

ORGANOPHOSPHORUS REAGENTS IN ACTINIDE SEPARATIONS:
UNIQUE TOOLS FOR PRODUCTION, CLEANUP AND DISPOSAL

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ABSTRACT

Interactions of actinide ions with phosphate and organophosphorus reagents have figured prominently in nuclear science and technology, particularly in the hydrometallurgical processing of irradiated nuclear fuel. Actinide interactions with phosphorus-containing species impact all aspects from the stability of naturally occurring actinides in phosphate mineral phases through the application of the bismuth phosphate and PUREX processes for large-scale production of transuranic elements to the development of analytical separation and environment restoration processes based on new organophosphorus reagents. In this report, an overview of the unique role of organophosphorus compounds in actinide production, disposal, and environment restoration is presented. The broad utility of these reagents and their unique chemical properties is emphasized.

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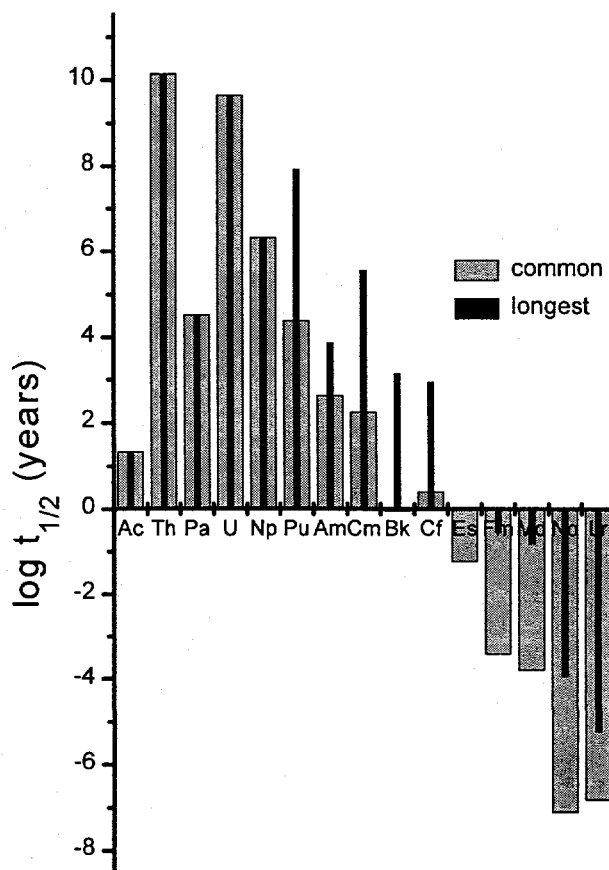
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Introduction

Prior to 1939, the transuranium actinides were unknown, though a substantial amount of research had been conducted to attempt the synthesis of elements heavier than uranium. Between 1939 and 1962, all members of the series were synthesized, fulfilling the alchemists dream of the transmutation of elements. At the end of the millennium, some actinides are quite well-known to the general public and in some cases have come to be considered at least a problem and possibly a curse. Though actinide production for defense purposes helped to preserve an often uneasy peace between 1946 and the present, an enormous legacy of environmental cleanup problems are a byproduct of this age. However, during that same period, the peaceful application of nuclear energy for electricity production has prevented the addition of billions of tons of CO₂ to the earth's atmosphere. Given the large uncertainty of the potential impact of global warming on human existence, it appears likely that the stigma presently worn by nuclear technology must fade in the coming decades. Before this sea-change can occur, reduction of the real and perceived risks associated with nuclear technology must be accomplished. Environmental cleanup and demonstration of safe waste disposal methods are essential for this shift in public perception to occur.

All of the actinide elements are radioactive, with half-lives of the most stable isotopes decreasing across the series (Figure 1). Only thorium and uranium have half-lives long enough to have persisted since the big bang. However, very low concentrations of naturally-occurring plutonium can be found in uranium ores as a result of the spontaneous fission of uranium and neutron capture by ²³⁸U. The heaviest members of the series are so unstable they can only be created a few atoms at a time (and so must be detected on the fly). Over the past 50 years, plutonium production for nuclear weapons has generated more than 100 metric tons in the U.S. and at least a similar amount in Russia of purified plutonium for weapons purposes. The plutonium produced in power reactors amounts to perhaps as much as 7000 metric tons worldwide, most of which is dilute and contained in spent reactor fuel. (1)

Figure 1. Half-lives of the most abundant and longest-lived actinide isotopes.



