CHAPTER TWENTY FOUR

ACTINIDE SEPARATION SCIENCE AND TECHNOLOGY

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24.1 INTRODUCTION

Both the science and technology of the actinides as we know them today owe much to separation science. Conversely, the field of metal ion separations, solvent extraction, and ion exchange in particular, would not be as important as it is today were it not for the discovery and exploitation of the actinides. Indeed, the synthesis of the actinides and the elucidation of their chemical and physical features required continuous development and improvement of chemical separation techniques. Furthermore, the diverse applications of solvent extraction and ion exchange for metal ion separations as we know them today received significant impetus from Cold War tensions (and the production of metric tons of plutonium) and the development of nuclear power for peaceful uses.

Solvent extraction, precipitation/coprecipitation, and ion exchange procedures have played a central role in the discovery and characterization of the 5f transition elements. Each of these separations techniques likewise has shaped progress in technological applications of actinides for electricity production and for nuclear weapons. Recent decades have seen the rise of pyroelectrometallurgical separations, wherein the long-term future of actinide separations may lie.

Efficient chemical separations are an essential feature of actinide science and technology because (1) aside from U and Th there are no primordial transuranic actinides and so no natural mineral deposits from which to isolate them and (2) the nuclear techniques employed to create actinides also induce fission in the heavy metal target atoms producing mixtures that can include up to one-third of the periodic table. Whether for scientific purposes or technological applications, high degrees of purification of actinides from diverse solid solutions containing small amounts of the desired material in a complex solid matrix are required. This chapter addresses the details of these chemical separation processes and describes what the exercise of these separation processes has taught us about the chemistry of the actinides.

Four specific separation tasks had to be accomplished to enable the discovery of the 5f elements and then to support creation of sufficient amounts of these elements to sustain their practical application: isolation of natural uranium from its mineral sources, isotope enrichment to increase the relative percentage of fissile ^{235}U above that of natural uranium, separation of actinides from a diverse mixture of fission products, and separation of individual members of the series. The accomplishment of these tasks required innovative solutions to demanding problems. Setting aside the technologically essential process of isotope enrichment (not discussed in this chapter), separations of actinides can be considered at two scales: analytical-scale separations conducted at low concentrations or with small amounts of the analyte, and large-scale separations conducted on kilogram quantities of materials in large shielded facilities. Each of these carries unique opportunities and challenges. Analytical separations are best served by reagents that are both highly specific and very efficient (i.e. capable of quantitatively separating the target species in a single (or small number of) contact(s)). Plant-scale separations also perform best with highly specific reagents, but extremely high phase-transfer efficiency typically is not preferred because materials must also be readily recovered from the separation matrix. Weak chemical separations processes can be overcome at plant scale by adding more repeat contacts (stages) of reagents.

In a once through nuclear fuel cycle, there are no large-scale separations subsequent to the preparation of the enriched uranium fuel. However, in the operation of a closed loop fuel cycle, it is necessary to separate the transuranium actinides individually or as a group from uranium and fission products. For the purpose of scientific discovery, it was (and is) necessary to isolate individual members of the series. The diverse redox chemistry of uranium, neptunium, and plutonium is the primary feature of processes for their isolation and purification. For the actinides beyond americium and in most applications for americium as well, the trivalent oxidation state predominates. The trivalent oxidation state is also prevalent in the lanthanides, which are produced in about one-third of thermal neutron-induced fission events in ^{235}U and ^{239}Pu. Most features of the chemistries of the trivalent transplutonium actinides and lanthanides are nearly identical.

Aside from the unique demands of trivalent actinide/lanthanide group separations, the discussions of separations systems below will consider features of lanthanide separations as representative of the behavior of trivalent actinides. The separation of individual trivalent actinides relies on the predominantly electrostatic bonding characteristics of the ions and on the steady reduction that is seen in the trivalent cation radii with increasing atomic number, a behavior paralleling that of the lanthanides. This small but (more-or-less) regular decrease in cationic radii provides an adequate driving force for ion exchange-based separations of the individual members of the series, as will be described below.

The actinides are as a group readily separated from most fission products, based on their unique chemistry as compared with the great diversity of species present. Typically, only Ru, Mo, Zr (under some circumstances), and the ubiquitous lanthanides represent a significant separations challenge. The isolation of individual trivalent transplutonium actinides from trivalent lanthanides can be readily achieved if the species to be separated are sufficiently differentiated based on cation radii. Specifically, the transplutonium elements can be readily separated from the light lanthanides, but with greater difficulty from those in the middle of the series. For an effective separation of the trivalent actinides from the lanthanides as a group or for ions having similar cation radii, it has proven essential to incorporate into the separation scheme donor atoms 'softer' than oxygen or fluoride. Poly-aza ligands of complex geometries, chloride ions, thiocyanate ions, or species containing sulfur donor atoms have proven the most viable candidates. These soft-donor reagents can appear in the separation schemes either as lipophilic extractant molecules or as water-soluble complexing agents.

Nearly 60 years of industrial scale implementation of aqueous processing schemes has produced both considerable insight into the ways and means of conducting these separations, and large waste disposal/environmental restoration challenges at the sites where such large-scale processing has been conducted. The legacy of the massive volume of waste generated during these many years of aqueous processing to recover actinides from spent fuel has spurred efforts to develop radically different approaches. In particular, separations developed conceptually in the 1960s based on molten salts, molten metal, including electrochemical processing in these media, have received considerable attention in recent years for their potential as alternative large-scale separations methods for spent fuel processing. Such methods tend to strongly favor reduced actinide species and radically different (though fundamentally simple) coordination chemistry for the actinide species in these media. Far less is known about the chemistry of actinides in supercritical fluids, room-temperature ionic liquids, or other non-conventional media, but any of these methods could play a central role in future nuclear fuel cycles. Processes based on volatility of certain actinide compounds have also received some attention and possess some interesting features. However, each of these concepts is far behind aqueous processing, both because of the number of years of experience that have been accumulated for the aqueous option, and the unknowns always attendant to developing new science and technology.

24.1.1 Prior literature reviews/useful reference volumes

There are two categories of previous studies each serving a complementary role in describing actinide separation science: those providing 'recipes' for conducting separations of radioactive materials and those explaining the underlying principles. In the beginning, the chemical properties of the transuranium elements were a matter of informed speculation, so underlying principles were not known except by inference. Their discovery and the ultimate elucidation by Seaborg of the actinide hypothesis was a clear demonstration of the correctness (and utility) of Mendeleev's periodic table. The chemical separation procedures that enabled actinide science as we know it today were based on belief in chemical periodicity. One remarkable aspect of actinide separation science is the enduring quality of many of the separations developed during the days of actinide discovery. This is a tribute to the talents and abilities of those early practitioners of actinide separation science.

Perhaps the most useful (even today 40 or more years after their publication) detailed experimental separation procedures are those found in the National Academy of Science Series on radioanalytical chemistry. This series, published in the 1950s and 1960s, still constitutes a useful primary reference for formula separation schemes for the entire periodic table, including the actinides. Though individual bound volumes of these separation procedures are widely available, the series is long out of print. These volumes are however presently available online (http://lib-www.lanl.gov/radiochemistry/elements.htm).

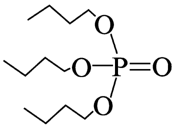
Of course, the insights gained from these initial explorations have allowed the development of more general reference works and a better understanding of the chemical features of the processes. The classic reference book for aqueous separations chemistry (both ion exchange and solvent extraction) has long been *Ion Exchange and Solvent Extraction of Metal Complexes* by Marcus and Kertes (1969). In this book, the theory and practice of separation science is discussed in great detail. Solvent extraction chemistry has been reviewed by Sekine and Hasegawa (1977). In addition to concentrating on solvent extraction, this work differs from the Marcus and Kertes volume in that it has references to many more specific examples. Helfferich (1962) published a volume that is generally considered as the most authoritative discussion of the unique theoretical aspects of ion exchange-based separations. Two 'how-to' manuals have been published which describe in detail useful ion exchange separation procedures for the lanthanides and actinides (Korkisch, 1986a,b).

Updates on the state of the art of f-element separations have appeared in the literature at regular intervals. Jenkins (1979, 1984) reviewed ion exchange applications in the atomic energy industry. Symposium volumes entitled

Actinide Separations (Navratil and Schulz, 1980), *Lanthanide/Actinide Separations* (Choppin *et al.*, 1985) and *Separations of f Elements* (Nash and Choppin, 1995) are collections of papers from several authors covering various aspects of lanthanide and actinide separations. Additional specialized reviews of specific topics have also appeared frequently. Most of these are considered below.

The subject of lanthanide/trivalent actinide separations has been reviewed previously (Weaver, 1974; Nash, 1993a). Weaver's review is an excellent source for a comprehensive discussion of solvent extraction separations of the lanthanides and trivalent actinides. Weaver discusses many of the historical aspects of lanthanide/actinide separations, and considers both the successes and failures in the separation of trivalent lanthanides and actinides. Nash's review complements and updates the observations of Weaver, emphasizing the critical role played by soft-donor ligands in the development of efficient processes for the selective separations of the trivalent 4f and 5f elements.

Arguably, the most important reagent for actinide separations is tri(*n*-butyl) phosphate (TBP – structure a). This compound is the subject of a four-volume handbook entitled *The Science and Technology of Tributyl Phosphate* (Schulz *et al.*, 1990). Many chapters in this collection address important features of the application of TBP for nuclear fuel processing and actinide recovery. On the subject of large-scale separations of actinides, the current state of the art in hydrometallurgical processing of actinides from spent fuel or radioactive wastes has been reviewed recently (Horwitz and Schulz, 1999; Mathur *et al.*, 2001).



Structure a

These reports describe and critically evaluate water-based actinide partitioning research activities being conducted around the world. The diversity of activities being pursued worldwide is in some respects surprising. However, it does reflect the increasingly important nature of these separations. In truth, aqueous separations still dominate the actinide separations landscape. Contemporary research attempts to take a 21st century perspective on nuclear fuels processing, emphasizing the importance of closing the fuel cycle while minimizing the generation of wastes requiring geological disposal.

24.1.2 Scope of the chapter

The space available to this chapter simply does not allow for a comprehensive treatment of all aspects of the subject of actinide separations. Some selectivity will therefore be applied in the following discussion. All essential features of actinide separations will be discussed, but it will not be possible to include detailed step-by-step descriptions of all of the well-known separation systems.

The reader will find such information among the several reviews noted above. Greater emphasis will be placed on the details of newer science and technologies, those currently being considered for advanced applications, and on those most appropriate methods to preserve long-term options for nuclear fuels recycling in the 21st century.

Because chemical separations have played such an important role in the discovery of the actinides, the chapter begins with a discussion of the early history of actinide separations. This discussion will be followed by some consideration of the fundamental chemistry of separation systems and of actinide behavior in phase transfer systems. The fundamental chemistry of actinides in aqueous solutions has been described in the previous chapter. It will therefore not be necessary to address the details of actinide behavior in solution in detail here. However, some aspects of the aqueous chemistry of actinides (redox, solvation, complexation) do play an important role in actinide separations, and so will receive an appropriate emphasis wherever needed in this chapter. The general features of phase transfer reactions will be discussed briefly, focusing on the differences between the classic solvent extraction, ion exchange, and precipitation methods. Unconventional techniques, those still at the developmental/exploration stage, including those related to the use of supercritical fluids (mainly CO_2), molten metals/molten salts, and more exotic (and less extensively tested) techniques like those based on the use of room temperature ionic liquids (RTILs) or volatility will then be addressed. The issue of scale will be considered with coverage of analytical separations followed by a detailed description of the current state of the art in hydrometallurgical (industrial-scale) separations for actinide recovery, recycle, and transmutation. The chapter concludes with some consideration of future directions.

24.2 HISTORICAL DEVELOPMENT OF ACTINIDE SEPARATIONS

Actinide separations had its beginnings with the discovery of radioactivity. Crookes and Becquerel found that the addition of carbonate to a solution containing uranium caused the formation of a precipitate that 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, "While carrying out these operations (separations by precipitation), more active products are obtained. Finally, we obtained a substance whose activity was 400 times larger than that of uranium. We therefore believe that the substance whose activity we have isolated from pitchblende is a hitherto unknown metal. If the existence of this metal can be affirmed, we suggest the name polonium" (Choppin *et al.*, 2002). The separation method used by these pioneers was precipitation/coprecipitation, which remained the predominant separation technique through the Manhattan Project of World War II. A historical perspective on the development of this science and technology through the end of World War II is available in *The Making of the Atomic Bomb* (Rhodes, 1986).

Between 1934 and 1939, about 50 research papers claimed the discovery and reported studies of transuranium elements with $Z = 93, 94, 95, 96$. In 1939, Hahn and Strassmann conducted very careful separations on neutron-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 separated. 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, establishing a link with the 4f elements.

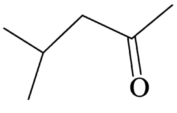
Within the context of world politics in the 1930s and 1940s (and as it turned out the following decades), it was perhaps inevitable that the discovery of fission would be first valued for its potential military applications. Two approaches to the assembly of a critical mass were immediately recognized: isotope enrichment to increase the atom percentage of the fissile uranium isotope ^{235}U and transmutation of ^{238}U by neutron capture and β^- decay to produce ^{239}Pu. The former option required a many theoretical plate isotope separation process wherein the stage-wise efficiency is limited by the small difference in mass of the two principal isotopes. Plutonium production instead relies on neutron capture in a reactor fueled by uranium (the ratio of ^{239}Pu production to fission of ^{238}U after capture of a thermalized neutron is about 14 to 1 (Choppin and Rydberg, 1980) and chemical separation of different elements. Differences in the redox chemistries of uranium and plutonium facilitate their mutual separation. Neither isotope enrichment nor plutonium production were considered to have an advantage in the race to produce a critical mass for the first nuclear weapon in time to affect the outcome of the war, so both methods were pursued with equal vigor in the Manhattan Project.

Two approaches to uranium isotope enrichment were proposed for full investigation and process development: electromagnetic isotope separation, proposed by E. O. Lawrence at Berkeley, and gaseous diffusion, championed by John Dunning at Columbia University (Rhodes, 1986). The latter was considered the more likely to succeed on an industrial scale because it was based on technology that was better established. It also offered the advantage of continuous operation, which was not deemed possible in the electromagnetic separation option. Electromagnetic isotope separation received equal consideration because of the greater per-stage separation potential of the technique. Each method relied on the low-temperature volatility of UF_6 (Cotton and Wilkinson, 1988).

As research continued on both approaches, groundbreaking occurred on the Clinch River in eastern Tennessee in 1942, leading to the establishment of the Clinton Engineering Works in Oak Ridge. The Gaseous Diffusion Plant (K-25) required the co-siting of a dedicated coal-fired power plant and occupied about 0.2 sq. km under a four-stories-high roof. The electromagnetic isotope separations plant (Y-12) occupied half that space and required 13 tons of silver (borrowed from the U.S. Treasury) for the electromagnets. In the end, K-25 provided feedstock of up to 50% enriched ^{235}U to the Y-12 plant for completion of the high enrichment needed for weapons production. These two plants working in tandem produced the ^{235}U for the Hiroshima weapon (Rhodes, 1986).

Industrial scale plutonium production was first accomplished at the Hanford site on the Columbia River near Richland, Washington (Anonymous, 1996). It began with commissioning of B reactor in September 1944 and continued through the lifetimes of eight single-pass reactors, N reactor (the only dual-use Hanford reactor that produced both usable steam and Pu), and the fast flux test facility (FFTF) ending in the early 1980s. The isolation of plutonium from uranium and fission products was initially accomplished by precipitation with $BiPO_4$. The process, pioneered by S. G. Thompson (Thompson and Seaborg, 1956, 1957; Seaborg and Thompson, 1960), involves coprecipitation of Pu(IV) by $BiPO_4$ followed by oxidation to Pu(VI), which does not carry on $BiPO_4$. The process was repeated several times and followed by a LaF_3 precipitation to increase the purity of the product. This batch process is inherently inefficient and has the additional disadvantage of losing uranium to the waste stream. At the time, the loss of uranium to the waste stream was particularly damaging to process efficiency because of the limited amount of purified uranium that was available. However, precipitation/coprecipitation was the only viable technology that could be readily scaled up to production plant dimensions within the demanding time constraints of the Manhattan Project. In fact, the $BiPO_4$ coprecipitation process was first demonstrated using microgram quantities of plutonium, hence the scale-up was by a factor of 10^9. Because of the consistency and reproducibility of the chemistry involved, this scale-up occurred without significant complications. After the war, additional separations of $BiPO_4$ wastes were conducted to recover the rejected uranium for recycle to reactors.

$BiPO_4$ was eventually replaced at Hanford by solvent extraction processes based on the use of methyl(isobutyl)ketone (hexone, Structure b) for extraction of uranium and plutonium from slightly acidic $Al(NO_3)_3$ solutions (REDOX process) and later using TBP to selectively extract (and mutually separate) uranium and plutonium from nitric acid solutions (PUREX process). Great improvements in efficiency were achieved with each successive development, though the PUREX process produced a far smaller volume of secondary wastes than the REDOX process. Fifty years later, PUREX remains the principal method for processing of spent nuclear fuel.



Structure b

In the spirit of scientific discovery and at several laboratories around the world, though primarily at Berkeley and under the supervision of Glenn Seaborg, research in the 1950s and 1960s continued to extend the actinide series from plutonium and americium towards the final element of the series ($Z = 103$). The identification of new elements demands satisfaction of "...The basic criterion for the discovery of a new element is the experimentally verified proof that the atomic number of the new element is different from the atomic numbers of all previous elements. Establishment of the atomic number can be by chemical means, by identification of the characteristic X-rays in the decay of the new species, or by establishment of genetic decay relationships through α-particle decay chains in which the new element is identified by the observation of previously known decay products" (Seaborg and Loveland, 1990). To respond to the demand for predictable chemistry, it was essential that the separations process behave in a systematic fashion.

