shift toward new horizons. Many opportunities exist for improvements in existing procedures or the development of new methods for actinide isolation.

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### REFERENCES

1. M. S. Gerber, *Legend and Legacy: Fifty Years of Defense Production at the Hanford Site* Westinghouse Hanford Report WHC-MR-0293.

2. G. R. Choppin and J. Rydberg, *Nuclear Chemistry: Theory and Applications* Pergamon Press, Oxford, England, (1980) pp. 22-33.
3. E. M. McMillan and P. A. Abelson, *Phys. Rev.* **57**, 1185 (1940).
4. G. T. Seaborg, A. C. Wahl and J. W. Kennedy, *Phys. Rev.* **69**, 367 (1946).
5. A. Ghiorso, R. A. James, L. O. Morgan and G. T. Seaborg, *Phys. Rev.* **78**, 472 (1950).
6. G. T. Seaborg, *Chem. Eng. News* **23**, 2190 (1945).
7. S. G. Thompson, K. Street, Jr., A. Ghiorso and G. T. Seaborg, *Phys. Rev.* **78**, 472 (1950).
8. S. G. Thompson, A. Ghiorso and G. T. Seaborg, *Phys. Rev.* **78**, 298 (1950).
9. A. Ghiorso, S. G. Thompson, G. H. Higgins, G. T. Seaborg, M. H. Studier, P. R. Fields, S. M. Fried, H. Diamond, J. F. Mech, G. L. Pyle, J. R. Huizenga, A. Hirsch, W. M. Manning, C. I. Brown, H. L. Smith and R. W. Spence, *Phys Rev* **99**, 1048 (1955).
10. A. Ghiorso, B. G. Harvey, G. R. Choppin, S. G. Thompson and G. T. Seaborg, *Phys Rev* **98**, 1518 (1955).
11. A. Ghiorso, T. Sikkeland, J. R. Walton and G. T. Seaborg, *Phys Rev Lett.* **1**, 18 (1958).
12. A. Ghiorso, T. Sikkeland, A. E. Larsh and R. M. Latimer, *Phys Rev Lett.* **6**, 473 (1961).
13. R. M. Diamond, K. Street, Jr. and G. T. Seaborg, *J. Am. Chem. Soc.* **76**, 1461 (1954).
14. K. L. Nash, *Solv. Extr. Ion Exch.* **11**, 729 (1993).
15. G. R. Choppin and R. J. Silva, *J. Inorg. Nucl. Chem.* **3**, 153 (1956).
16. D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).
17. J. Stary, *Talanta* **13**, 421 (1966).
18. B. Weaver and F. A. Kappelmann, *J. Inorg. Nucl. Chem.* **30**, 263 (1968).
19. W. W. Schulz and E. P. Horwitz, *Sep. Sci. Technol.* **23**, 1191 (1988).
20. T. H. Siddall, III, *J. Inorg. Nucl. Chem.* **25**, 883 (1963).
21. T. H. Siddall, III, *J. Inorg. Nucl. Chem.* **26**, 1991 (1964).
22. K. D. Abney, A. B. Pinkerton, R. C. Staroski, N. C. Schroeder, K. R. Ashley, J. M. Adams and J. R. Ball, "Sorption Behavior of Uranium onto Reillex™-HPQ Anion Exchange Resin from Nitric and Hydrochloric Acid Solutions" in *Separations of Elements* (K. L. Nash, G. R. Choppin, Eds.) Plenum Press, New York (1995) pp. 209-223.

23. A. Clearfield, R. A. Cahill, S. B. Wright, P. C. Bellinghausen and B. Shpeizer, "Use of Selective Inorganic Ion Exchangers for Separation of Rare Earths" in *Separations of Elements* (K. L. Nash, G. R. Choppin, Eds.) Plenum Press, New York (1995) pp. 165-176.
24. Chiarizia, E. P. Horwitz and S. D. Alexandratos, Solvent Extr. Ion Exch. 12, 211 (1994).
25. K. L. Nash and P. G. Rickert, Separation Science and Technology 28, 25 (1993).
26. K. L. Nash, E. P. Horwitz, H. Diamond, P. G. Rickert, J. V. Muntean, M. D. Mendoza and G. di Giuseppe, Solv. Extr. Ion Exch. 14, 13 (1996).
27. G. R. Choppin and K. L. Nash, "Actinide Separation Science" Submitted for publication in *Radiochim. Acta* (1996).
28. Y. Inoue and O. Tochiyama, J. Inorg. Nucl. Chem. 39, 1443 (1977)..
29. A. Kobashi and G. R. Choppin, J. W. Morse, *Radiochim. Acta* 43, 211 (1988).
30. P. A. Bertrand and G. R. Choppin, *Radiochim. Acta* 31, 135 (1982).
31. A. Saito and G. R. Choppin, *Anal. Chem.* 55, 2454 (1983).
32. E. P. Horwitz, M. L. Dietz, R. Chiarizia, H. Diamond, S. L. Maxwell, III and D. R. Nelson, *Anal. Chim. Acta* 310, 63 (1995).
33. J. T. Bell and L. H. Bell, "Separations Technology: The Key to Radioactive Waste Minimization", in *Chemical Pretreatment of Nuclear Waste for Disposal* (W. W. Schulz and E. P. Horwitz, eds.) Plenum, New York (1994), pp. 1-15.