Chemically, the actinides are strongly acidic metal ions that are readily hydrolyzed and form strong complexes with common chelating agents. The actinides between U and Am have a moderately diverse redox chemistry which is utilized in their chemical separation from reactor fuels. The transplutonium actinides have a less diverse redox chemistry and behave quite similarly to the

trivalent lanthanides. This factor is important in their separations chemistry, as will be explained below. One of the most abundant naturally-occurring ores of the lanthanides (and thorium) is the simple stoichiometric phosphate, monazite ($\text{Ln}(\text{Ca,Th})\text{PO}_4$). Uranium is readily oxidized to the hexavalent state and is stabilized in the terrestrial environment principally as oxides or vanadates, but uranium phosphate mineral phases are also known.

Phosphate and organophosphorus complexing agents have figured prominently in the industrial scale production of transuranium elements and, to a lesser degree, in their discovery and development of an understanding of their chemical properties. Though phosphate in defense wastes is incompatible with industry-standard high-level waste glass formulations and so is considered a problem in cleanup of the weapons complex and in high-level waste disposal, both inorganic phosphate and organophosphorus compounds may have a unique role to play in both the cleanup of contaminated environments and in the development of safe materials for their geological disposal. The purpose of this report is to summarize some of the most important research results and technological applications of this important class of reagents in actinide science, and to illustrate the means by which these species could help in preserving this important energy production option in the next millennium.

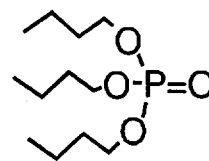
Actinide Discovery and Separations

The discovery of the actinides began with the irradiation of natural uranium to produce first neptunium (1939) and subsequently plutonium (1940). The scientific and technological significance of the latter event was anticipated and led directly to the establishment of the Manhattan Project that produced the world's first nuclear weapons. Because actinide production is always accompanied by some fission, chemical separations processes to isolate the newly synthesized actinides from the matrix that included fission products and uranium were central to this effort.

To satisfy the anticipated demand for an industrial-scale separation process for plutonium produced in uranium-fission reactors, more efficient separation processes than the ether extraction/lanthanum fluoride precipitation methods were needed. Glenn Seaborg and his research team were assigned the task of identifying a separation process suitable for plutonium production.(2) This research culminated with the development by Stan Thompson of a co-precipitation method based on bismuth phosphate. Bismuth phosphate was observed to carry reduced Pu with about 98% efficiency, thus separating it from the uranium and most fission products. The crystalline precipitate was readily redissolved in HCl and the plutonium oxidized to the hexavalent state, which does not carry on BiPO_4 . A combination of several stages of oxidation state adjustments and precipitation procedures were used to accomplish the final purification of Pu.

The BiPO_4 process proved suitable for the rapid production of pure Pu demanded by the Manhattan project, but suffered the defect of losing the valuable purified uranium to the process waste stream. The development of solvent extraction processes, first the Redox process and subsequently the Purex process overcame this limitation and simultaneously resulted in a dramatic increase in the throughput of the plutonium production process. The Redox process is based on the extraction of uranium and plutonium nitrates from $\text{Al}(\text{NO}_3)_3$ with methyl(isobutyl)ketone (MIBK). Purex substitutes tributylphosphate (TBP, Figure 2) in a kerosene diluent for MIBK. The stronger extracting power of TBP eliminates the need for the salting-out effect of $\text{Al}(\text{NO}_3)_3$ allowing extraction from HNO_3 and resulting in a significantly cleaner

Figure 2. Tributyl Phosphate



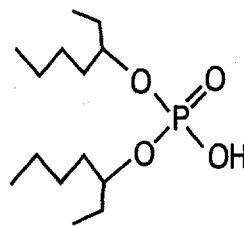
process. TBP extracts both hexavalent uranium and tetravalent plutonium away from the fission products, the transplutonium actinides and most of the neptunium. Plutonium is recovered from this solution by reduction to the trivalent state, leaving the excess uranium in the extractant phase for subsequent recovery and recycle. The latter feature both allows reuse of the uranium and simultaneously reduces the volume of high level wastes created. Though not without problems, the Purex process remains today the industry standard for efficient plutonium production and uranium recycle.