As the postwar research on actinide syntheses progressed, it was quickly learned that the rich redox chemistry of the light actinides, which was central to most of the successful separations of the light members of the series, did not persist beyond americium. In aqueous solutions, the elements beyond americium behaved chemically more like the 4f analog lanthanides than the light members of the series, strongly preferring to remain in the trivalent oxidation state.

Because synthesis of successive members of the series (beyond Cm) required the isolation and irradiation of a previous member of the series, the task of identifying the later members of the series was hindered not only by the ability to analyze for new species produced, but also by the rate at which target elements could be produced (and how quickly they decayed). The difficulty is demonstrated in Table 24.1 in which the nuclear reaction, target element, and product are noted. The process was further complicated by the increasingly short half-lives of the elements produced, and the low efficiency of the reactions leading to their production. For the elements beyond einsteinium, only a few atoms at a time were created and detected. The procedures of one-atom-at-a-time chemistry have been described in some detail by Seaborg and Loveland (1990) and can be found in Chapters 13 and 14 of this work.

The particle capture reactions that yielded new elements were also always accompanied by some fission. Yields for lanthanides in heavy element fission are high thus the dissolution of irradiated targets led to the creation of solutions that contained not only small amounts of the target transamericium elements but also significant concentrations of lanthanides. This complication impacted both the identification of new elements and the creation of appropriate target materials.

Two challenging separation problems resulted from this circumstance: the need for mutual separation of the two groups (5f from 4f), and of adjacent metal ions (in the 5f series) of identical charge and similar cationic radii. Because

Table 24.1 *Summary of original actinide synthesis methods, means, and materials.*

Actinide	*Target*	*Half-life*[a] (*Target*)	*Half-life*[a] (*Product*)	*Projectile*	*Method*
^{239}Np	^{238}U	4.47×10^9 yr	2.35 d	n	cyclotron
^{238}Pu	^{238}U	4.47×10^9 yr	87.74 yr	^{2}H	cyclotron
^{241}Am	^{239}Pu	24 100 yr	432.7 yr	n	reactor
^{242}Cm	^{239}Pu	24 100 yr	162.7 d	^{4}He	cyclotron
^{243}Bk	^{241}Am	432.7 yr	4.5 h	^{4}He	cyclotron
^{245}Cf	^{242}Cm	162.9 d	43.6 min	^{4}He	cyclotron
^{253}Es	^{238}U	4.47×10^9 yr	20.47 d	n	fusion explosion
^{255}Fm	^{238}U	4.47×10^9 yr	20.47 h	n	fusion explosion
^{256}Md	^{253}Es	20.47 d	1.27 h	^{4}He	cyclotron
^{254}No	^{244}Cm	18.11 yr	55 s	^{12}C	HILAC[b]
^{258}Lr	$^{249–252}$Cf	351, 13.08	3.9 s	^{10,11}B	HILAC[b]
	–	898, 2.645 yr	–	–	–

[a] Appendix II.
[b] Heavy ion linear accelerator.

of the minute amounts of materials being used as targets and produced in irradiations, and the absence of multiple oxidation states, many standard separation procedures (e.g. precipitation/coprecipitation) were simply not useful. The emergence of polymeric ion exchange materials proved essential to accomplishing both of these separations.

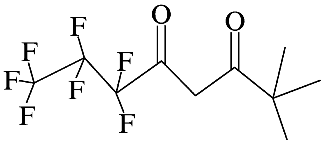
Though cation exchange resins bearing readily deprotonated sulfonic acid groups adsorbed the trivalent f-elements strongly, even from moderately acidic solutions, these sorbents exhibited little inherent facility for accomplishing either separation, i.e. there was insufficient differentiation between cations of similar size. Lanthanides and trivalent actinides were absorbed by the resin under the same conditions and with most inorganic eluants exited the column together. The secret to attaining selectivity was proper choice of the eluting solution. Two distinctly different classes of eluting agents were applied to these separation problems, soft-donor ligands, and hydroxycarboxylate complexants. Their use enabled the positive identification of the remaining members of the series thus confirming the basic correctness of the actinide hypothesis. Each of these separations methods is discussed in greater detail in Section 24.3.3.

24.3 FUNDAMENTAL FEATURES OF ACTINIDE SEPARATION SYSTEMS

To isolate an actinide ion from a complex mixture, some procedure must be devised to transport the target metal ion from its starting condition into a separate phase and then recover the target metal ion from that separate phase. For analytical-scale separations, a highly efficient process that can be accomplished in a single (or small number of) contact(s) between the phases is most desirable. For large-scale separations, complex series of processes are typically combined to accomplish the separation. As a result, less efficient single-stage chemical processes are acceptable (and in fact often preferred) for hydrometallurgical applications. Selectivity becomes a more important feature than extractant strength. The key features needed for large-scale separations of nuclear materials are: (1) reversibility of phase transfer (mass transport) reactions with a shift in extraction conditions, (2) sufficient reliability to be readily adaptable to remote (i.e. no human contact) operations, (3) rapid chemical reaction and phase-transfer kinetics, and (4) the ability to operate in a continuous rather than batch fashion. The first three features are absolutely essential; the fourth is highly desirable. Materials must also demonstrate physical and chemical stability in contact with strongly acidic aqueous solutions and in a high radiation environment. General features of selected separation techniques will be discussed in the following sections.

24.3.1 Volatility-based separations methods

Choppin (2002) has provided an overview of the subject of separation processes based on the volatility of actinides and selected fission products. He suggests possible approaches to selective removal of Zr, Tc, and Ru fission products (or cladding material) through their volatile oxides (Tc, Ru) or chlorides (Zr). There are also reports on the potential use of volatile β-diketone complexes of trivalent lanthanides for gas phase based separations. For example, tetra- and hexavalent actinide cations are known to form volatile compounds with FOD (6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione, Structure c), which could form the basis for a separation of uranium and plutonium from americium (Anonymous, 1995). This same reagent will appear again in the discussion of actinide separations methods based on supercritical CO_2 (Section 24.3.10). No separation system based on the volatility of either fission product oxides or β-diketonate complexes has received extensive development at the process scale.



Structure c

The most extensively researched system for volatility separations is based on the same volatile fluorides that are the basis of isotope separations. A separation based on the volatility of uranium and plutonium fluorides was demonstrated by Hyman *et al.* (1956) and investigated in greater detail at Oak Ridge National Laboratory for reprocessing as a part of the molten salt reactor project (Rosenthal *et al.*, 1972). The overall effectiveness of the process is limited principally by the simultaneous production of volatile fluorides of fission products Tc, Te, and I. The volatile fluorides can be separated by distillation, though the lower volatility of PuF_4 (arising from the decomposition of PuF_6) leads to Pu deposition problems. In principle, this approach should produce minimal volumes of wastes, though operations combining fluorine compounds and radioactive materials always present challenging materials handling and safety issues. The application of fluorinated compounds to volatility separations is mimicked in many separations that rely on supercritical CO_2, as will be discussed in Section 24.3.10.

24.3.2 Precipitation/coprecipitation methods

In the laboratory, precipitation and coprecipitation processes are a regular and accepted feature of radioanalytical chemistry. Several applications of precipitation and coprecipitation techniques for conducting investigations of the redox speciation of actinides at radiotracer concentrations are discussed in Section 24.4.1a. For the cleanup of aqueous media containing low concentrations of actinides, ultrafiltration has also been employed to collect ultrafine actinide-containing solids (Cecille *et al.*, 1987; Senentz and Liberge, 1998; Smith *et al.*, 1998, 1999; Bisset *et al.*, 2003). Though a number of precipitation processes have been advanced over the years to assist in selected actinide separation scenarios (Bertozzi *et al.*, 1976; Mousty *et al.*, 1977; Pietrelli *et al.*, 1987; Spurny and Heckmann, 1987; Grossi *et al.*, 1992a,b; Sinha *et al.*, 1992; Strnad and Heckmann, 1992; Felker *et al.*, 1995; Tomiyasu and Asano, 1995; Harada *et al.*, 2001), precipitation is no longer practiced as the primary means of separations for large-scale actinide production purposes.

Because the actinides are acidic cations, they readily undergo hydrolysis and precipitate as hydroxides. If complexing agents are kept from the solution, actinide hydroxides can be readily precipitated in the trivalent ($K_{sp} \approx 10^{-20}$), tetravalent ($K_{sp} \approx 10^{-54}$), pentavalent ($K_{sp} \approx 10^{-10}$), and hexavalent ($K_{sp} \approx 10^{-25}$) oxidation states (Martell and Smith, 1998). Hydroxides are generally avoided at the production scale and are unreliable for radioanalytical purposes, but often prove quite convenient avenues to the purification of actinide ions at the milligram to gram level for research purposes. Their most notable feature is the ready reversibility of the precipitation through the addition of mineral acid solutions, thus hydroxide precipitation can be used to readily convert from (for example) chloride to nitrate salts. The cautionary note here is to avoid the formation of tetravalent plutonium hydroxide, which has an extremely low K_{sp} and is redissolved only with difficulty, and often not cleanly, particularly if the precipitate is aged. The presence of carbonate or strong complexing agents (e.g. aminopolycarboxylates) can seriously interfere with hydroxide precipitation processes.

Other species that are readily precipitated are the phosphates of actinide ions in any oxidation state and under a wide range of conditions, and the fluorides and the oxalates of trivalent and tetravalent actinide ions. The latter two reagents can be employed for oxidation state-based separations, as the pentavalent or hexavalent actinide cations do not form insoluble species under most conditions with these anions while both the trivalent and tetravalent ions precipitate readily from acidic solutions. In the remanufacture of plutonium from nuclear weapons pits (fission core of a thermonuclear device), the selective precipitation of tetravalent plutonium as the peroxide was an essential feature of operations at the Rocky Flats Plant (Cleveland, 1970).

The most technologically important coprecipitation process (no longer used in practice) is that based on bismuth phosphate, as noted above in Section 24.2 and again later in more detail in the discussion of process chemistry. For actinide oxidation state speciation in radioanalytical applications, the actinides themselves are present at concentrations too low to challenge solubility limits in a reliable fashion. The introduction of cations and anions that combine to form insoluble species that carry the actinides down are useful analytical or laboratory-scale purification procedures. This is the case of lanthanum fluoride (LaF_3) whose solubility product is reported as about $10^{-18.7}$ (Martell and Smith, 1998). This compound is readily precipitated from comparatively dilute acidic fluoride solutions. LaF_3 (actually, most any lanthanide will serve) quantitatively carries trivalent and tetravalent actinide ions. Care must be exercised for quantitative LaF_3 carrier precipitation to avoid excess HF, as the resultant formation of soluble metal fluoride complexes can interfere with the efficiency of precipitation. Partly as a result of the unique coordination geometry of the dioxo actinide (v) and (vi) cations, there are no reliable coprecipitation procedures for their analysis or macroscale separation, though there are a number of insoluble adsorbents that will remove these ions from solutions (though with limited selectivity). These adsorption reactions will be discussed in Section 24.4.1.

24.3.3 Ion exchange methods

The development of solid materials capable of capturing and reversibly releasing the metal ions back into the contacting solution, ion exchange materials, was a great step forward in separating elements with similar properties. The earliest non-crystallization separation processes for individual trivalent lanthanide ions based on inorganic ion exchangers demonstrated separation factors for adjacent ions of 1.01–1.05, barely acceptable for chromatographic separations using large columns. For the production of actinides in microscopic amounts, such separation factors are simply too low to be useful. The selectivity limitations of inorganic ion exchange materials were only slightly improved with the development of polymeric organic ion exchange materials, though the latter offered superior reproducibility and resistance to dissolution. Radiation stability is an issue for either class of sorbents, but more problematic for the polymeric materials. Clearly, more efficient procedures were required to cope with submicroscopic amounts of the new transplutonium elements being produced.

The separation of trivalent actinides from lanthanides was first achieved by cation exchange from concentrated chloride media. Street and Seaborg (1950), Diamond *et al.* (1954), and later Choppin and Chetham-Strode (1960) demonstrated that the behavior of lanthanides and actinides on cation exchange columns was identical below 6 M HCl, but diverged between 6 and 12 M (as shown in Fig. 24.1). Separation factors of about 10 were achieved at 12 M HCl. Separation efficiency was increased when the separation was carried out from salt solutions (dilute acid) or from alcohol–water mixtures of HCl. Diamond and coworkers proposed that the separation of promethium and americium at high concentrations of HCl was a manifestation of f-orbital covalency to the bonding of Am^{3+} to Cl^- (which is not present in the Pm system). The origin of the effect is still a matter of discussion and debate, but it has become abundantly clear over the intervening decades that the most effective trivalent actinide and lanthanide separations are based on the contribution of ligand donor atoms softer (i.e. more polarizable) than oxygen.

Separation efficiency was slightly greater when anion exchange was employed. Thompson *et al.* (1954) found actinide/lanthanide separation factors above 10 for anion exchange separation from 10 M LiCl aqueous solutions.

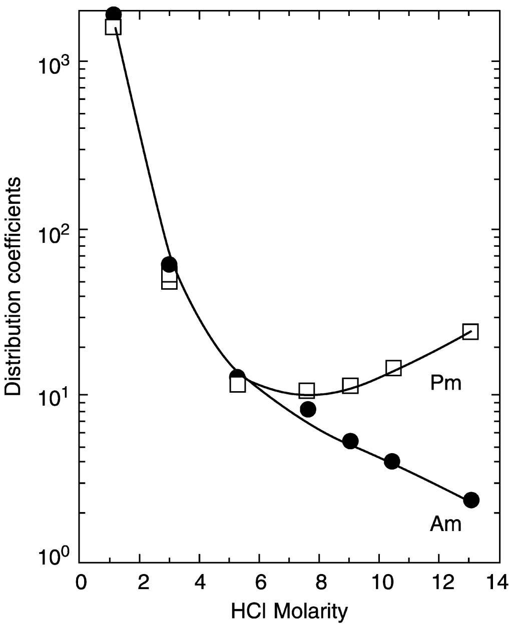


Fig. 24.1 *Distribution of Pm(III) and Am(III) onto Dowex* 50 *cation exchange resin as a function of hydrochloric acid concentration (Diamond* et al., 1954).

In this case, higher order (anionic) actinide chloride complexes are formed which preferentially associate with the resin. Introduction of 20% ethanol improved the separation factor, presumably through a modification of the hydration characteristics of the metal ions or their complexes. In this system, the actinides were eluted within a few column volumes while the lanthanides required much larger volumes. In another procedure using a Dowex 1 anion exchange resin column and eluting with 9.9 M LiCl (0.11 M HCl), Hulet *et al.* (1961) achieved an excellent separation of Ln–An. Surls and Choppin (1957) reported that similar results could be achieved in thiocyanate solution at significantly lower concentrations than is required for chloride (Fig. 24.2). This is a result of the increased interaction strength of the actinide with the 'less-soft' nitrogen donor atom of SCN^- relative to the very soft Cl^- anion. The LiCl anion exchange process is still used for actinide/lanthanide separation at Oak Ridge National Laboratory for actinide production (King *et al.*, 1981).

The results of Guseva and Tikhomirova (1972) indicate a significant improvement in the group separation from 4% cross-linked Dowex 50 using 10.5 M HCl

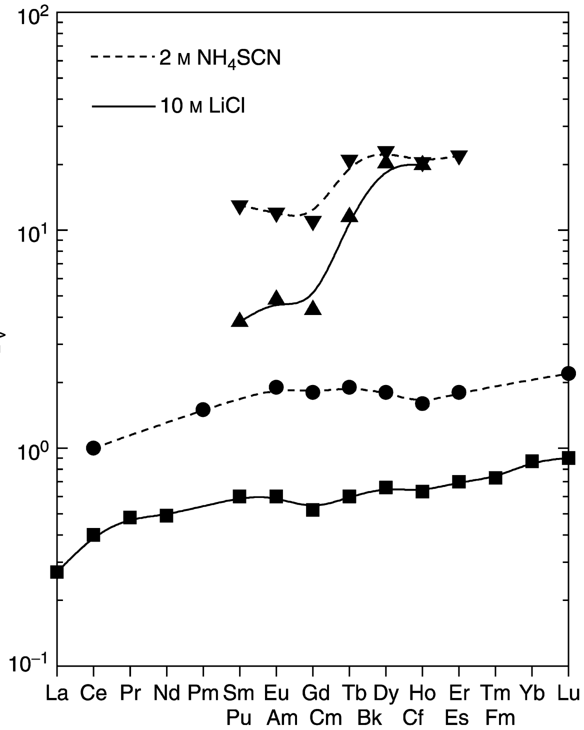


Fig. 24.2 *Partitioning of trivalent actinides and lanthanides onto Dowex* 1 *anion exchange resin from* 10 M *lithium chloride* (*Hulet* et al., 1961) *and* 2 M *ammonium thiocyanate* (*Surls and Choppin,* 1957) *solutions* (▼, ▲, *actinides,* ●, ■, *lanthanides*).

in 40% ethanol as the eluant as compared with 12.5 M HCl in water. Guseva *et al.* (1987a,b) subsequently demonstrated an efficient separation of trivalent actinides from all matrix elements (lanthanides and other fission products) with both cation and anion exchange from aqueous–ethanol solutions of sulfuric acid. Usuda and coworkers (Usuda, 1987, 1988; Usuda *et al.*, 1987) have proposed a separation scheme for trivalent actinides using a three-step ion exchange partition from light actinides and fission products. Though little fundamental solution chemistry research has been done to probe the impact of alcohol–water mixtures on actinide separations, the effects cited above clearly indicate an important role for the interactions between solvent and solute molecules in these systems.