The chemistry of the actinide elements heavier than americium is dramatically different from the light members of the series. For the trans-amerium actinides, the trivalent oxidation state predominates. In fact, though americium can be oxidized in production-suitable solutions to the pentavalent or hexavalent oxidation states, the trivalent species Am^{3+} dominates its chemistry. Nucleosynthesis for actinide discovery relied substantially on cation exchange from lactic or citric acid solutions for the identification of these species. Because of the declining lifetimes of the isotopes, production and detection became increasingly difficult as the atomic number increases. To confirm the discovery of mendelevium, for which individual atoms were detected, another standard technique, the α -hydroxyisobutyric acid (HIBA) cation exchange procedure was developed.(3) This process produced the most consistent separation of individual members of the lanthanide and transplutonium actinides, having separation factors (ratios of distribution coefficients of adjacent ions) averaging about 1.5. The separation of individual members of the trivalent actinide and lanthanide series occur more-or-less in parallel.

In Purex process chemistry, dibutylphosphoric acid (HDBP) was produced as a result of the hydrolytic and radiolytic decomposition TBP. This lipophilic acidic molecule was capable of extracting metal ions without the need for transferring nitrate ions to the organic phase. This species unfortunately interfered with the stripping stage of the Purex process and so process operation was modified to clean up the Purex process solvent by doing an alkaline scrub to remove DBP as a water-soluble sodium salt. Research into the extraction properties of HDBP led to the development of a series of acidic extractants that were more stable esters of phosphoric, phosphonic, and phosphinic acids. The technologically most important of these species is bis(2-ethylhexyl) phosphoric acid (HDEHP, Figure 3). The work of

Peppard and Mason (4) examined the separation of adjacent lanthanide and trivalent actinide ions by HDEHP in solvent extraction. The comparative separation factors for trivalent lanthanide and actinide ions by HIBA cation exchange and HDEHP

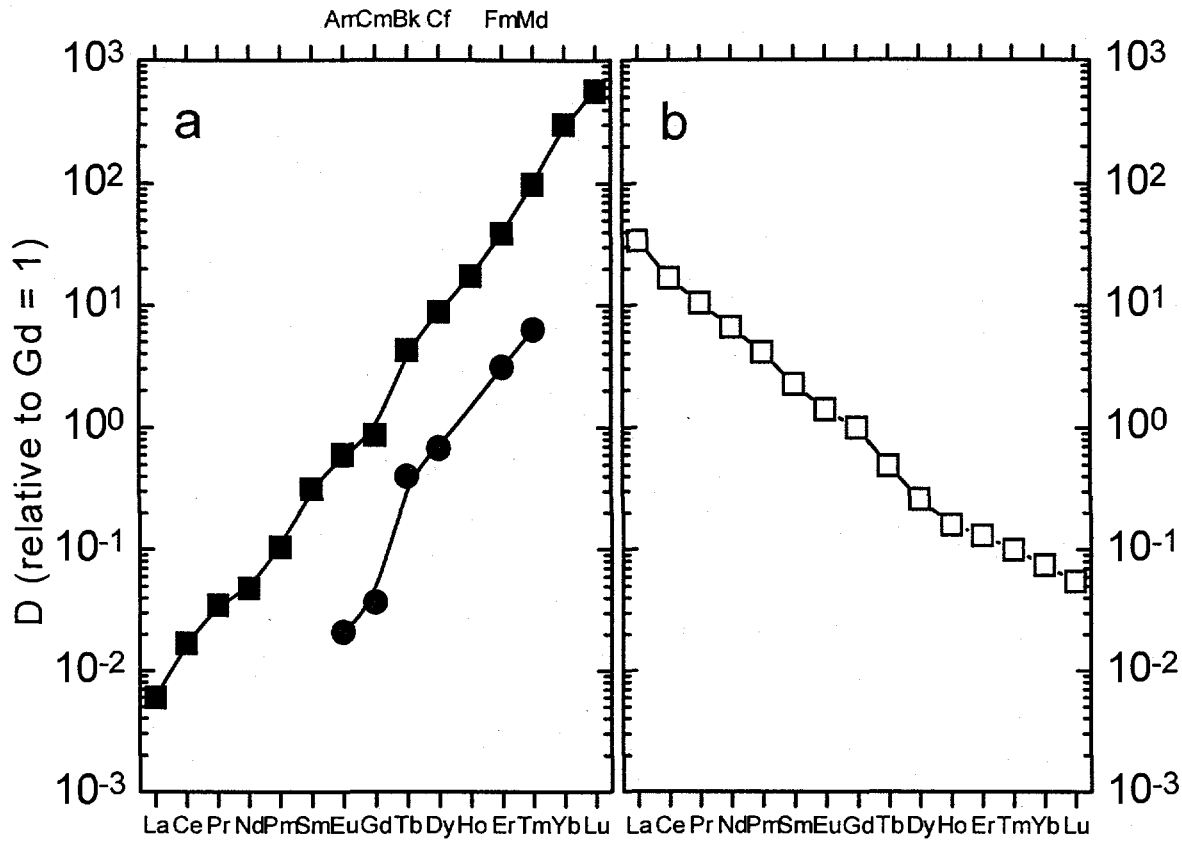
Figure 3. bis(2-ethylhexyl)phosphoric acid (HDEHP)



solvent extraction separations are shown in Figure 4. Separation factors for adjacent lanthanide cations average about 2.5 for HDEHP. This reagent has been adapted for use on extraction chromatographic materials.(5) Dialkyl phosphinic and phosphonic acids give similar performance in this separation. Several processes for treatment of high level wastes based on acidic organophosphorus compounds have been summarized recently. (6)

The Purex process rejects the trivalent (and pentavalent) actinides, leaving these species with the bulk of the fission product wastes. During the age of Pu production, this was a desirable feature of the process, as it allowed straightforward pathways to separation of Pu and removal of the

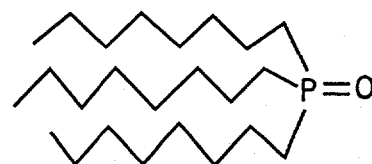
Figure 4. Separation factors for trivalent lanthanide and actinide metal ions in (a) HDEHP solvent extraction and (b) α -hydroxyisobutyric acid cation exchange.



undesirable Np, Am, and Cm from the desired Pu product. However, in modern processing of nuclear fuels, the dispatch of the minor actinides to the fission product waste stream is no longer desirable, as it increases the length of time the radioactive wastes must be sequestered from the environment. Put another way, isolation of the minor actinides from fission products and their separate disposal will greatly reduce the volume of wastes requiring disposition to a mined geological repository, the most expensive alternative for radioactive waste disposition. Beginning in the late 1970's, a considerable research effort was mounted world wide to remedy this feature of the Purex process (now seen as a weakness, though it was once considered a desirable feature).

A number of parallel research avenues have been traveled in a search for the best extractant for selective isolation of the trivalent actinides. The most important species technologically are Am and Cm, which are produced at long irradiation times in reactor fuels due to the successive neutron capture reactions of ^{238}U , ^{239}Pu , and ^{241}Am . In France, the development of actinide extractants has focused on the development of amide complexants, which contain no phosphorus and thus support the French philosophy of the CHON (carbon, hydrogen, oxygen nitrogen) principal for completely incinerable reagents. Research in China has emphasized trialkyl phosphine oxides (Figure 5), neutral extractants more basic and less prone to radiolytic and hydrolytic destruction than TBP, for this task. In Russia some effort