The separation of adjacent trivalent actinides represented an even more challenging task. The inherent selectivity of Dowex 50 cation exchange resin for adjacent lanthanide cations (in this case, behaving analogously with the trivalent actinides under all conditions) is demonstrated in Fig. 24.3. Separation factors for adjacent lanthanide cations average about 1.007. The coupling of water-soluble chelating agents (also demonstrated in Fig. 24.3) with the ion

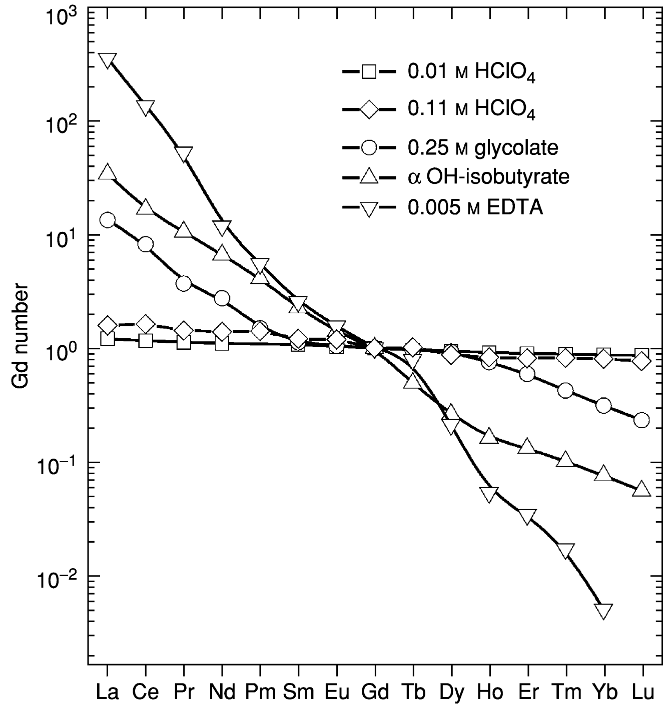


Fig. 24.3 *Partitioning of trivalent lanthanide ions onto Dowex* 50 *cation exchange resin from various aqueous acid solutions.* (*Gd number is the distribution ratio of the element normalized relative to* $D_{Gd} = 1.0$, *created from data in Marcus,* 1983.)

exchange systems by Thompson and coworkers (Thompson *et al.*, 1950, 1954; Choppin *et al.*, 1956) was the enabling science that made the identification of the new transplutonium elements possible.

The combination of a buffered solution of, in particular, a hydroxycarboxylic acid with a strong acid cation exchange resin like Dowex 50 made it possible to take advantage of the relative stability of the aqueous complexes of the actinide ions (which generally increase in proportion to those of the analogous lanthanide complexes across the series). This effect can be readily understood given a little consideration of the monophasic and biphasic equilibria involved in the process. Assuming that the water-soluble metal complexes present in the eluant are not sorbed by the resin, the distribution of the metal ion onto the acidic resin phase is governed by the following equilibrium (taking a trivalent cation as the example):

$$\mathrm{M^{3+} + 3H(Resin) \rightleftarrows M(Resin) + 3H^{+}} \tag{24.1}$$

In the aqueous phase the metal complexation equilibria with a ligand HY can be written as:

$$\mathrm{M^{3+}} + n\mathrm{HY} \rightleftarrows \mathrm{MY}_n^{(3-n)^+} + n\mathrm{H^+} \tag{24.2}$$

The distribution ratio (*D*) for the metal ion is the ratio of the amount of metal species in the resin phase, $[\mathrm{M}]_\mathrm{R}$ to that in the aqueous phase $[\mathrm{M}]_\mathrm{a}$. Most commonly, these values are normalized to 1 ml of solution and 1 g of resin, respectively.

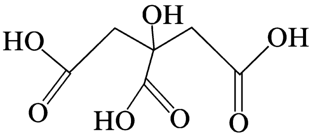
$$D = [\mathrm{M}]_\mathrm{R}/[\mathrm{M}]_\mathrm{a} = [\mathrm{M(Resin)}]/([\mathrm{M^{3+}}] + \Sigma_1^n(\mathrm{MY}_n^{(3-n)^+})) \tag{24.3}$$

The distribution ratio is directly proportional to the resin's affinity for the metal ion and inversely proportional to the degree of complex formation in the aqueous phase. In general, the separation factor (*S*), the ratio of distribution ratios, determines whether a separation of two species is successful or not. Written in terms of the respective one- and two-phase complexation equilibria, the separation factor is:

$$S_{\mathrm{M}'}^{\mathrm{M}} = \frac{D_\mathrm{M}}{D_{\mathrm{M}'}} = \frac{K_\mathrm{ex}^\mathrm{M}\ \cancel{[\mathrm{HR}]}^3/\cancel{[\mathrm{H}^+]}^3(1+\Sigma\,\beta_i^{\mathrm{M}'}[\mathrm{Y}]^i)}{K_\mathrm{ex}^{\mathrm{M}'}\ \cancel{[\mathrm{HR}]}^3/\cancel{[\mathrm{H}^+]}^3(1+\Sigma\,\beta_i^{\mathrm{M}'}[\mathrm{Y}]^i)} \tag{24.4}$$

wherein $K_\mathrm{ex}^{\mathrm{M,M}'}$ represents the equilibrium coefficient for the partitioning of the cation onto the resin phase, and $\beta_i^{\mathrm{M,M}'}$ represents the complexation equilibrium constants for species present in the eluant solution. In fact, multiple complexants can be used in the aqueous phase to enhance separations, in which case additional complexation equilibria can be used to predict separation performance.

First attempts relied on citric acid (Structure d) as the eluant. As the synthesis of new actinides proceeded across the series, the product nuclides had progressively shorter half-lives, and in passing the middle of the series, the actinide equivalent of a gadolinium break (differentiation of the stability constants of adjacent actinide complexes, predominant at the beginning and end of the lanthanide series, disappeared in the middle of the series) reduced the effectiveness of citrate as an eluant. These combined features resulted in smaller separation factors between the newest nuclides and in their early exit from the column, hampering analysis and detection. Substitution of lactic acid for citric acid improved performance. The comparative elution positions of Am, Cm, Bk, Cf, Es, and Fm from Dowex 50 cation exchange resin when the eluting solution was 0.25 M ammonium citrate or 0.4 M ammonium lactate are shown in Table 24.2.



Structure d

Ultimately, the demands of the chemistry and the radiochemistry required a 'better' eluant (i.e. one yielding more consistent (i.e. linear) trends of elution with decreasing radii while retaining rapid kinetics). To satisfy this demand, Choppin and Silva (1956) introduced α-hydroxyisobutyric acid (Structure e), α-HIBA, which also came to be known colloquially as the 'BUTT' eluant. This complexant differs from lactate in the substitution of a second methyl group for H at the alpha position. The α-hydroxyisobutyric acid provides average separation factors for adjacent lanthanides or trivalent actinides of about 1.3–1.5 and very consistent elution positions even through the middle of the series where many reagents fail to give acceptable results. Parallel performance between trivalent lanthanides and actinides in cation exchange separations was a key factor in the identification of most of the transplutonium actinides. Fig. 24.4 shows the elution profile of trivalent actinides and lanthanides with ammonium α-hydroxyisobutyrate and shows the consistency in separation factors for adjacent cations across the series. It should be noted that if the data were plotted in terms of cationic radii rather than atomic number, the lanthanide and actinide results would overlap. Table 24.3 compares $S_{\mathrm{M}}^{\mathrm{M}'}$ of adjacent actinides with lactic acid, α-hydroxyisobutyrate, ethylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid (EDTA) and further relates those data to the separation factors observed for

Table 24.2 *Elution of transplutonium elements from Dowex* 50 *cation exchange resin using ammonium carboxylate salts at* 87°C, pH 3.0–4.5, 2 min/drop, 2 mm *by* 10–20 mm *column* (*Thompson* et al., 1950, 1954).

			Retention time (*drop number*)			
Carboxylic acid	*Am*	*Cm*	*Bk*	*Cf*	*Es*	*Fm*
0.25 M ammonium citrate	94.0	80.8	56.0	38.3	32.5	26.7
0.4 M ammonium lactate	58.5	49.0	33.0	22.0	18.0	13.6

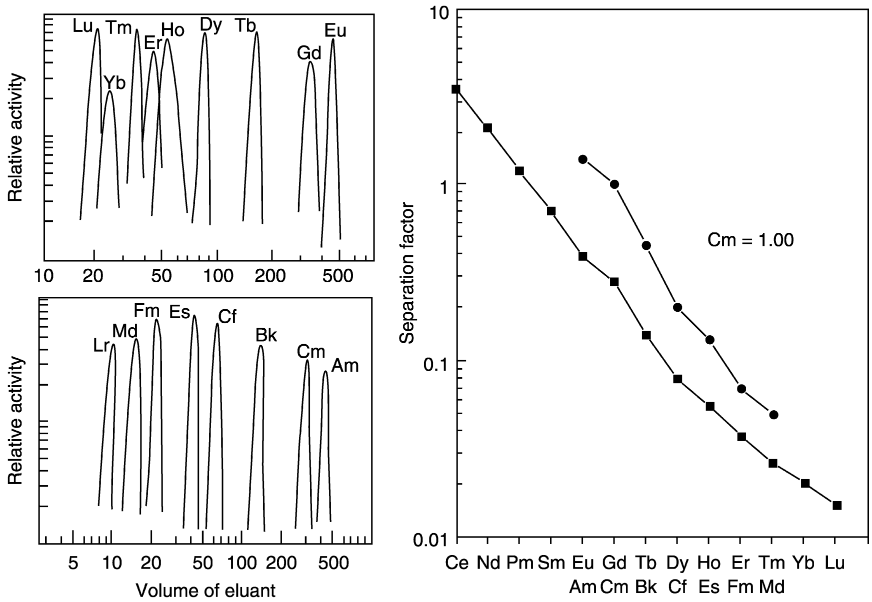
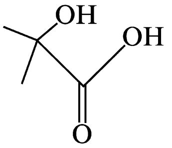
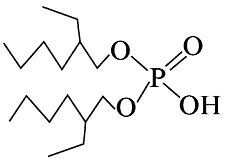


Fig. 24.4 *Elution profiles for trivalent lanthanide and actinide ions and separation factors (relative to Cm* = 1.0) *for α-hydroxyisobutyrate elution from Dowex* 50 *cation exchange resin (Choppin and Silva*, 1956).

solvent extraction separations using bis(2-ethylhexyl)phosphoric acid (HDEHP, Structure f), which will be considered further in Section 24.3.4a



Structure e



Structure f

Improvements in separations have been achieved with cation exchange systems of this type using very finely divided resin beds and high-pressure elutions (Campbell, 1970). Kilogram amounts of americium and gram amounts of curium have been purified from each other by using nitrilotriacetic acid (NTA) and diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (DTPA, Structure g) as

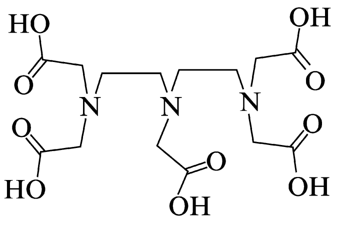
Table 24.3 *Separation factors for adjacent trivalent actinides with solvent extraction and cation exchange column using different reagents.*

	Reagents			
		Cation exchanger		
Element	*Solvent extration. HDEHP/HNO*$_3$	*EDTA*	*Lactic acid*	*α-HIBA*
Am/Cm	1.24	2.0	1.21	1.4
Am/Bk	8.3	3.1	1.54	1.7
Bk/Cf	2.7	2.0	1.55	2.2
Cf/Es	1.02	–	1.25	1.5
Es/Fm	2.2	–	1.45	1.7
Fm/Md	4.4	–	–	1.4

α-HIBA = α-hydroxyisobutyric acid.

the eluants (Baybarz, 1970). The kinetics of the metal complexation/ion exchange equilibration on the Dowex 50 column with α-hydroxyisobutyrate eluant was also found to be superior to that for the several other ligands that had been previously employed. For example, aminopolycarboxylic acid ligands like EDTA demonstrated comparable or even superior separation factors (to α-hydroxyisobutyrate; see Fig. 24.3), but slower equilibration rates, which required longer residence times for the solutions on the column. The need for longer equilibration times on the column was a definite handicap in the search for short-lived actinide species. Like TBP and PUREX, the BUTT column remains today one of the most effective ion exchange separation method for trivalent f-elements from a mixture of like elements (Nash and Jensen, 2000).

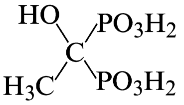
It should be noted that the intrinsic affinity of cation exchange resins increases for actinides in the order An(v) < An(iii) < An(vi) < An(iv), in accord with the comparative electrostatic attraction of the cations for the anionic sulfonate functional groups of the resin. The differences are sufficiently large to allow the mutual separation of the ions in different oxidation states; however, all but the pentavalent oxidation state are bound too strongly for effective separation procedures to be routinely used. Where necessary and possible, sorption of strongly bound ions is generally reversed using oxidation state adjustment or chelating agents.



Structure g

To avoid the elution difficulties of the cation exchange resins, ion exchange separations for the purification of the tetravalent and hexavalent actinides more frequently rely on anion exchange techniques. A variety of separation methods based on the use of tetraalkylammonium or methyl pyridinium polymeric resins have been developed. Introduction of the Reillex resins, based on methylpyridinium functional groups, is among the more significant recent advances in anion exchange separations for actinides (Abney *et al.*, 1995). Perhaps the most important application of anion exchange resins is in the purification of plutonium. Pu(IV) is selectively sorbed onto Dowex 1 from 8 M HNO_3, allowing the passage of other contaminants through the resin. Pu(IV), which is retained on the resin as the hexanitrato complex ($Pu(NO_3)_6^{2-}$), is readily eluted using more dilute nitric acid. Anion exchange separations for An(IV) and An(VI) are facile because these cations readily form anionic complexes with simple inorganic anions like NO_3^- and Cl^-. However, higher order complexes are formed in the presence of the resin than are observed in the same solution in its absence. This is due to the superposition of the phase transfer equilibrium upon the typical aqueous phase complexation reactions, which tends to drive the process. In essence, anionic complexes are sorbed to the resin whether or not they are present in the aqueous solution phase contacting the resin.

A new chelating ion exchange resin (Diphonix) that exhibits high affinity for actinide cations in all oxidation states from strongly acidic solutions has been developed jointly at Argonne National Laboratory and the University of Tennessee as a spinoff of the development of the transuranium extraction (TRUEX) solvent extraction process (Alexandratos *et al.*, 1993; Chiarizia *et al.*, 1993, 1994, 1996, 1997; Horwitz *et al.*, 1993, 1994; Chiarizia and Horwitz, 1994, 2000; Trochimczuk *et al.*, 1994). Diphonix resin combines a methylenediphosphonic acid chelating group with carboxylic and benzene sulfonic acid groups in a styrene–divinylbenzene matrix. This combination results in a chelating resin that exhibits good metal ion uptake kinetics (Chiarizia *et al.*, 1994) and effectively sorbs actinide metal ions in all oxidation states from moderate to strong acid solutions and even in the presence of moderately strong complexants. The hexavalent and tetravalent species are so strongly retained by the resin even from 10 M HNO_3 that they can only be removed upon elution with a moderately concentrated solution of a structurally related diphosphonate chelating agent (1-hydroxyethane-1,1-diphosphonic acid, HEDPA; Structure h) or by applying a reducing agent. The distribution ratios for Am(III), U(VI), Pu(IV), Np(IV), and Th(IV) onto Diphonix as a function of [HNO_3] are shown in Fig. 24.5. The acid dependence for Am(III) uptake indicates normal cation exchange behavior while that for Th(IV) and U(VI) has been interpreted in terms of coordination of these cations by the phosphoryl oxygens of the fully protonated methylenediphosphonate groups. The principal feature of the Diphonix resin is the strength of cation uptake rather than selectivity, though the resin demonstrates significant selectivity for Pu(IV) and U(VI) over Am(III) from concentrated nitric acid media. The principal advantage of this resin may be in the separation of actinides from less-strongly-bound fission product and cations present as a result of matrix dissolution.



Structure h

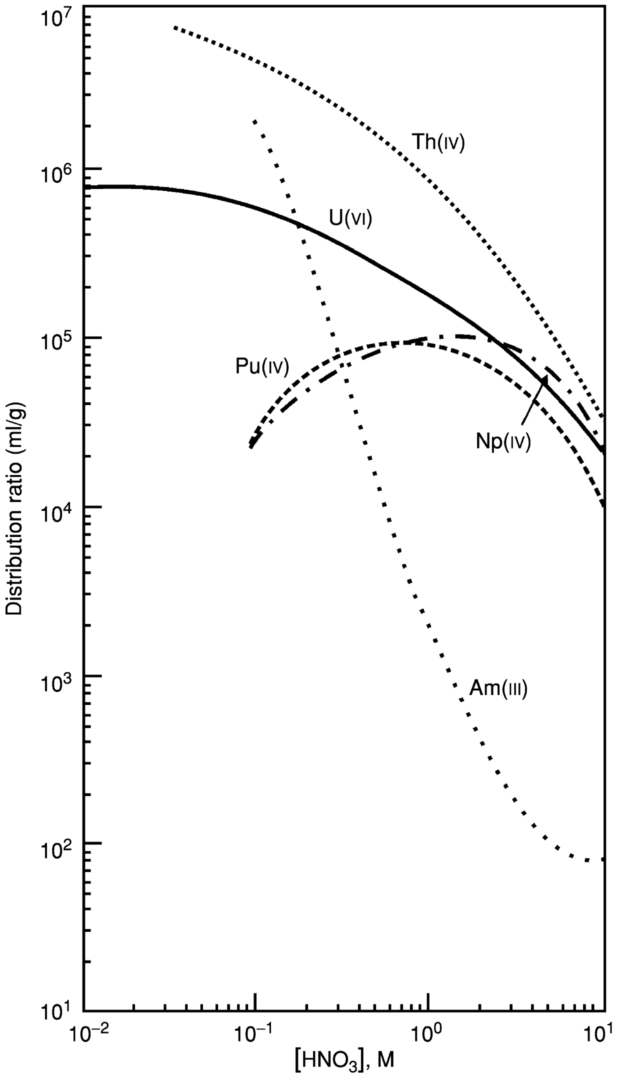


Fig. 24.5 *Distribution of selected actinide ions onto Diphonix resin from nitric acid solutions* (*Chiarizia* et al., 1997).