Figure 5. Trioctylphosphine Oxide



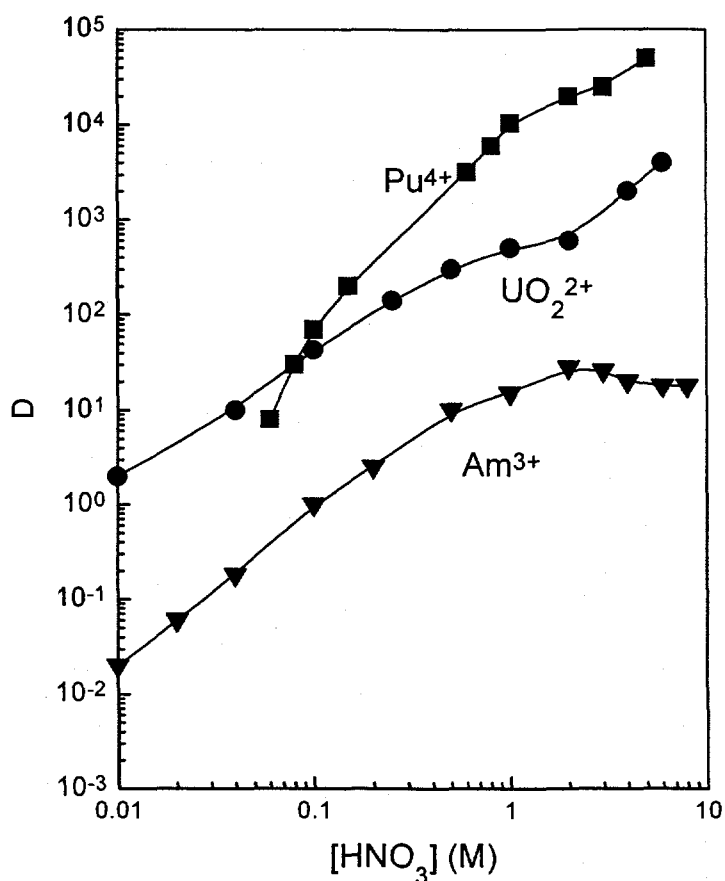
has been expended on the design and characterization of bis-phosphonate extractant molecules for minor actinide extraction. More recent research in Russia has focused on derivatives of carbamoylmethylphosphine oxides (CMPO) developed at Argonne National Laboratory.

The development of CMPO and carbamoylmethylphosphonate (CMP) extractants during the past two decades can be traced ultimately to the work of Siddall in the mid 1960's.(7) Considerable research effort was expended at ANL and elsewhere on the optimization of the basic CMP-CMPO extractant structure. One major

purpose of the research was to design a reagent that would be readily compatible with the Purex process solvent, which relies on TBP, so that it could be easily interfaced with the Purex process in a hydrometallurgical processing plant. At ANL that effort led to the extractant octyl(phenyl)-N,N-diisobutylcarbamoylmethyl phosphine oxide and the TRUEX process. In TRUEX, U(VI), Pu(IV) and Am/Cm(III) are co-extracted as their respective neutral nitrate complexes from 1-2 M HNO₃ (Figure 6). The actinides can be stripped together or in principle can be selectively stripped by successive contacts with appropriate aqueous solutions. The extractant has been extensively tested as to its stability and physico-chemical properties. The TRUEX process has been demonstrated at five laboratories in the U.S. and two foreign laboratories, and has been shown capable of successfully handling a variety of different waste streams.

(6)

Figure 6. Extraction of Am³⁺, Pu⁴⁺, and UO₂²⁺ by 0.25 M CMPO in dodecane.



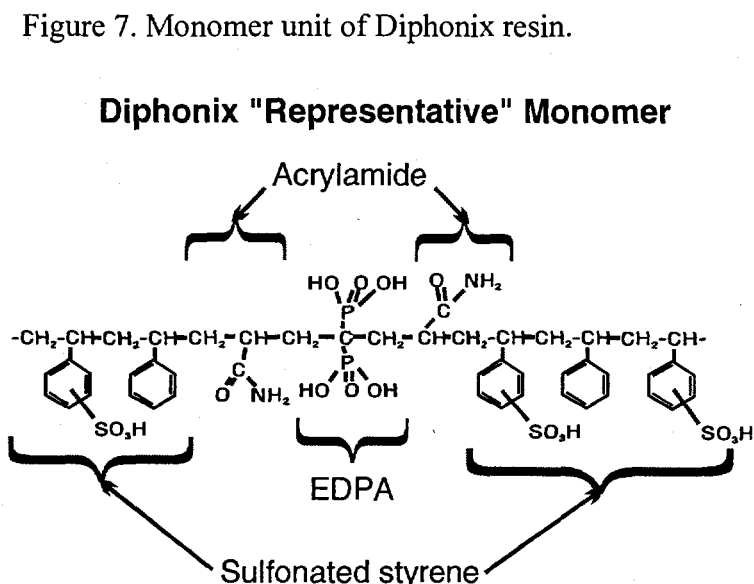
Though CMPO is moderately resistant to radiolytic and hydrolytic degradation, the acidic extractants that are produced in the extractant solution as a byproduct of degradation are moderately effective complexing extractants in dilute acid solutions. As acidic organophosphorus extractants become more effective in dilute acid, their presence in the extractant phase can seriously impair the "stripability" of the actinides from the loaded solvent. While the degradation products can be handled much as they are in Purex, removal of the residual actinides from the extractant solution prior to its recycle in the process is best accomplished using water soluble complexing agents. In process applications, it is usually desirable to minimize the amount of adjustments applied between stages of the process. Since TRUEX solvent extracts actinides from a moderately acidic solution, the ideal complexing agent would strongly bind the metal ions to be stripped strongly in such solutions. Among commonly known complexants, only oxalic acid has the appropriate combination

of properties to accomplish actinide stripping under these conditions. Our research on water-soluble complexing agents based on methanediphosphonic acid (MDPA) has revealed another possible approach to the stripping of process solvents.

Our investigations began with studies of the complexing power of the commercially available diphosphonate 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). We observed reduction of actinide distribution ratios as great as 10^7 for contacts between TRUEX solvent and 0.5 M HEDPA in 1 M HNO_3 .(8) An additional concern associated with the application of such complexants was their potential environmental persistence, which could lead to undesirable migration of radionuclides in soils and natural waters. We therefore approached the design of these complexants with the idea that decomposability could be designed into the complexing agent. The complexants are collectively referred to as Thermally Unstable Complexants or TUCS. (9) Procedures for their ready destruction using wet chemical techniques (rather than incineration) have been developed.(10) Though one of the complexant destruction methods demonstrated applies equally well to species that do not contain phosphorus, the presence of phosphate as a degradation product may have desirable implications for actinide solubility control, as will be discussed below.

One of the water soluble diphosphonates prepared during this research was vinylidene-1,1-diphosphonic acid (VDPA). VDPA was readily decomposed in hot HNO_3 and formed surprisingly soluble actinide complexes. The most important feature of VDPA is the unsaturation in the alkyl backbone, which represents an attractive target for further derivatization. Though a number of water-soluble diphosphonate derivatives of VDPA have been synthesized and investigated for their potential applicability in actinide processing, the preparation of a chelating cation exchange resin based on diphosphonate groups is the most important development to flow from the preparation of VDPA. In joint research between ANL and the University of Tennessee, a multifunctional diphosphonate resin, Diphonix™, was prepared and characterized for its ability to adsorb polyvalent metal ions from solutions of various compositions.(11) The monomer structure of the original Diphonix copolymer is shown in Figure 7. A number of additional multifunctional resins combining diphosphonate and other purpose-built functional groups have been synthesized, as has a Diphonix resin on a silica core (Diphosil™). These resins have found numerous practical applications.

Figure 7. Monomer unit of Diphonix resin.