24.3.4 Solvent extraction methods

Successful solvent extraction processes depend on the *selective* transport of the target metal ion (or group of metal ions) from an aqueous solution containing contaminants into an immiscible organic solution. When the target metal ion is removed from that organic phase, it will have undergone some degree of purification, often characterized in terms of a 'decontamination factor' (D_f). Additional purification processes may subsequently be engaged, depending on the D_f required for the product. Strongly acidic, extensively hydrated metal ions like actinides and most of their complexes with typical mineral acid anions or other hydrophilic complexants have minimal intrinsic tendency to partition spontaneously from aqueous into non-polar organic solutions. The driving force for phase transfer is provided by the introduction of a lipophilic complexant (extractant) into the organic phase. Usually, new complexes possessing a hydrophobic external 'shell' are formed at the oil–water interface and transferred to the non-polar (or less polar) organic phase. Chemical reactions occurring in the aqueous phase, including oxidation–reduction, hydrolysis, and the formation of water-soluble complexes, all affect the phase transfer equilibrium position as well.

Of all separation techniques that have been applied for actinide separations, solvent extraction offers the greatest number of options and adjustable parameters to finetune performance. Further, it is perhaps the separations technique best adapted to the continuous operations, high throughput, and remote handling that are essential to the processing of nuclear fuels. Of course, this flexibility can also introduce complications, including rather long development time for the creation of a new solvent extraction-based process. Historically, industrial scale aqueous processes have also produced waste streams noteworthy for both their complexity and volume.

It is important at this stage to make the clear distinction between the chemistry of actinides in the organic media relevant to solvent extraction and the chemistry generally termed as organoactinide chemistry, which is covered in Chapters 25 and 26. In solvent extraction, metal ions in organic solutions *never* engage in bonding to *carbon* atoms, as they do in most true organometallic complexes. Direct bonding interactions between actinide ions and lipophilic complexants *do* play an important role in most solvent extraction systems, except for those based on molecules that organize in organic solutions to form reverse micelles. For the actinides in extraction processes, bonding is always to oxygen, nitrogen, or occasionally sulfur donor atoms in organic compounds or to chloride or thiocyanate anions, sometimes in combinations.

In solvent extraction, some dissolved water molecules are always present in the organic phase. For actinide separations, these solutions will often also bear mineral acid molecules that have been extracted by the same lipophilic reagents that remove the actinides from the aqueous phase. In some systems, a specific interaction can occur between the metal cation and solvent molecules, but only with compounds like methyl(isobutyl)ketone (MIBK) or (neat) tri(*n*-butyl) phosphate (TBP) which are moderately strong Lewis bases and so capable of competing with adventitious water molecules in the organic phase of solvent extraction systems.

It would be impossible to catalog all of the various reagents whose actinide extraction properties have been investigated in the space allocated for this overview. In the following discussion, the general characteristics of the classes of selected extraction systems are considered. The objective here is to illustrate the general features of the techniques. There are at least five different classes of solvent extraction systems that have been employed for actinide separations. The classes and representative biphasic extraction equilibria are:

Liquid cation exchangers/chelating agents,

$$\mathrm{M}^{3+}_{\mathrm{aq}} + n\mathrm{HL}_{\mathrm{org}} \rightleftarrows \mathrm{ML}_{n,\mathrm{org}} + 3\mathrm{H}^{+}_{\mathrm{aq}} \tag{24.5}$$

Micellar extractants,

$$\mathrm{M}^{3+}_{\mathrm{aq}} + (\mathrm{HL})_{n,\mathrm{org}} \rightleftarrows \mathrm{MH}_{n-3}\mathrm{L}_{n,\mathrm{org}} + 3\mathrm{H}^{+}_{\mathrm{aq}} \tag{24.6}$$

Solvating extractants,

$$\mathrm{M}^{3+}_{\mathrm{aq}} + 3\mathrm{X}^{-}_{\mathrm{aq}} + n\mathrm{S}_{\mathrm{org}} \rightleftarrows \mathrm{MX}_3\mathrm{S}_{n,\mathrm{org}} \tag{24.7}$$

Ion pair forming extractants (or liquid anion exchangers),

$$\mathrm{M}^{3+}_{\mathrm{aq}} + 3\mathrm{X}^{-}_{\mathrm{aq}} + \mathrm{A}^{+}\mathrm{X}^{-}_{\mathrm{org}} \rightleftarrows \mathrm{MX}_4\mathrm{A}_{\mathrm{org}} \tag{24.8}$$

Synergistic extractants,

$$\mathrm{M}^{3+}_{\mathrm{aq}} + 3\mathrm{HL}_{\mathrm{org}} + n\mathrm{S}_{\mathrm{org}} \rightleftarrows \mathrm{ML}_3\mathrm{S}_{\mathrm{n,org}} + 3\mathrm{H}^{+}_{\mathrm{aq}} \tag{24.9}$$

Species present in the aqueous and organic solutions are designated by the subscripts aq and org, respectively. In solvent extraction systems, the metal ion distribution ratio is a dimensionless quantity defined as $D = [\mathrm{M}]_{\mathrm{org}}/[\mathrm{M}]_{\mathrm{aq}}$. D is not a species-specific term but rather defines the analytical concentrations of the metal ion in the aqueous and organic phases. The stoichiometric features of the equilibria outlined above are most relevant at low concentrations of the metal ions. Under conditions near the stoichiometric limits of concentrations, the phase transfer equilibria can be substantially more complex than these simple equilibria indicate.

Each class of extraction system accomplishes the phase transfer by a slightly different chemical process. However, these systems share the following general characteristic: while the high dielectric constant of water readily supports the presence of charged ionic species as discrete molecules, the low polarity of organic solutions demands close contact between cations and anions. Most solutes in most organic solvents are expected to be discrete electroneutral entities. The liquid cation exchangers, chelating agents, and micellar extractants each exchange a number of monovalent cations (usually H^{+}) equivalent to the formal charge on the cation extracted to maintain electroneutrality in both phases. In these systems, transfer of the metal ion into the organic phase is favored by low acidity, implying that the metal ion can be stripped from the loaded organic solution into concentrated acid solutions (as H^+ competes with the metal ion for the extractant). Some acidic extractants have a tendency to self organize (aggregate), even in the absence of the extracted metal ion, to form dimers or higher order aggregates. Sulfonic acid extractants in particular behave in this manner, forming reverse micelles in the organic phase.

Solvating extractant systems are technologically the most important for actinide purification. They accomplish phase transfer by solvating electroneutral metal complexes with mineral acid anions, hence the net phase transfer reaction includes the necessity to dehydrate and resolvate in the organic phase both the metal ion and a sufficient number of conjugate base anions of mineral acids to neutralize the cation charge. In solvating extraction systems, the phase transfer reaction is favored by high concentrations of the counter-ion (preferably introduced as an acid solution to minimize the generation of secondary wastes) and stripped from the loaded organic solution by contact with dilute acid solutions, a change in oxidation state, or washing with a water-soluble complexant.

Primary among the solvating extractant systems that are technologically the most important actinide separations systems in operation today are those based on the solvating ability of TBP. More than 50 years of cumulative industrial scale experience exists on the PUREX process. This solvent extraction process accomplishes the selective removal of both plutonium [as Pu(IV)] and uranium [as U(VI)] from dissolved spent fuel solutions (3–6 M HNO_3) as their electroneutral nitrate salts with minimal complication (Fig. 24.6). Most fission products and the trivalent and pentavalent actinides [Am(III), Cm(III), Np(V)] are rejected by TBP.

Plutonium is selectively recovered from the extractant phase through its reduction to the trivalent oxidation state in which its extraction performance is comparable to that of Am(III). In PUREX processing, changes in neptunium oxidation state speciation causes partitioning of this element to undesirable locations within the process flow scheme. Until recent years, it has been most advantageous to try to maintain Np(V) in the aqueous phase so that it remains with the fission product raffinate. The emergence of full recycle fuel cycles for actinide transmutation in recent years has brought greater attention to the means of controlling Np speciation in PUREX-style separations. The details of neptunium's speciation complexity are discussed in Section 24.4.4f.

Synergistic systems generally combine acidic extractants, usually and most effectively multidentate chelating agents, with solvating extractants, hence they share some features of both liquid cation exchangers and solvating extractant molecules. Ion pair-forming extractants tend to be micellar in most organic solutions and to exchange simple anions for negatively charged metal coordination complexes. For actinide extraction by liquid anion exchangers, the

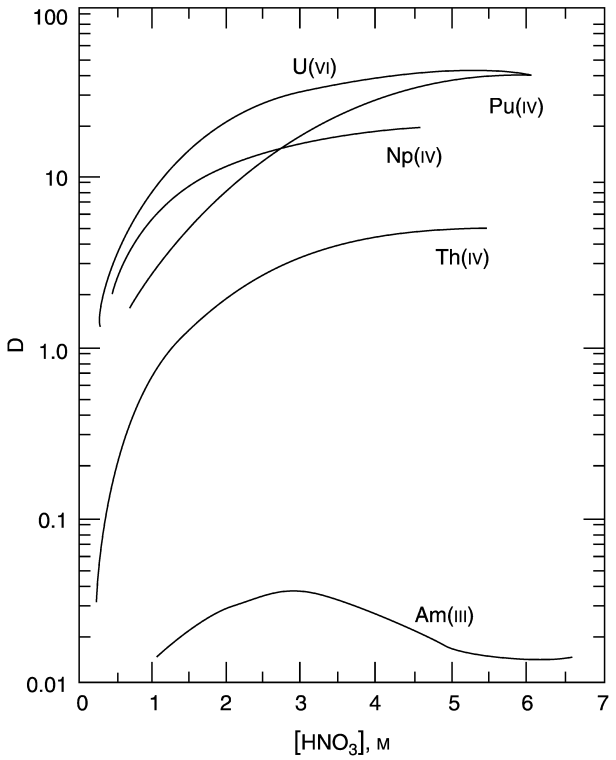


Fig. 24.6 *Extraction of actinides into tri*(n-*butyl*)*phosphate/dodecane as a function of nitric acid concentration.*

anionic complex (e.g. $AmCl_4^-$) exists only in the organic phase in the presence of the lipophilic counter-ion and is usually not an important species in the aqueous phase. These extractants are the soluble analogs of anion exchange resins and so exhibit relative actinide affinities in the order: An(iv) > An(vi) > An(iii) > An(v).

As a general (though not universal) rule, the greatest selectivity for metal ions having similar properties (like adjacent trivalent lanthanides or actinides) is seen in acidic extractant systems, particularly those involving the formation of multidentate complexes. Solvating extractant systems tend to exhibit their greatest selectivity only for metal ions differing in charge (for interactinide separations, this implies the presence of the metal ions in different oxidation states), but extract chemically similar species without much selectivity. Such behavior is also generally seen for micellar reagents, i.e. minimal selectivity is demonstrated for series of closely related metal ions. Synergistic systems achieve increased extraction strength, usually at the price of decreased selectivity (though there are some exceptions).

Table 24.4 *Am and Eu extraction with* 20% *triisooctyl amine from* 11.9 M *LiCl*/0.1 M *HCl* (*Moore,* 1961).

Diluent	*Percent extracted* *Am*	*Eu*	*Separation factor* S_{Eu}^{Am}
xylene	91.7	15.7	59
toluene	87.0	10.1	60
benzene	80.8	7.0	56
mesitylene	94.2	23.4	53
hexone	87.3	2.7	47
β,β′-dichloroethyl ether	97.1	63.1	20
o-Dichlorobenzene	80.6	7.5	51
nitrobenzene	87.2	11.8	51
n-Hexane	98.4	54.8	51
CH_2Cl_2	99.7	91.3	32
CCl_4	23.4	0.9	34
$CHCl_3$	0.6	<0.3	–
xylene-$CHCl_3$			
1:1	<1.0	<1.0	–
3:1	10.3	<0.5	–
20:1	71.2	4.3	55
50:1	83.4	8.7	53

$S_{Eu}^{Am} = D_{Am}/D_{Eu}$ = (% org Am/%AqAm)/(% org Eu/%AqEu)

The organic molecule almost always used to solubilize or dilute the extractant[1] is commonly considered to be 'inert', but, as the data in Table 24.4 indicates, this inertness is relative. Considering a single extractant system that transfers the metal ion in a straightforward equilibrium process, several orders of magnitude variation in extraction efficiency can be seen to result simply from a change in the diluent. For analytical separations, different classes of diluents can be employed, though many techniques favor volatile species like chloroform. For hydrometallurgical separations, issues of phase compatibility at high solute loading, low flammability, and low toxicity are primary considerations in the selection of a diluent.

Phase modifiers, secondary solute molecules that may or may not enter into specific interaction with the metal ion, the extracted complex, or the extractant itself are often employed simply to improve solubility characteristics. In hydrometallurgical separations of actinides, the phenomenon of third phase formation (also known as phase splitting), in which the biphasic system

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[1] Typically this organic compound is referred to as the diluent for historic reasons – the solution containing the extractant molecule in a diluent is referred to as the "solvent" in solvent extraction.

becomes a ternary liquid system, complicates process operations under conditions of high solute loading of the organic phase. This phenomenon has been most extensively studied in the TBP–PUREX system from an operational perspective (Rao and Kolarik, 1996) and empirical correlations have been developed. More recent work by Chiarizia and coworkers (Borkowski *et al.*, 2002, 2003; Jensen *et al.*, 2002a; Chiarizia *et al.*, 2003a,b, 2004) and by Tondre and coworkers (Erlinger *et al.*, 1998; Lefrancois *et al.*, 2001a,b) has attempted to provide a more fundamental understanding of the physical chemistry of the phenomenon.

Subtle variations in the properties of the aqueous phase can alter both extraction efficiency and selectivity patterns, as illustrated by the work of Sekine on the TBP extraction of Am^{3+} and Eu^{3+} by tri(*n*-butyl)phosphate from thiocyanate and mixed thiocyanate/perchlorate solutions [Fig. 24.7 (Sekine, 1965)]. The salting out effect of added perchlorate reduces the degree of order in the aqueous solution, which leads to a more efficient phase transfer process. However, the penalty paid is a reduction in the selectivity of the thiocyanate extractant system for Am over Eu. This system is discussed in more detail in Section 24.3.9. Note that in this example, Am(III) and Eu(III) are extractable into TBP solution because the aqueous acid solution has been replaced by a salt solution of higher pH.

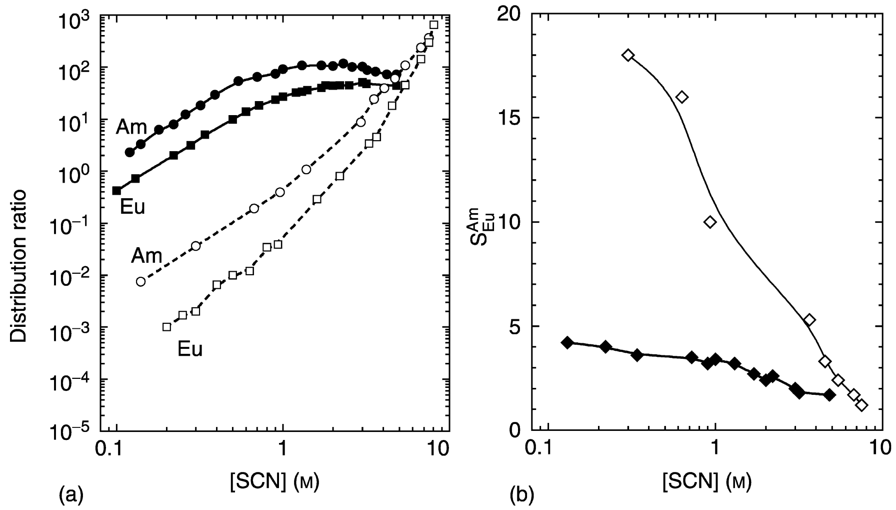
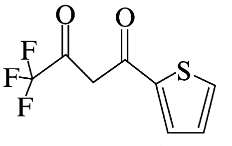


Fig. 24.7 (*a*) *Distribution of Am*(III) *and Eu*(III) *between sodium thiocyanate or sodium thiocyanate/perchlorate solutions and tri*(n-*butyl*)*phosphate/benzene solutions* (*open symbols thiocyanate only, closed symbols thiocyanate–perchlorate mixtures – from data in Sekine*, 1965); (*b*) *Am/Eu separation factors from thiocyanate alone* (◇) *and from thiocyanate/perchlorate mixtures* (◆).

(a) Acidic extractants

The extraction of actinides (and lanthanides) by thenoyltrifluoroacetone (TTA, Structure i) was one of the first solvent extraction methods for the isolation of individual An(III) ions (Stary, 1966). The separation factors for adjacent ions are slightly greater than in α-HIBA elution, but they are less constant throughout the series. TTA extraction from 1 M acid solutions is highly specific for tetravalent actinide ions, and is often employed in studies of oxidation state speciation of actinides in environmental samples (Choppin and Bond, 1996; Choppin and Wong, 1998; Nash *et al.*, 1988a; Rollin, 1999). Because of the photolytic instability of TTA and its appreciable solubility in aqueous solutions, it is employed almost exclusively in research rather than in hydrometallurgical separations. For analytical applications, this reagent should be prepared fresh frequently and always protected from ambient light and air. Structurally similar pyrazolone compounds extract actinide ions in patterns similar to those demonstrated by the β-diketones represented by TTA. They differ from β-diketones in that they are slightly more acidic, thus able to accomplish actinide phase transfer from more acidic solutions.



Structure i

Acidic organophosphorus extractant molecules have been used extensively in actinide separations. The first important acidic organophosphorus extractant was dibutylphosphoric acid (HDBP), which is produced spontaneously during the use of TBP (solvating-class extractant) for nuclear fuel processing. In TBP-based extraction systems, the presence of HDBP in the extractant phase caused considerable difficulty in the stripping of actinides from loaded and degraded TBP solutions into dilute acid solutions. From the above extraction equilibrium equations, it is clear that conditions needed for stripping of metal complexes from solvating extractants favor the phase transfer of the acidic analog, hence the simultaneous presence of both solvating and acidic extractants can have an important negative impact on the efficiency of solvent extraction separations. In the case of HDBP, the complications introduced by its presence were readily overcome by the development of careful procedures for removing HDBP from the TBP-extractant phase as its water-soluble sodium salt by scrubbing of recycled process solvent with sodium carbonate (Schulz *et al.*, 1990).

Realization of the special features of HDBP extraction touched off efforts to develop similar extractants less prone to degradation or able to function under different sets of conditions. One of the current principal methods for isolation of individual lanthanides commercially is solvent extraction with HDEHP mentioned above (Structure f), a reagent first reported by Peppard *et al.* (1957).

Adjacent lanthanide separation factors are up to twice as high for HDEHP separations as for α-hydroxyisobutyrate cation exchange. Trivalent actinides likewise are separated from one another by this reagent. A representative plot of actinide extraction in the most common oxidation states is shown in Fig. 24.8. This extractant is the phase transfer reagent for the TALSPEAK process for lanthanide/trivalent actinide separation (Weaver and Kappelmann, 1964, 1968).

Many long years of research were invested in systematic studies of monofunctional acidic organophosphorus extractants containing different alkyl groups designed to alter both the solubility of the reagent and the basicity of the functional group. Dialkylphosphoric acids like HDEHP $[(RO)_2P(O)(OH)]$ are characterized by the presence of two alkyl ester bonds. The P–O–C linkage is far more susceptible to hydrolytic and radiolytic degradation than P–C bonds. To increase the long-term stability of the extractant (and its suitability for application to the separation of radioactive materials) while simultaneously modifying its basicity (and so the effective range of pH operation), phosphonic $[(RO)(R)P(O)(OH)]$ and phosphinic $[(R)_2P(O)(OH)]$ acids replace alkoxide groups with alkyl groups, resulting in reagents of steadily increasing hydrolytic stability and greater basicity of the functional groups. Higher basicity translates into stronger metal ion bonding but typically forces operation under less acidic conditions due to the increased affinity of the extractants for H^+.

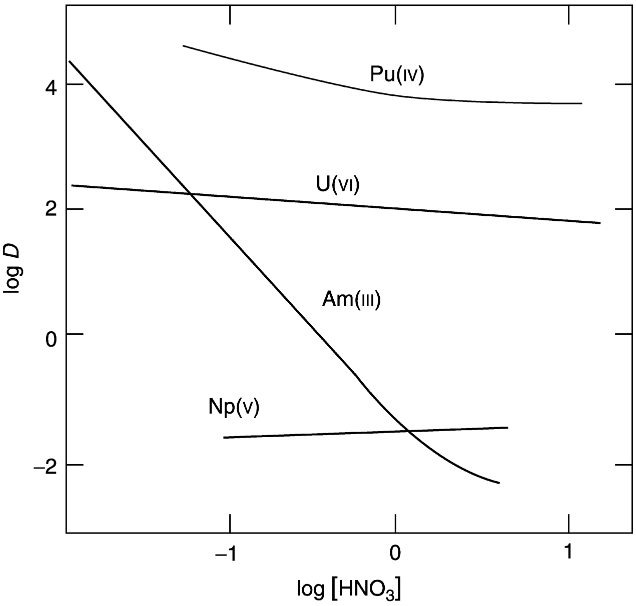
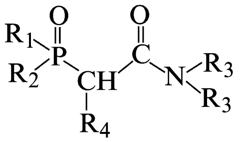


Fig. 24.8 *Dependence of extraction of Pu*(IV), *U*(VI), *Am*(III), *and Np*(V) *into* 0.5 M *HDEHP/iso-octane on nitric acid concentration* (*Myasoedov* et al., 1974).

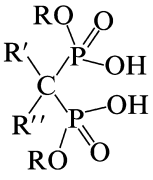
Many variations on these general structures are commercially available. They have found application for actinide/lanthanide separation and for actinide partitioning, as will be described in Section 24.3.9.

If one acidic organophosphorus binding site is good, might not two be better? In the 1960s, work in the water-treatment/detergent industry led to the production of alkyldiphosphonic acid complexing agents as substitutes for pyrophosphates in detergent formulations (Irani and Moedritzer, 1962; Carroll and Irani, 1967, 1968; Elesin *et al.*, 1972; Wada and Fernando, 1972). These complexants followed the same operational philosophy as the extractant development activity discussed in the previous paragraph: replacement of P–O–C bonds with P–C bonds increases hydrolytic stability and thereby utility of this arrangement of ligand donor groups. During the development of CMPO (most typically referring to octyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide, but the term CMPO is used to refer to carbamoylmethylphosphine oxide extractants generally; generic Structure j) and the TRUEX process, research at Argonne National Laboratory addressed the use of diphosphonate complexants as efficient actinide-stripping reagents (Nash and Horwitz, 1990; Nash, 1991, 1993b). An additional feature of these compounds is that selected representatives were devised to be readily decomposable to minimize waste volumes in process applications. The latter ligands were given the acronym TUCS, meaning thermally unstable complexants (Schulz and Kupfer, 1991; Horwitz *et al.*, 1992; Nash and Rickert, 1993).



Structure j

Chiarizia and coworkers (Chiarizia *et al.*, 1998; McAlister *et al.*, 2002; Otu and Chiarizia, 2002; Otu *et al.*, 2002) have prepared and characterized a number of dialkyl diacidic actinide extractants based on diphosphonic acids, derived from symmetric partial esterification of water-soluble diphosphonates (Structure k). These extractants have proven uniquely capable actinide sequestrants, finding unique application in analytical separations. Neutron scattering and osmometric studies of these extractants reveal unexpected patterns of extractant aggregation and cation size selectivity as the length of the alkyl chain bridging the phosphonate monoester groups changes from 1 to 6.

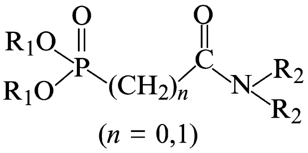


Structure k

(b) Solvating extraction systems

The ability of TBP to reject the so-called minor actinides (Np, Am, Cm) present in dissolved spent fuel was recognized as a desirable feature of this extractant system when maximizing production of plutonium and recovery of uranium were the primary motivations for processing spent nuclear fuels. However, for actinide separations in the 21st century, minimizing the toxicity of the wastes exiting a production facility must become an equally important factor in process operations. In most countries operating a closed loop nuclear fuel cycle today, recovery of the minor actinides for isolation or transmutation has become more desirable. To recover americium and curium from spent nuclear fuel using TBP would demand reduction of the acidity of the aqueous feed and the addition of salting out reagents like $NaNO_3$. Both of these actions will increase the volume of wastes and therefore are unacceptable. Neptunium can in principle be recovered as either Np(IV) or Np(VI), but neither oxidation state has adequate stability in nitric acid to prevent its dispersal to undesirable portions of the process under the ambient conditions prevailing in a process facility (i.e. moderate concentrations of nitric acid, radiolysis). Within the structure of a modern processing facility, what is needed is a reagent that will complement TBP (most probably a solvating extractant) by accomplishing the complete and selective recovery of the minor actinides from strongly acidic solutions. A significant fraction of research on actinide separations today seeks to develop such reagents and processes for their use.

In the early 1960s, a few bidentate carbamoyl phosphonate compounds (Structure 1) were synthesized (Siddall, 1963a, 1964) and their utility for the extraction of trivalent americium, cerium, and promethium from moderately acidic solutions demonstrated. The bifunctional nature of the extractant reduces the impact of competition between HNO_3 and the target metal ion for the primary extractant binding site ($P=O$). Schulz and coworkers (Schulz and McIsaac, 1975; Schulz and Navratil, 1982) revived interest in synthesis of new compounds of this class and in their utilization for the extraction of actinides and lanthanides. Since that time, several groups in the United States (of greatest note, the Horwitz group at Argonne National Laboratory) and other parts of the world have synthesized numerous derivatives of CH_2-bridged (CMPs) and unbridged (CPs) extractants and studied the extraction behavior of hexavalent, tetravalent, and trivalent actinides and a few lanthanides using the extractant alone (Martella and Navratil, 1979; Navratil and Thompson, 1979; Petrzilova *et al.,* 1979; Horwitz *et al.*, 1981, 1982; Kalina *et al.*, 1981b; Hugen *et al.*, 1982; McIsaac, 1982; McIsaac and Baker, 1983; Kalina and Horwitz, 1985; Akatsu and Kimura, 1990; Rapko, 1995) or in combination with TBP in various diluents (Mathur *et al.*, 1991, 1992a).



(n = 0,1)

Structure 1

Slope analysis studies at radioanalytical concentrations established the stoichiometry of the extracted complexes of trivalent actinides and lanthanides from NO_3^- and SCN^- media, and those of U(VI) and Th(IV) from the NO_3^- medium by CMP from the equilibria:

$$M^{3+}_{aq} + 3NO^-_{3\,aq} + 3CMP_{org} \rightleftarrows M(NO_3)_3 \cdot 3CMP_{org} \tag{24.10}$$

$$M^{3+}_{aq} + 3SCN^-_{aq} + 4CMP_{org} \rightleftarrows M(SCN)_3 \cdot 4CMP_{org} \tag{24.11}$$

$$UO^{2+}_{2\,aq} + 2NO^-_{3\,aq} + 2CMP_{org} \rightleftarrows UO_2(NO_3)_2 \cdot 2CMP_{org} \tag{24.12}$$

$$Th^{4+}_{aq} + 4NO^-_{3\,aq} + 3CMP_{org} \rightleftarrows Th(NO_3)_4 \cdot 3CMP_{org} \tag{24.13}$$

where M^{3+} = trivalent actinides and lanthanides. In the case of the Am system, the slope of the straight line for log D vs log [CMP] plot was only 3.6 in the thiocyanate system implying the presence of both tri- and tetra-solvate complexes. However, while using the mixture of CMP and TBP, americium and promethium were extracted from a NO_3^- medium as $M(NO_3)_3 \cdot (2.6)$ CMP·0.4 TBP. Complete coordination of all possible ligand donor atoms (bidentate nitrate and CMP molecules) would require unusually large complex coordination numbers. It is believed in general that the denticity of the CMP ligands is less than two in most of these species with the P=O group preferentially coordinated.

Ultimately, the CMP and CP extractants proved inadequate for the task of trivalent actinide recovery from nitric acid solutions of moderate concentration as are encountered in the raffinate from the first stages of PUREX processing. Ligand development procedures conducted over an extended period led Horwitz and coworkers to conclude that the extractant CMPO represents the best combination of features around which to build an effective industrial-scale process for total actinide recycle, including their extraction in the trivalent oxidation state. The greater basicity of the phosphine oxide overcomes the principal weakness of the CP and CMP class of ligands.

The nature of U(VI) and Pu(IV) species extracted into the organic phase from NO_3^- medium with CMPO can be given by the following equilibria:

$$\mathrm{UO_{2\,aq}^{2+} + 2NO_{3\,aq}^{-} + 2CMPO_{org} \rightleftarrows UO_2(NO_3)_2 \cdot 2CMPO_{org}} \tag{24.14}$$

$$\mathrm{Pu_{aq}^{4+} + 4NO_{3\,aq}^{-} + 2CMPO_{org} \rightleftarrows Pu(NO_3)_4 \cdot 2CMPO_{org}} \tag{24.15}$$

There has been a lot of interest in the extraction of Am(III) and Eu(III) by CMPO from aqueous media containing NO_3^-, SCN^-, ClO_4^- or $NO_3^- + ClO_4^-$. The extraction equilibria can be given as:

$$\mathrm{M_{aq}^{3+} + 3NO_{3\,aq}^{-} + 3CMPO_{org} \rightleftarrows M(NO_3)_3 \cdot 3CMPO_{org}} \tag{24.16}$$

$$\mathrm{M_{aq}^{3+} + 3SCN_{aq}^{-} + 3CMPO_{org} \rightleftarrows M(SCN)_3 \cdot 3CMPO_{org}} \tag{24.17}$$

$$\mathrm{M_{aq}^{3+} + 3\,ClO_{4\,aq}^{-} + 3\,CMPO_{org} \rightleftarrows M(ClO_4)_3 \cdot 3CMPO_{org}} \tag{24.18}$$

$$\mathrm{M_{aq}^{3+} + NO_{3\,aq}^{-} + 2ClO_{4\,aq}^{-} + 3CMPO_{org} \rightleftarrows M(NO_3)(ClO_4)_2 \cdot 3CMPO_{org}} \tag{24.19}$$

The thermodynamic features of these reactions will be discussed in Section 24.3.5. The work of Dozol and coworkers (Delmau *et al.*, 1998, 1999; Arduini *et al.*, 2000; Dozol *et al.*, 2000; Garcia-Carrera *et al.*, 2001; Gruener *et al.*, 2002; Teixidor *et al.*, 2002; Arnaud-Neu *et al.*, 2003; Schmidt *et al.*, 2003) and of Scott (Peters *et al.*, 2002) has sought to introduce an element of molecular recognition into CMPO–actinide coordination complexes with the creation of polydentate podand structures based on rigid alkyl backbones and calixarenes. These intriguing structures have yet to produce startling advances in actinide separations.

The process based on the use of CMPO is the TRUEX process (Vandegrift *et al.*, 1984, 1993; Horwitz and Schulz, 1990; Horwitz and Chiarizia, 1996). The TRUEX process solvent consists of 0.2–0.25 M CMPO and 1.0–1.4 M TBP (depending on the nature of the diluent, with a normal paraffinic hydrocarbon preferred). Because this solvent can simultaneously extract the actinides in the oxidation states important in technological processes, it could have significant impact in the reduction of the volume of high-level waste requiring burial in a geological repository. There has been one report that proposes an oxidation state selective separation of actinides based on the use of TRUEX extraction and a diphosphonic acid complexant (Nash and Rickert, 1993).

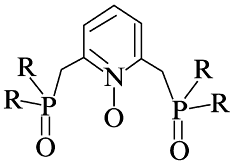
The neutral bifunctional extractants (CMPs, CMPOs, and related compounds) have been applied to a few analytical-scale separations as well. Horwitz *et al.* (1981) studied the separation of the trivalent actinides from Am to Fm (Table 24.5) using dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP) and aqueous nitrate solutions. Steadily decreasing distribution ratios are observed for the lanthanides, but a much smaller decrease is found for the trivalent actinides. These results suggest possible interlanthanide

Table 24.5 *Separation factors (relative to Am) for solvent extraction of trivalent lanthanides and actinides with* 0.817 M *DHDECMP/DIPB/*1.0 M *HNO_3 from (Horwitz* et al., 1981). *For separation factors of adjacent elements, M represents the higher, M′ the next lower value in the table. (i.e. next lower atomic number).*

Actinides	S_M^{Am}	$S_M^{M'}$	*Lanthanides*	S_M^{Am}	$S_M^{M'}$
Fm	0.575	–	Lu	0.048	–
	–	1.04		–	1.41
Es	0.595	–	Yb	0.067	–
	–	1.15		–	1.34
Cf	0.685	–	Tm	0.090	–
	–	1.05		–	1.15
Bk	0.719	–	Y	0.103	–
	–	0.90		–	1.29
Cm	0.649	–	Er	0.133	–
	–	1.54		–	1.40
Am	1.00	–	Ho	0.186	–
				–	1.43
			Dy	0.266	–
				–	1.32
			Tb	0.351	–
				–	1.15
			Gd	0.403	–
				–	1.49
			Eu	0.602	–
				–	1.22
			Sm	0.735	–
				–	1.16
			Pm	0.855	–
				–	1.12
			Nd	0.962	–
				–	1.26
			Pr	1.21	–
				–	1.12
			Ce	1.36	–
				–	1.04
			La	1.41	–

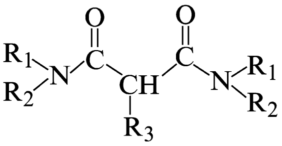
(but probably not interactinide) separations. The adaptation of CMPOs to extraction chromatography has led to the development of additional selective separations methods based on these reagents, to be discussed in Section 24.4.4b. Continued development of phosphine oxide ligand types and processes based on their use has produced a simplified version of the CMPO ligands (and an alternative TRUEX process, discussed in Sections 24.4.4b(i)–(iv)) and tridentate pyridine-*N*-oxide bisphosphine oxide reagents (Structure m) that exhibit useful actinide separations properties (Paine, 1995; Bond *et al.*, 1997, 1998; Nash *et al.*, 2002). Chmutova *et al.* (1975) have demonstrated that alkylene phosphine dioxides exhibit some ability to enhance the separation of californium from americium ($S_{\mathrm{Cf}}^{\mathrm{Am}} \approx 25$), and berkelium from curium ($S_{\mathrm{Bk}}^{\mathrm{Cm}} \approx 10$).