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The success of the diphosphonate group in a covalently fixed configuration of a polystyrene-divinylbenzene matrix led naturally to consideration that the preparation of a lipophilic chelating agent based in diphosphonic acid would perhaps represent the next logical step in the evolution of diphosphonate groups for actinide separations. Introduction of 2-ethylhexyl groups at each of the phosphonate groups of methane-, ethane-, and butanediphosphonic acid produced lipophilic extractant molecules with exceptional affinity for actinide ions from acidic aqueous solutions. (12)

In fact, the extractants proved to be such powerful reagents for actinide extraction into normal paraffinic hydrocarbon solvents that are considered optimum for hydrometallurgy of actinides that it was necessary to employ water soluble diphosphonate chelating agents for effective stripping. This enormous strength of interactions provides a great opportunity for the development of highly selective separations with the adjustment of the diluent properties or of the bridging backbone of the extractant. These compounds have been found to be particularly effective when adapted to extraction chromatographic separations.(5)

Transmutation and Lanthanide-Actinide Separations

Instead of direct disposal of actinides in a geological repository, an alternative approach is to transmute these elements into shorter-lived fission products which become less hazardous in a shorter period of time. Transmutation can be accomplished either by incorporating the actinides in reactor fuels or by the application of accelerator-based techniques. Both approaches result in the fissioning of the actinides and extract at least some portion of the energy released during the fission process for power production. The neutron physics of the processes are such that processing of the actinide targets or fuel rods will be needed to remove neutron poisons that build up and decrease the efficiency of the fuel or actinide target. The most problematic of these species are the rare earths (lanthanides plus yttrium), which are produced in about 40% of fission events and have chemistry nearly identical to the transplutonium actinides. The parallel chemistries make this group separation one of the most difficult tasks in separation science.

It was observed first by Diamond et al.,(13) that trivalent actinide cations interact somewhat more strongly with chloride ion than the lanthanides, thus enabling a cation exchange resin-based separation of moderate efficiency. This effect was attributed to covalency in the actinide-chloride complex that is essentially absent in the lanthanides. Subsequent research demonstrated a similar effect in ion exchange separations based on thiocyanate. We have recently reported Am/Eu separation factors of about 10 for CMPO extraction of these metal ions from NH_4SCN solution.(14) Though the concept of covalency in actinide coordination complexes is still a matter of some debate, all effective group separations rely on the stronger interactions of actinide with soft donor atoms like Cl^- , S, or N. (15)

There are two examples of trivalent actinide-lanthanide separations based on organophosphorus reagents for phase transfer. The first of these is the TALSPEAK process, developed at Oak Ridge National Laboratory. (16) The most common extractant in this process is HDEHP, though several other phosphonic acid or phosphoric acid extractants perform similarly. The TALSPEAK process solvent preferentially extracts lanthanide cations while the trivalent actinides remain in the aqueous phase due to the combined actions of 1 M ammonium lactate and 0.05 M diethylenetriamine- $\text{N,N,N}',\text{N}'',\text{N}'''$ -tetraacetic acid (DTPA), which accounts for the group separation. The "soft" donor atom that accounts for the separation is the amine nitrogens on DTPA. Group separation factors of about 10 are typically observed in TALSPEAK.

More recently, Zhu and co-workers (17) have reported that dithiophosphinic acid extractants like Cyanex 301 exhibit a preference for trivalent actinide ions of 3000-6000. Jarvinen and co-workers have reported a similar result for dicyclohexanodithiophosphinic acid, which they report as being readily prepared and easily purified.(18) The dithiophosphinic acids are susceptible to hydrolytic and radiolytic degradation to product oxygenated extractants, but they are substantially more stable than dialkyldithiophosphoric acids that were investigated earlier.(19) Zhu et al (17) report that the extraction of Am by Cyanex 301 is substantially more exothermic than that of Eu^{3+} indicating a

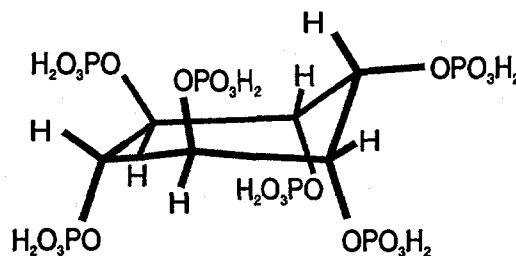
stronger covalent contribution to the bonding in the Am complex, though there still seems to be some uncertainty as to the species that are extracted.