A considerable body of research has been developed by Karandashev and coworkers (Turanov *et al.*, 2000, 2002, 2004) on the subject of lanthanide extraction by bisphosphine oxide (and structurally similar) podands that should have strong analogies to actinide separations, though this latter opportunity has not been extensively investigated.



Structure m

A new class of solvating extractants has been introduced during the past decade as non-phosphorus-containing alternatives to CMPO for total actinide recycle. Amidation of the well-studied lanthanide/actinide complexant malonic acid yields lipophilic complexants that exhibit affinity for actinides in the trivalent, tetravalent, and hexavalent oxidation states. Malonamide extractants (Structure n) were proposed initially by Musikas and coworkers in the 1980s and have seen extensive investigation during the intervening years (Musikas, 1987; Cuillerdier *et al.*, 1991a; Nakamura *et al.*, 1995; Nigond *et al.*, 1995; Berthon *et al.*, 1996, 2001; Delavente *et al.*, 1998, 2001, 2003; Erlinger *et al.*, 1998, 1999; Mahajan *et al.*, 1998; Iveson *et al.*, 1999; Madic *et al.*, 2002). These extractants, functionalized at the α-carbon atom with either long chain alkyl groups or alkoxides to improve phase compatibility, compare favorably with CMPO in many respects. The process built around these extractants is referred to as the DIAMEX process.



Structure n

The DIAMEX system has a steeper nitric acid dependence than is seen for CMPO, requiring that the aqueous feed be maintained above 3 M HNO_3 for adequate phase transfer. However, a steep acid dependence also implies more facile stripping of the actinides from the loaded organic phase. The primary advantage of this class of reagents, containing only carbon, hydrogen, oxygen, and nitrogen (CHON), is their ability to be completely incinerated leaving no ash behind when the end of their useful lifetime arrives. A further and in some respects equally important advantage of the malonamides is the innocuous character of the degradation products of diamides. Unlike the phosphinic acid, compounds that are produced as CMPO is degraded (to be discussed in Section 24.4.4b(iv)) or the dibutylphosphoric acid from TBP, the carboxylates and amines resulting from the degradation of diamides do not appear to interfere appreciably with the ease of stripping of actinides from the loaded extractant phase. This positive feature is counterbalanced by a slightly faster rate of radiolytic degradation than is seen for CMPO or TBP. Phase compatibility issues in large-scale tests to date have indicated a moderate tendency toward (third-phase formation) and led to adjustments in both the extractant and diluent.

Extraction of Am(III), U(VI), Np(IV), Fe(III), Sr(II), and Cs(I) from solutions of different HNO_3 concentrations using 1 M dimethyldibutyltetradecylmalonamide (DMDBTDMA in *n*-dodecane and that of americium from a synthetic PHWR–HLW (pressurized heavy water reactor–high level waste) has been reported (Mahajan *et al.*, 1998). It is suggested that this amide is very promising for the extraction of americium and other actinides from 3–4 M HNO_3, particularly under high loading of Nd or a mixture of Nd and U. The extraction of trivalent, tetravalent, and hexavalent actinides from HNO_3 medium by DMDBTDMA/*n*-dodecane can be represented by the equilibria:

$$\mathrm{Am}^{3+}_{\mathrm{aq}} + 3\mathrm{NO}^{-}_{3\,\mathrm{aq}} + 2\mathrm{A}_{\mathrm{org}} \rightleftarrows \mathrm{Am(NO_3)_3}\cdot 2\mathrm{A}_{\mathrm{org}} \qquad (24.20)$$

$$\mathrm{Pu}^{4+}_{\mathrm{aq}} + 4\mathrm{NO}^{-}_{3\,\mathrm{aq}} + 3\mathrm{A}_{\mathrm{org}} \rightleftarrows \mathrm{Pu(NO_3)_4}\cdot 3\mathrm{A}_{\mathrm{org}} \qquad (24.21)$$

$$\mathrm{UO}^{2+}_{2\,\mathrm{aq}} + 2\mathrm{NO}^{-}_{3\,\mathrm{aq}} + 2\mathrm{A}_{\mathrm{org}} \rightleftarrows \mathrm{UO_2(NO_3)_2}\cdot 2\mathrm{A}_{\mathrm{org}} \qquad (24.22)$$

These species have very similar stoichiometries to those observed for CMPO. The same diamide when adsorbed on an inert support is also efficient for the uptake of trace quantities of actinide ions from 3–5 M HNO_3. Batch studies show reasonable uptake of actinides from synthetic PHWR–HLW, only when it has been given two contacts with 20% TBP/*n*-dodecane (Mohapatra *et al.*, 2000).

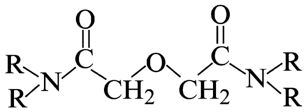
Hydrolytic and radiolytic degradation of *n*-dodecane solutions of three malonamides, DMDBTDMA, *N*,*N*′-dimethyl-*N*,*N*′-dibutyldodecyloxyethyl malonamide (DMDBDDEMA), and *N*,*N*′-dimethyl-*N*,*N*′-dioctylhexyloxyethyl malonamide (DMDOHEMA), in the presence of HNO_3 have been conducted (Berthon *et al.*, 2001). The results of a similar investigation of *N*,*N*,*N*′,*N*′-tetraoctyl-3-oxapentane-1,5-diamide (TODGA) has also been reported (Sugo *et al.*, 2002). Degradation products were identified using gas chromatography coupled to Fourier transform infrared spectroscopy (FTIR) or mass spectrometry. The primary degradation products are a variety of amide–acid species and secondary amines $R'–CH_3NH$. The amide–acids are thermally unstable and decarboxylate to form monoamides. The other products such as amide–lactone, diamides, carboxylic acids, and alcohol are formed but their concentrations in the organic phase are much lower than the three mentioned above. It has been observed that D_{Am} and D_{Ln} values decrease with increasing irradiation doses. In a comparative study on the radiolysis of 1 M solution of

TBP, DMDBTDMA, and DMDOHEMA in TPH (hydrogenated tetrapropene or 4,4-dipropyl heptane) in contact with 4 M HNO_3 with an integrated dose of 0.7 M Gy, the concentrations found after radiolysis were respectively 0.95, 0.68, and 0.57 M. For these process representative conditions, the stability of malonamides is lower than that of TBP by a factor of 6–9.

DMDBTDMA/*n*-dodecane has been used as carrier in supported liquid membranes (SLM) studies for the facilitated transport of Am(III) using 1–5.5 M of HNO_3 as the feed solution and 0.01 M HNO_3 as the strip solution (Sriram *et al.*, 2000). It is interesting to note that under similar conditions, the permeability of Fe(III) was significantly lower than that of Am(III). In another study (Sriram and Manchanda, 2002), several other diluents apart from *n*-dodecane were used to prepare solutions of DMDBTDMA and the transport of U(VI), Pu(IV), Am(III), and Eu(III) from HNO_3 medium using a SLM technique was carried out. The stripping agent containing a mixture of 0.4 M formic acid, 0.4 M hydrazine hydrate, and 0.1 M DTPA was most promising.

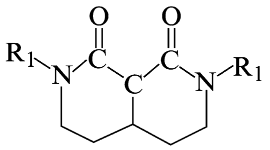
Madic and coworkers (Spjuth *et al.*, 2000) have synthesized seven new compounds in the malonamide series by introducing an ether oxygen into the alkyl chain attached to the bridging methylene group or of phenyl substituents on the nitrogen. These modifications reduce the basicity of the new derivatives to less than that of DMDBTDMA. The extraction of Am from HNO_3 by different malonamides in *t*-butylbenzene diluent has shown that the D_{Am} is higher for the malonamides with low basicity than that for DMDBTDMA.

Taking the cue from the malonamide work, researchers at the Japan Atomic Energy Research Institute (JAERI) have synthesized six diglycolamides (Structure o) having the generic formula R,R–N–CO–CH_2–O–CH_2–CO–N–R,R where R is an alkyl group having carbon atoms ranging from 3 to 10 (Sasaki *et al.*, 2001). Of these, only two compounds, namely, *N*,*N*,*N*′,*N*′-tetra(octyl)-3-oxapentanediamide (TODGA) and *N*,*N*,*N*′,*N*′-tetradecyl-3-oxapentanediamide (TDDGA) showed adequate solubility in *n*-dodecane to be useful for process development. Using TODGA the *D* values of actinides increased with increasing HNO_3 concentrations and the number of diglycolamide molecules attached to the extracted actinide ions (derived from slope analysis at radioanalytical concentrations of the metal ions) were three for Th(IV), U(VI), and Pu(IV) and four for Am(III) and Cm(III). TODGA in *n*-dodecane has been shown to extract both actinides and lanthanides completely from HNO_3 solutions.



Structure o

Additional basic work continues on this class of reagents on many fronts in France, in Japan with the development of diglycolamide extractants (Sasaki *et al.*, 2001; Sasaki and Tachimori, 2002) and in the U.S., with the report of a structurally–hindered diamide (Lumetta *et al.*, 2002, 2003) that exhibits greater affinity for trivalent actinides than the free rotation analogs (Structure p). Work also progresses on monoamides as possible replacements for TBP in a PUREX-like extraction system. The ultimate potential of this class of extractant molecules has perhaps not yet been reached.



Structure p

(c) Ion pair formation systems

Two classes of alkyl amine extraction systems are known, tertiary and quaternary amines. Tertiary amines are electroneutral species that are readily protonated to form lipophilic salts ($R_3NH^+X^-$) while quaternary amines are tetraalkylammonium ions (R_4N^+) bearing a permanent positive charge and always associated with an anion in the organic phase. Both extractant classes have a tendency toward the formation of reverse micelles in organic solutions.

Tertiary amines require preequilibration with concentrated acid to create the ion pair. However, this protonation reaction introduces an additional means of adjusting the extraction chemistry of such systems. The efficiency of this class of extractants is impacted by both the salt concentration in the aqueous contacting solution and its acid concentration. Quaternary ammonium extractants are analogous to tetraalkylammonium based anion exchange resins and bear some kinship to the room temperature ionic liquids that will be discussed in Section 24.3.10.

Moore (1964) first applied quaternary amines to lanthanide/actinide group separations examining the system Aliquat 336[2]/xylene/H_2SO_4–NH_4SCN.

A principal advantage of this method is the relatively low concentration of salts required to attain a usable separation. Several other applications of the method have been summarized (Weaver, 1974). This class of extractants can be immobilized on an inert support to create extraction chromatographic materials that combine the best features of the extractants with the increased efficiency of extraction chromatography. Horwitz *et al.* (1995) have reported the application of the effect of thiocyanate for the selective separation of actinides from lanthanides using such resins (Fig. 24.9). When loaded from a solution 1.0 M NH_4SCN/0.1 M HCO_2H, trivalent actinides (represented by Am^{3+}) are quantitatively sorbed while lanthanides (from La to Eu) are rejected. Americium can be eluted from the column with 0.25 M HCl for a very selective actinide/lanthanide separation.

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[2] Aliquat 336-nitrate is tri(C8-10 alkyl)methylammonium nitrate

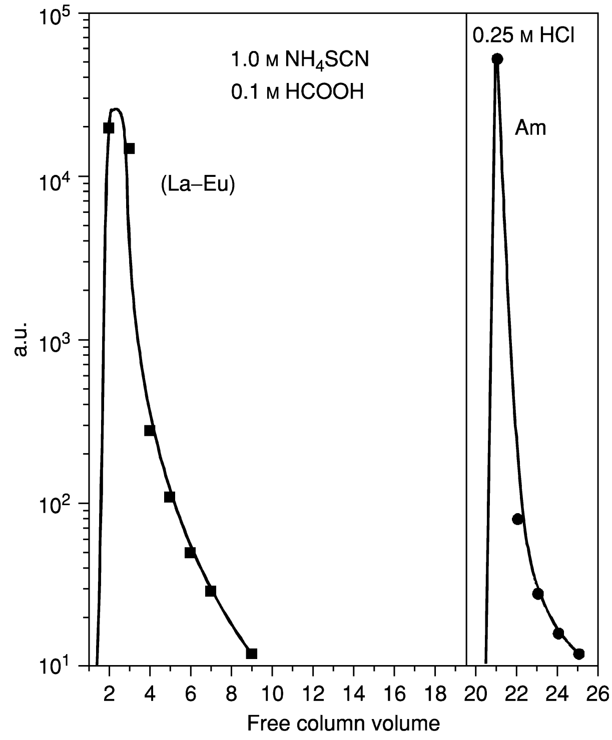


Fig. 24.9 *Partitioning of trivalent lanthanides and actinides on U-TEVA resin™* (*Horwitz* et al., 1995).

(d) Synergistic systems

The principal feature of synergistic extraction systems is increased extraction strength. Improved extraction efficiency often comes at the expense of selectivity. This is seen in the extraction of lanthanides from xylene solutions of TTA and TTA/TBP mixtures for which the separation factors (normalized to Lu^{3+}) are shown in Fig. 24.10. A linear correlation is observed between the separation factors and the position of the lanthanide ions through the series for the extraction of $Ln(TTA)_3$, whereas for extraction of $Ln(TTA)_3(TBP)_2$ separation of adjacent cations is observed for the light lanthanides only but not for the latter members of the series. The relevant literature on trivalent lanthanide/actinide separations by synergistic systems was reviewed by Mathur (1983).

Extensive investigations of 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone (PMBP, Structure q) by Chmutova *et al.* (1973) indicate that the synergistic enhancement for TBP and TOPO adducts (in benzene) of the trivalent actinides (extracted from nitric acid) increase in the order Am < Cm < Bk < Cf. However, Khopkar and Mathur (1982) do not observe any particular order in

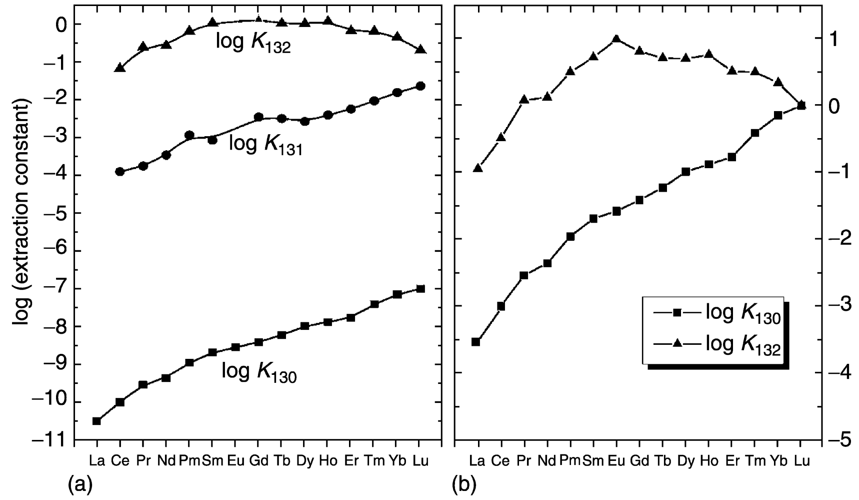
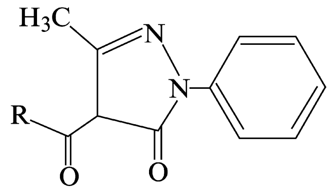


Fig. 24.10 *The effect of adding a synergist on extraction efficiency and comparative extraction of trivalent lanthanides in the TTA–TBP system*: (*a*) *extraction equilibrium constants for the reactions* $M^{3+} + 3\ HTTA \rightleftarrows M(TTA)_3 + 3\ H^+$ (K_{130}) (*Poskanzer and Foreman*, 1961), $M(TTA)_3 + TBP \rightleftarrows (M(TTA)_3TBP$ (K_{131}), *and* $M(TTA)_3 + 2\ TBP \rightleftarrows M(TTA)_3(TBP)_2$ (K_{132}) (*Farbu* et al., 1974). (*b*) *Comparative data normalized to log* $K_{Lu} = 0$.

the extraction of these metal ions from hydrochloric acid solutions into the same extractant mixtures with xylene as diluent.



Structure q

While such reagents possess interesting cation coordination properties, ligands designed for size-selective metal ion coordination, the crown ethers (CE), calixarenes, and related species have been employed primarily as synergists for An(III) separations. As yet, no important separations of actinides have been developed based on the application of such species as a primary extractant. The use of benzo-15-crown-5 (Bz15-C-5), and dicyclohexano-18-crown-6 (DCH18-C-6) as synergists for lanthanide and actinide extraction with 1-phenyl-3-methyl-4-trifluoroacetyl-5-pyrazolone (PMPFT)/chloroform suggest some potential for such mixtures to accomplish certain specific group and inter-actinide separations (Mathur and Khopkar, 1988). Aly *et al.* (1985) studied synergistic extraction using TTA and 15-crown-5 synergist for lanthanide and trivalent actinide extraction. They found significant enhancement of the extraction, but little separation of individual ions. The extracted complex is $M(TTA)_3(CE)_2$ for the 15-crown-5 synergist and $M(TTA)_3(CE)$ for the 18-crown-6.

There is also evidence that non-cyclic polyethers can function as synergists in lanthanide/actinide separations. Ensor and Shah (1983, 1984) report that 1,13-bis[8-quinolyl]-1,4,7,10,13-pentaoxatridecane (Kryptofix-5, or K-5) enhances the extraction of Ce(III), Eu(III), Tm(III), Am(III), Cm(III), and Bk(III) into chloroform solutions of TTA. The extracted complex has the stoichiometry $R(TTA)_3 \cdot K\text{-}5$, and the synergistic enhancement is comparable to that of TBP under the conditions studied. The separation factors reported for TTA alone are $S^{Cm}_{Am} = 1.1$, $S^{Bk}_{Am} = 5.25$, $S^{Cf}_{Am} = 11$, while for the mixture of TTA and K-5 the values are $S^{Cm}_{Am} = 0.87$, $S^{Bk}_{Am} = 3.4$, $S^{Cf}_{Am} = 2.5$, clearly indicating a decrease in separation efficiency.