Phosphate in Cleanup of the Weapons Complex

As noted above, the presence of phosphate in the underground waste tanks in the DOE weapons complex complicates waste disposal. Because phosphate is incompatible with the preferred borosilicate waste glass, present plans call for an alkaline scrub of tank sludges prior to the vitrification of the actinide-bearing sludges in part to reduce the concentration of phosphate in the sludge, which will result in a reduction in the total volume of wastes produced. As a result, phosphate and organophosphorus compounds have acquired a reputation for being problematic in radioactive waste disposal. However, the inherent insolubility of actinide and lanthanide phosphate mineral species suggests that perhaps phosphate and organophosphorus compounds could have a positive influence on the isolation of actinides from the biosphere. Several reports have investigated actinide sorption by hydroxyapatite and other phosphate mineral forms. Lanthanide and actinide phosphate mineral forms also are incorporated in geochemical thermodynamic models as important species for solubility control.

We have recently completed a laboratory demonstration of a waste disposal technique based on a naturally occurring organophosphorus compound as a potential pathway for decreasing actinide mobility in ground waters using a comparatively simple technique.(20) The organophosphorus complexant is phytic acid (myo-inositolhexakisphosphoric acid, Figure 8), a compound produced in great abundance by certain legumes. Phytic acid is a known chelating agent for polyvalent metal ions, is fairly easily decomposed at neutral pH (either spontaneously or by microbiological processes) to release phosphate and the cyclic sugar inositol as byproducts. This compound is produced in the U.S. at a rate of about 10^5 tons as a byproduct of fermentation.

Figure 8. Phytic acid.



The in situ isolation process relies first on the cation exchange behavior of the calcium salt of phytic acid (which is moderately insoluble) which exchanges Ca^{2+} for actinide cations to remove them from the solution phase, thus immediately reducing their mobility. Because the phytate is readily decomposed, it is expected that it will slowly release phosphate to foster the development of calcium-actinide-phosphate mineral phases that will represent a thermodynamically stable long-term disposition medium for the actinides. Details of the laboratory demonstration of the basic principals of the process have been described in previously.(20) This method of in situ disposal creates an opportunity for low-cost control of the environmental mobility of actinides in the subsurface. There is also a large, as yet uninvestigated, potential for application of such technology to the stabilization of uranium mill tailings and for possible applications in the sequestration of non-radioactive toxic heavy metals.

Conclusions and Future Opportunities

The future of nuclear energy in the developed world is at present very much in doubt. Problems associated with the disposal of high level wastes, the cleanup of contaminated environments left over from 50 years of plutonium production for defense purposes, a public perception that the technology may not be safe, and concerns about plutonium proliferation combine to account for the current state.

Organophosphorus complexing agents and inorganic phosphates have figured prominently in the generation of some of the waste problems, as they have in the production of the tons of plutonium that now are present on the earth. However, the unique chemical properties of organophosphorus compounds presently in existence and similar species that could be developed may ultimately have a significant positive impact on the outstanding problems of nuclear technology.

Purex technology is likely to remain the industry standard for nuclear fuels processing for at least the next decade. It is a well-known and generally successful technology that, while not perfect, has enjoyed substantial success. In both France and the United Kingdom Purex processing of nuclear fuels is being done with comparative safety and moderate profitability. The development of more efficient (zero-emission?) processes based on Purex technology is a reasonable goal. The production of phosphate wastes from Purex processing may in the end prove desirable, as the long-term stability of actinide ions in radioactive waste glasses has been questioned. If these valuable energy production resources (actinides) are not to be recycled, a ceramic phosphate waste form may ultimately prove the ideal waste disposal medium for these elements.

Full-scale application of TRUEX technology could substantially reduce the volume of wastes requiring disposal in a geological waste repository. The complete design of such a process might also include water soluble organophosphorus complexing agents for both solvent recycle and potentially for environment restoration problems. If actinide burnup and/or recycle is to increase in importance, recent research results suggest that thio-phosphorus organic complexants may prove quite valuable. Analytical separations for environmental and bioassay of actinides might also be uniquely carried out with organophosphorus compounds. Despite the current disdain being expressed for organophosphorus reagents in nuclear fuels processing, these compounds appear to have too many favorable characteristics to be eliminated from consideration for future developments of nuclear technologies.

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