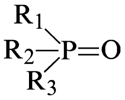
24.3.5 Thermodynamic features of actinide solvent extraction reactions

The transfer of a metal ion from an aqueous medium to an organic extractant solution and back is governed by the relative positions of several competing reversible equilibria. In the aqueous phase, hydration and protonation equilibria of metal cations, chelating agents, and metal complexes, as well as the complexation equilibria of metal ions and ligands control the relative extractability of metal ions. In the organic phase, metal–ligand bonding, non-specific and specific solvation of complexes, and ligand–ligand interactions are the most important processes contributing to the net thermodynamics of phase transfer (Nash, 2001). Because solvent extraction reactions are fundamentally mass-transfer processes, they can be driven against an unfavorable Gibbs energy gradient by manipulation of phase transfer conditions, as will be demonstrated in the discussion of trivalent ion extraction by Cyanex 301 below.

Most investigations of the thermodynamics of f-element solvent extraction reactions have been performed relying on the change in the extraction equilibrium constant (K_{ex}) as a function of temperature with application of the Van't Hoff relationship $[\partial(\ln K_{ex})/\partial(1/T) = -\Delta H/R]$. Second order thermodynamic effects resulting from changes in ΔC_p generally do not complicate the application of this technique, as the temperature range is restricted by solubility and volatility considerations to the region of 0–60°C, often significantly less. There have been several reports of enthalpy changes measured calorimetrically in synergistic systems. In these experiments, measured enthalpies describe the addition of a co-extractant to the primary chelate complex of the extracted metal ion in a homogeneous organic phase. The experimental results described below are derived from a variety of literature reports. The reader is referred to the original references for details of the experimental procedures.

The most thoroughly investigated synergistic extraction systems involving f-elements are those in which TTA is the primary extractant. Neutral organophosphorus compounds, aliphatic amines, crown ethers, bipyridyl, phenanthroline, and aliphatic sulfoxide extractants have all been investigated thermochemically as synergistic reagents for lanthanide and actinide extraction by TTA. Most of the thermodynamic data were determined using the temperature variation method, some were investigated by calorimetry, and a few systems have been studied using both techniques. Adduct formation reactions are generally exothermic (ΔH between –20 and –70 kJ mol^{-1}) while the entropies cover a wide range of both favorable and unfavorable contributions to the net equilibrium, dependent primarily on the nature of the synergist (Nash, 2001).

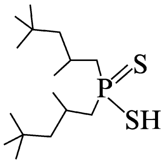
The tris-TTA complex of the lanthanides is a dihydrate or trihydrate in most organic diluents, thus the entropy change upon formation of the adduct partly reflects the ability of the synergist to displace this residual hydration. Using calorimetry, Choppin and coworkers (Caceci *et al.*, 1985) studied the addition of both TBP and trioctylphosphine oxide (TOPO, Structure r, where $R_1 = R_2 = R_3 = n$-octyl) to the neutral TTA complexes of UO_2^{2+}, Nd^{3+}, and Th^{4+} in benzene. The enthalpies of adduct formation were 10–20 kJ mol^{-1} more exothermic in the dry solvent than the water-saturated equivalent. The corresponding variations in the entropy changes almost fully compensated the variations in enthalpy changes, resulting in a constant Gibbs energy of adduct formation. Crown ether adducts on the corresponding TTA complexes (Mathur and Choppin, 1993) were characterized by negligible entropy changes in the trivalent lanthanide adducts, but moderately unfavorable entropy changes for the UO_2^{2+} and Th^{4+} complexes.



Structure r

Addition of pyridine-based donors like bipyridyl to lanthanide TTA complexes or dipivaloylmethane (also a β-diketone) is characterized by a strongly exothermic enthalpy (–40 to –70 kJ mol^{-1}) partially compensated by an unfavorable entropy change (Kassierer and Kertes, 1972; Kertes and Kassierer, 1972; Dakternieks, 1976). The synergistic extraction of lanthanides by mixtures of TTA and trialkyl amines exhibits no temperature dependence implying that the formation of the adduct from $Ln(TTA)_3$ is characterized by an enthalpy change of the same magnitude but opposite in sign to that of the extraction of the lanthanide by TTA alone. This curious observation has been made for the combination of tertiary amines and pyrazolone extractants as well.

The greater affinity of actinides for donor atoms softer than oxygen is at the heart of all successful separations of the trivalent ions of the transplutonium elements from the lanthanides (Nash, 1994). This difference in interaction strength has been attributed to a greater tendency for the actinides towards covalency in their bonding, which should, in principle, be manifested thermodynamically by exothermic complexation heats. Dithiophosphinic acid extractants [e.g. Cyanex 301, bis(2,4,4-trimethylpentyl)dithiophosphinic acid, Structure s] have been shown to exhibit separation factors of greater than 10^3 for trivalent actinide ions over lanthanides of comparable size. Cyanex 301 when purified and used for the extraction of Am(III) and Eu(III) from nitrate medium gave an $S_{\mathrm{Eu}}^{\mathrm{Am}}$ of 5.9 × 10^3 (Zhu *et al.*, 1996). The $S_{\mathrm{M}}^{\mathrm{M}'}$ for other lanthanides was found to be Am/La ~3500, Am/Ce ~1000, Am/Pr ~1000, Am/Nd ~1900, Am/Sm ~4500. The average Am/Ln $S_{\mathrm{M}}^{\mathrm{M}'}$ being greater than 2300.



Structure s

The work of Tian *et al.* (2001) has demonstrated that Am/Eu separation factors above 10^3 can be seen even in partially degraded solvents when excess lanthanides are present in the aqueous phase. Excess non-radioactive lanthanides tend to mask the deleterious effect of degradation products of Cyanex 301 (oxygenated phosphinic acid extractant molecules in particular) on Am/Eu separation factors by competing more strongly than Am for the oxygenated species. Lanthanide saturation of the oxygenated degradation products allows the soft-donor interaction between Am and the thio phosphinates to be maintained.

These authors also have calculated thermodynamic parameters based on the measurement of distribution ratios as a function of temperature the enthalpy associated with extraction of Am^{3+} and Eu^{3+} from 1.0 M Na/HNO_3 by purified Cyanex 301. Tian *et al.* report $\Delta H_{\mathrm{Am}} = +18.1$ kJ mol^{-1}, $\Delta H_{\mathrm{Eu}} = +43.6$ kJ mol^{-1} with corresponding entropy changes of $\Delta S_{\mathrm{Am}} = -87$ J K^{-1} mol^{-1}, $\Delta S_{\mathrm{Eu}} = -66$ J K^{-1} mol^{-1}. Though both phase transfer reactions are characterized by unfavorable endothermic enthalpic effects and negative entropies, analysis of the data indicates that the enthalpy difference between the americium and the europium extraction is the principal source of the greater selectivity of Cyanex 301 for Am^{3+} [$(\Delta H_{\mathrm{Am}} - \Delta H_{\mathrm{Eu}}) = -25.5$ kJ mol^{-1}; $-T(\Delta S_{\mathrm{Am}} - \Delta S_{\mathrm{Eu}}) = +6.3$ kJ mol^{-1}]. Both the more exothermic heat and greater order implicit in the entropy contribution are consistent with increased strength of the Am–S bonding relative to that of Eu–S.

Jensen and Bond (2002a,b) have concluded based on a combination of EXAFS, osmometry, Karl Fisher titration, and UV–visible spectrophotometry that the complexes of lanthanide and trivalent actinide ions extracted into Cyanex 301 in xylene are octahedral containing no inner sphere water molecules. They interpret this result as indicating that the difference in thermodynamic parameters is most likely a result of increased Cm–S bonding strength relative to that of Sm. Tian *et al.* (2003) argue based on EXAFS, FTIR, and MS data for the presence of eight-coordination lanthanide and actinide complexes with Cyanex 301. The lanthanide complex contains an inner-sphere water molecule that is not present in the corresponding eight-coordinate Am complex.

The most common neutral extractants for f-elements are trialkyl-phosphates, -phosphonates, -phosphinates, and -phosphine oxides. As shown in equation (24.7) describing the extraction process for systems of this class, both an appropriate number of aqueous anions to neutralize the cation charge and a variable number of extractant molecules to make the complex lipophilic are needed. This assembly of a number of components to form a single product species suggests that the net extraction entropy for such reactions should be consistently negative. In fact, for extraction of trivalent lanthanides, actinides, Th^{4+}, and UO_2^{2+} by simple monodentate or complex bidentate organophosphorus extractants (which represent the bulk of such neutral extractant systems) the extraction entropies range between –40 and –150 J K^{-1} mol^{-1}independent of the nature of the counter ion X^-. Extraction enthalpies are exothermic and in the range of –30 to –90 kJ mol^{-1}, implying a net increase in bonding strength for the phase transfer reaction (though the origin of the increased bonding strength cannot be established from such investigations) (Nash, 2001).

The relative extraction of trivalent lanthanides and actinides in neutral systems has been examined by comparing Am^{3+} and Eu^{3+} extraction by CMPO (Mathur and Nash, 1998; Suresh *et al.*, 2001) and DHDECMP (Horwitz *et al.*, 1981; Muscatello *et al.*, 1982). The stoichiometries of the extraction equilibria are as described above. The thermodynamic data (ΔG, ΔH, and ΔS) for the extraction of Am(III) and Eu(III) species from NO_3^- and SCN^- media with CMP and NO_3^-, SCN^-, ClO_4^-, and $ClO_4^- + NO_3^-$ media with CMPO are given in Table 24.6. The thiocyanate systems demonstrate a greater selectivity for americium corresponding to an increased Gibbs energy change of 4–5 kJ mol^{-1} (a separation factor of 5–7). Substantially more exothermic extraction enthalpies are observed in both the Eu^{3+} and Am^{3+} thiocyanate systems than is seen in the corresponding nitrate reactions. This difference has been attributed, based on data tabulated by Marcus (1997), to the greater exothermicity of the transfer three SCN^- ions from the aqueous to a normal alkane organic phase as compared with the transfer of three nitrate anions (Mathur and Nash, 1998). Differences in the enthalpy of extraction of americium relative to europium are not substantial or consistent enough to attribute the enhanced extraction of the actinide to a soft donor-effect.

24.3.6 Aqueous biphasic systems

Some research has been done on liquid–liquid extraction systems that seek to eliminate hydrophobic organic materials. For example, polyethylene glycols can produce two-phase systems (called aqueous biphases) when equilibrated with concentrated salt solutions of water-structuring anions (Rogers *et al.*, 1993). The key characteristic of these systems is that the immiscible phases are both largely aqueous in nature. Myasoedov and Chmutova (1995) have reported conditions for the separation of transplutonium elements from uranium, thorium, and lanthanides. The aqueous biphase itself does not extract actinides

Table 24.6 *Thermodynamic parameters for Am*(III) *and Eu*(III) *extraction from nitrate, thiocyanate, perchlorate, and nitrate + perchlorate media using neutral donors CMPO and CMP at* 25°C.

System	ΔG (kJ mol^{-1})	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	*Reference*
$Am(NO_3)_3 \cdot 3$ CMPO	–24.3	–66.5	–142	Suresh *et al.* (2001)
$Eu(NO_3)_3 \cdot 3$ CMPO	–25.8	–65.3	–133	Suresh *et al.* (2001)
$Am(SCN)_3 \cdot 3$ CMPO	–42.3	–92.3	–168	Suresh *et al.* (2001)
$Eu(SCN)_3 \cdot 3$ CMPO	–37.8	–114.2	–256	Suresh *et al.* (2001)
$Am(ClO_4)_3 \cdot 3$ CMPO	–25.3	–39.1	–46	Suresh *et al.* (2001)
$Eu(ClO_4)_3 \cdot 3$ CMPO	–23.8	–67.4	–146	Suresh *et al.* (2001)
$Am(NO_3)(ClO_4)_2 \cdot 3$ CMPO	–32.3	–124.8	–310	Suresh *et al.* (2001)
$Eu(NO_3)(ClO_4)_2 \cdot 3$ CMPO	–30.6	–139.2	–365	Suresh *et al.* (2001)
$Am(NO_3)_3 \cdot 3$ CMPO	–32.2	–49.4	–58	Mathur and Nash (1998)
$Eu(NO_3)_3 \cdot 3$ CMPO	–32.8	–64.5	–106	Mathur and Nash (1998)
$Am(SCN)_3 \cdot 3$ CMPO	–57.4	–89.9	–109	Mathur and Nash (1998)
$Eu(SCN)_3 \cdot 3$ CMPO	–51.6	–83.8	–108	Mathur and Nash (1998)
$Am(NO_3)_3 \cdot 3$ CMP	–6.67	–42.3	–120	Horwitz *et al.* (1981)
$Eu(NO_3)_3 \cdot 3$ CMP	–6.68	–37.4	–103	Horwitz *et al.* (1981)
$Am(SCN)_3 \cdot 3.6$ CMP	–44.4	–87.4	–144	Muscatello *et al.* (1982)
$Eu(SCN)_3 \cdot 4$ CMP	–40.5	–94.1	–179	Muscatello *et al.* (1982)

strongly, but Arsenazo III (2,7-bis(2,2′-arsonophenylazo)-1,8-dihydroxy-naphthalene-3,6-disulfonic acid) is a highly effective carrier for these metal ions. A method for preparation of an isotope generator for ^{239}Np from ^{243}Am using an ammonium sulfate solution containing potassium phosphotungstate has also been reported (Molochnikova *et al.*, 1995). Overall, while the aqueous biphasic extraction approach brings forward some interesting features, the high salt concentrations needed to generate the biphase work against its utility for large-scale separations. Polyethylene glycols remain useful compounds when employed as phase modifiers in conventional solvent extraction.

24.3.7 Actinide separations from Alkaline Solutions

Alkaline conditions tend, in general, to lead to the precipitation of actinide hydroxides. However, much of the actinide inventory within the waste system in the U.S. is found in (or in contact with) such solutions, and the tendency of actinides to precipitate from alkaline solutions can be overcome by water-soluble chelating agents. There are a few examples of the separation of lanthanides and actinides from alkaline and carbonate solutions, as reviewed by Karalova *et al.* (1988). Both solvating and chelating extractants have been used in these studies. Ternary and quaternary amines, alkylpyrocatechols, β-diketones, pyrazolones, and *N*-alkyl derivatives of aminoalcohols are the extractants indicated as useful for alkaline extraction processes. A variety of diluents have been used, but their nature seems to have little effect on the extraction efficiency or separation factors.

The factors contributing to a successful separation procedure in alkaline media are not different from those relevant in acidic solutions, i.e. the efficiency is dependent on the nature of the extractant and the aqueous complexant, the pH of the aqueous solution, and the strength of aqueous complexes. Two advantages provided by this approach are the relative ease of back extraction (contact with neutral salt solutions is usually sufficient) and the potential for separations based on relative rates of phase transfer reactions. The disadvantage (from a practical standpoint) is the requirement of working with concentrated salt solutions, which creates waste disposal problems. However, the potential for reducing the transuranium element (TRU) content of alkaline wastes justifies a search for viable separation schemes based on alkaline solutions.

Extraction from alkaline and carbonate solutions is characterized by an unusual sequence of the distribution ratios favoring the trivalent oxidation state [in carbonate solutions the order of extraction is M(III) > M(IV) > M(V) > M(VI)]. A further benefit of operation in alkaline solutions is the greater tendency for air oxidation of some trivalent metal ions. Group separation factors for the trivalent actinides and lanthanides are about 2 for extraction by Aliquat 336-EDTA in contact with an alkaline EDTA aqueous solution (Bukina *et al.*, 1983). Eu–Am separation factors of 70 have been reported for a non-equilibrium extraction in the system 4-(α,α-dioctylethyl)-pyrocatechol/NaOH/DTPA (or DTPMPA, diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentamethylenephosphonic acid) (Karalova *et al.*, 1982). In contrast with most acid-medium separation systems, the separation factors are based mainly on the difference in the *rates* of the metal–DTPA (or DTPMPA) complexation reactions for europium and americium rather than chemical equilibria. They are, therefore, highly dependent on the contact time. A principal limitation to the practical application of separation schemes based on alkaline solutions is the relatively long contact times (more than 10 min) required for extraction.

24.3.8 Separations of actinides involving natural agents

Several natural agents present in plants (Dushenkov *et al.*, 1997; Huang *et al.*, 1998; Thulasidas *et al.*, 1999) or more generally biomass (Anonymous, 1951; Dhami *et al.*, 1998a,b; Banaszak *et al.*, 1999), jimson weeds (Anonymous, 1995), tannin biomolecules (Sakaguchi and Nakajima, 1987, Nakajima and Sakaguchi, 1990), siderophores (Whisenhunt *et al.*, 1993), chitosan (a natural biopolymer derivative of chitin) (Anonymous, 1995; Park *et al.*, 1999; Srinivasan *et al.*, 2001) etc. have been considered for actinide separations from very dilute solutions. Our emphasis here will be on non-living microbial biomass, a common fungus *Rhizopus arrhizus* (*RA*), which has chitin chains inside its cell walls, and chitosan which is a natural biopolymer derivative of chitin extracted from crab shell.

A detailed study on the biosorption of uranium and thorium by *RA* has been carried out by Tsezos and coworkers (Tsezos and Volesky, 1981, 1982; Tsezos, 1983) where they have reported very high uptake of uranium from aqueous solutions to the extent of 180 mg U per gram of *RA*. The highest uptake of the metal ions was between pH 4 and 5. The presence of Cu^{2+}, Zn^{2+}, and Fe^{2+} ions interfered in the biosorption of uranium and thorium. The mechanism of uranium sequestering by *RA* has been studied by using techniques like electron microscopy, X-ray energy dispersion analysis, and IR spectroscopy. It has been proposed that the total sorption of uranium is the cumulative effect of three processes: formation of uranium coordination compounds with the amine nitrogen of the chitin chains, adsorption of uranium to the polyalcohol surface of the chitin matrix, and hydrolysis of the U–chitin complex formed, resulting in the precipitation of the hydrolysis product in the cell wall (Tsezos and Volesky, 1982). Sorption of radionuclides ^{233}U, ^{239}Pu, ^{241}Am, ^{144}Ce, ^{147}Pm, ^{152,154}Eu, and ^{95}Zr from aqueous nitrate medium (pH 2–11) has been studied with *RA*: it was suggested that *RA* is an effective biomass for the removal of actinides and trivalent fission product lanthanides from low-level waste streams generated in PUREX process and also in the secondary wastes generated from the TRUEX process (Dhami *et al.*, 1998a,b).

The adsorption of uranyl ion on powdered chitosan is characterized by a high affinity in neutral pH range; however the adsorption capacity of chitosan at relatively high pH decreases due to the presence of negatively charged uranyl species in the solution (Park *et al.*, 1999). Chitosan has been found to be a good natural material for the sorption of ^{241}Am at a pH of 3 (Srinivasan *et al.*, 2001).

24.3.9 Trivalent actinide/lanthanide separation systems

The classic historical methods of separating trivalent actinides from fission product lanthanides are based on ion exchange, as discussed in Section 24.2.4. However, as is seen in Section 24.3.4, solvent extraction techniques have a wider range of applications. One approach to accomplishing trivalent actinide/lanthanide separation by solvent extraction is to apply consecutively two unrelated separation processes in a complementary fashion. Sekine and Dyrssen (1964) reported Eu/Am separation factors for 12 acidic extractants covering the spectrum of available materials (Table 24.7 is adapted from their work). Based on their separation factors, one can envision a counter-current separation procedure involving first extraction by dibutylphosphoric acid (HDBP) to

Table 24.7 *Europium/americium separation factors for a series of acidic extractants* (*Sekine and Dyrssen,* 1964).

Extractant	*Diluent*	S_{Am}^{Eu}
dibutylphosphoric acid	$CHCl_3$	22.9
dioctylphosphoric acid	$CHCl_3$	14.1
1-phenyl-3-methyl-4-acetylpyrazolone-5	$CHCl_3$	3.47
thenoyltrifluoroacetone	$CHCl_3$	3.02
neocupferron	$CHCl_3$	1.74
N-benzoylphenylhydroxylamine	$CHCl_3$	1.66
N-2,4-dichlorobenzoylphenylhydroxylamine	$CHCl_3$	1.32
β-isopropyltropolone	$CHCl_3$	0.98
1-hydroxy-2-napthoic acid	hexone	1.07
2-hydroxy-1-napthoic acid	hexone	1.02
3-hydroxy-2-napthoic acid	hexone	0.95
5,7-dichloroxine	$CHCl_3$	0.10

preferentially remove americium, followed by contact of the aqueous phase with 5,7-dichloroxine to extract europium. Substituting bis(2-ethylhexyl)phosphoric acid (HDEHP) for HDBP, Kasting *et al.* (1979) suggest that such a separation procedure could give actinide/lanthanide separation factors of several thousand.

From a process-scale application perspective, combinations of extraction systems are generally considered undesirable because of the complexity they introduce into the separations process. The more widely accepted approach to the separation of trivalent actinides from lanthanides is to rely upon the slightly stronger interaction that the trivalent actinides exhibit with ligands containing soft-donor bases (S, Cl, or N), as reported by Diamond *et al.* (1954). The soft-donor atoms may be present as free ions (SCN^-, Cl^-) or in a complexant/extractant molecule either water-soluble or lipophilic. This condition was recognized early in the race to produce new actinides, and formed the basis of separations techniques developed between 1945 and 1960, several of which still constitute the 'state-of-the-art' in actinide separations. Both ion exchange and solvent extraction techniques figure prominently in these separations.

The efficiency of lanthanide/actinide separations through the agency of soft-donor complexants is highly dependent on the strength of the interaction between the hydrated metal cation and the bulk water structure in the aqueous phase as well. The results reported by Sekine (1965) illustrate this in showing the combined effect of soft-donor ligands (SCN^-) and of water-structure disrupting anions (both SCN^- and ClO_4^-) on Am/Eu separation using a solvating extractant (Fig. 24.7). Both the extraction and mutual separation of americium and europium with 5% TBP in hexane from 5.0 M $NaClO_4$/NaSCN, and from NaSCN solutions without supporting electrolyte (pH 4–5) exhibit strong dependence on the concentration of SCN^-. In each case, separations factors ($S_{\mathrm{Eu}}^{\mathrm{Am}}$) decline with increasing thiocyanate concentration, though they are lower throughout the range of observation in the mixed salt system than in the thiocyanate-only system. However, in the thiocyanate-only system, distribution ratios overall are significantly lower for both metal ions, particularly at low total thiocyanate.

Distribution ratios are significantly higher in the mixed salt system due to the 'perchlorate effect' (Marcus and Kertes, 1969). The Gibbs energy for extraction of either Am or Eu in the presence of perchlorate (for example, at 1 M NaSCN) is 12–17 kJ mol^{-1} more favorable than when perchlorate is absent. At the highest SCN^- concentrations, separation factors are about unity because the disrupting effect of SCN^- and ClO_4^- on the water structure essentially diminishes the importance of the effect of the soft-donor interaction in actinide binding to the SCN^-. It appears that cation/complex solvation effects dominate the relative interactions under these conditions. Effectively, water activity is increased by the disruptive effect of the large anions and thus the soft-donor thiocyanate can no longer effectively distinguish between Am and Eu (as it clearly does at lower salt concentrations).

The bifunctional extractants (CMPs and CMPOs discussed in Section 24.3.4b) are designed for process applications to permit complete recovery of all actinides in oxidation states 3+, 4+, and 6+ from nitric acid solutions. Their extraction strength does not readily lend itself to selective separations. However, Muscatello *et al.* (1982) reported that substitution of dilute NH_4SCN for HNO_3, in the extraction of trivalent f-elements from 0.244 M DHDECMP (dihexyl)diethylcarbamoylmethylphosphonate) yielded americium/europium separation factors as high as 10.8. The thermodynamic features of these and related systems have been discussed in Section 24.3.5.

A more efficient, but considerably more complex, approach to actinide/lanthanide separation was developed by Weaver and Kappelmann (1964). If the normal mineral acid aqueous phase is replaced by a 1 M carboxylic acid (pH 1.8) solution, HDEHP extraction of Am is depressed relative to that for the lanthanides. At higher pH values (~3.0), the separation factors are increased, with the most consistent enhancement observed for lactic acid. Addition of only 0.05 M DTPA to the solutions of carboxylic acids at pH 3 resulted in dramatically improved separation factors. For extraction from 1 M lactic acid/0.05 M DTPA at pH 3 with 0.3 M HDEHP/diisopropylbenzene, the worst actinide/lanthanide separation factor is for $S_{\mathrm{Cf}}^{\mathrm{Nd}} \approx 10$. Separation factors for lanthanides over americium and curium were greater than 100. In this system, up to one lactic acid molecule appears in the extracted complex. The DTPA complexes remain in the aqueous phase.

This separation process has acquired the acronym TALSPEAK (Trivalent Actinide Lanthanide Separation by Phosphorus reagent Extraction from Aqueous Komplexes). The generic applicability of the concept is demonstrated by the work of Baybarz (1965), who finds only slightly reduced efficiency upon substitution of 2-ethylhexyl(phenyl)phosphonic acid/diethyl benzene (H(EH(Φ)P)/DEB) for HDEHP/DIPB. The impact of substitution of DTPA

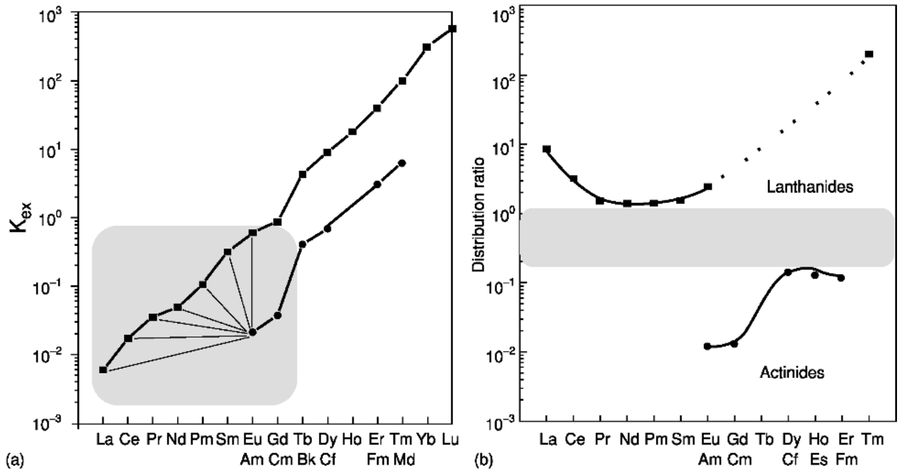
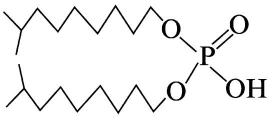


Fig. 24.11 *Distribution of lanthanide* (▪) *and trivalent actinide* (•) *cations between* (*a*) *nitric acid and* 0.5 M *HDEHP* (*Peppard* et al., 1957) *and* (*b*) 0.3 M *HDEHP/DIPB*, 1 M *lactic acid*, 0.05 M *DTPA at pH* 3 (*Weaver and Kappelmann*, 1964).

and lactate for nitric acid on group separations (as compared with HDEHP alone) is illustrated in Fig. 24.11. In a modification of the TALSPEAK process, known as the Reverse TALSPEAK process, trivalent actinides and lanthanides together are extracted by 1 M HDEHP from the 0.1 M HNO_3 feed solution. Americium and curium are then selectively stripped from the organic phase with a mixture of 0.05 M DTPA and 1.5 M lactic acid at a suitable pH adjusted with ammonia (Persson *et al.*, 1984).

A number of other reports have discussed applications, process experience, and modifications of TALSPEAK. Kosyakov and Yerin (1980) report that for curium extraction with TALSPEAK-type aqueous solutions using HDEHP/decane solutions both extractant (HDEHP) and acid dependencies (i.e. the number of extractant molecule dimers in the complex and the number of H^+ ions released to the aqueous solution) decreased from 3 to 2. This reduction indicates the extraction of a 1:1 M–lactate complex for the aliphatic diluent. Similar extractant dependencies were reported for Bk, Eu, and Ce. Bourges *et al.* (1980) report a comparison of TALSPEAK with TBP-nitrate and trilauryl ammonium nitrate extraction for Am/Cm separations using DTPA as aqueous complexing agent (in extraction chromatographic mode). Though TALSPEAK gives higher lanthanide/actinide separation factors, these authors cite favorable chromatographic kinetics and improved Am/Cm separation as justification for the choice of TBP/DTPA over TALSPEAK. Ishimori finds higher distribution ratios in a TALSPEAK type system using di-isodecylphosphoric acid (DIDPA, Structure t) in place of HDEHP (Ishimori, 1980). Bond and Leuze (1980) describe a lanthanide/actinide removal and separation scheme using a 1 M lactic acid–0.05 M DTPA stripping solution to separate trivalent actinides from the lanthanides.



Structure t

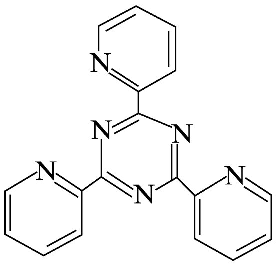
The TALSPEAK process is adaptable to liquid membrane separations (Novikov and Myasoedov, 1987). These authors report the use of a 'supported liquid membrane' impregnated with HDEHP for the separation of Am/Cm, Eu/Tb, and Am/Eu using DTPA, citric acid, and the potassium salt of a heteropolyacid ($K_{10}P_2W_{17}O_{61}$) as aqueous complexants. The optimum separation factors reported are $S^{\mathrm{Am}}_{\mathrm{Cm}} = 5.0$, $S^{\mathrm{Eu}}_{\mathrm{Tb}} = 10.8$, and $S^{\mathrm{Eu}}_{\mathrm{Am}} > 10^2$. Elements of the TALSPEAK (or reverse) still get periodic consideration in process chemistry of actinide recycle, as will be discussed in Section 24.4.4 g.

French researchers have investigated the use of soft-donor extractants and complexants to enhance actinide/lanthanide group separations (Musikas *et al.*, 1980; Musikas, 1985; Vitorge, 1985). The relative stability constants for lanthanide and actinide azide complexes reported by Musikas *et al.* (1980) suggest that hydrazoic acid (HN_3) could function as a useful reagent for this separation. This is confirmed in a later report on Am/Eu separation (Musikas, 1985) in which americium extraction is suppressed by complex formation with azide. The separation factors are similar to those reported by Sekine (1965) using SCN^- as the complexant in TBP extraction. As to the thermodynamic factors describing this system, Choppin and Barber (1989) find that, while the trivalent actinide–azide stability constants are somewhat larger than those of the trivalent lanthanides, the complexation enthalpies (calculated from the temperature coefficient of the stability constants) do not support the existence of a covalent bonding contribution.

A soft-donor extractant system, mixtures of *o*-phenanthroline and nonanoic acid (Musikas, 1985), extracts americium in order of magnitude more strongly than europium from 0.1 M $NaNO_3$ solutions at pH 4.5–5.1 [$S^{\mathrm{Am}}_{\mathrm{Eu}} = (17.4 \pm 0.9)$]. To accomplish the separation at higher acidity, research has been conducted on the complexant/extractant 2,4,6-tris(2-pyridyl)-1,3,5-triazine (TPTZ, Structure u), used in conjunction with carboxylate and sulfonate co-extractants. The latter is necessary because of the hydrophilicity of the $Am(NO_3)_3TPTZ$ complex. Replacement of nitrate by α-bromocaprate (with decanol as diluent) gives group separation factors ≈ 10 with little apparent variation in the distribution ratios for the members of the groups (Am, Cm, or Eu, Nd, Tb, and Yb) (Table 24.8) in the pH range of 2–3. Substitution of dinonylnaphthalenesulfonic acid (HDNNS) for α-bromocapric acid gives similar performance at 0.1 M acid.

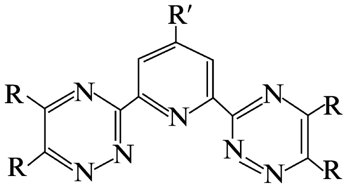
Table 24.8 *Extraction of selected trivalent actinides and lanthanides by* 2,4,6-*tris* (2-*pyridyl*)-1,3,5-*triazine* (*TPTZ*)/1 M α-*bromocapric acid* (*ABCA*)/*decanol, and TPTZ/ HDNNS/t-butylbenzene*(*TBB*) *nitric acid* (*Musikas*, 1985).

Metal	*D*(*TPTZ/ABCA*) pH 2.2	*D*(*TPTZ*/(*TPTZ/HDNNS*) [HNO_3] = 0.12 M
Am	0.85	1.35
Cm	0.80	1.40
Ce	–	0.158
Nd	0.08	–
Eu	0.10	0.199
Gd	–	0.178
Tb	0.11	0.14
Yb	0.10	0.22



Structure u

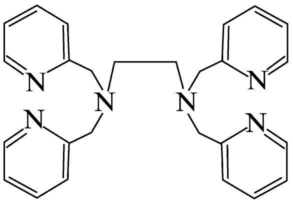
Structurally, TPTZ is perhaps not ideally suited as an extractant for this separation. Though there are a number of nitrogen donor atoms present in TPTZ, the planar nature of the ligand demands that no more than three nitrogen atoms be coordinated to a metal ion, leaving three additional potential donor atoms available for interactions (quite probably non-productive interactions) with other solutes in the organic phase. Continued research on the design, synthesis, and characterization of polyaza extractants led ultimately to the development by Kolarik *et al.* (1999) of the bistriazinylpyridine (BTP) class of ligands (Structure v). Work continues on the adjustment of the structure and properties of these ligands (Hägstrom *et al.*, 1999; Hudson *et al.*, 2003; Drew *et al.*, 2004a, b).



Structure v

In this ligand, pyridine rings have been substituted by triazines, in a geometry that favors at least tridentate coordination of the metal ion. Actinide/lanthanide separation factors as high as 100 have been reported. This ligand is receiving considerable attention as a candidate for process-scale lanthanide/actinide reagent (Madic *et al.*, 2002). To date, 75 derivatives of this class of reagents have been prepared and have undergone some degree of characterization. Lipophilic co-extractants (carboxylic or organophosphoric acids) and/or long-chain alcohol diluents are often employed to minimize partitioning of the BTP extractant to the aqueous phase.

Another polyaza ligand that has received some attention for its potential to accomplish actinide/lanthanide separation is the EDTA structural analog *N*,*N*,*N*′,*N*′-tetra(methylpyridyl)ethylenediamine (TPEN, Structure w). Investigations of the structure of lanthanide complexes (Morss and Rogers, 1997) and the thermochemistry (Jensen *et al.*, 2000) of the corresponding aqueous species confirm the existence of a hexadentate coordination mode and an apparent 100-fold selectivity for actinides over lanthanides in aqueous solutions. Separation-specific studies have been conducted by Takeshita and coworkers (Watanabe *et al.*, 2002). These authors have reported separation factors greater than 70 in a synergistic extraction system analogous to that employed in the BTP system. As with all polyaza ligands, extractant partitioning to the aqueous phase is a complication in these systems.



Structure w

In general, f-elements are poorly extracted by simple sulfur donor extractants. Furthermore, extractant molecules that incorporate sulfur as a donor atom are often plagued by poor stability when contacted with acidic (particularly nitrate) aqueous solutions. Certain types of extractants are more vulnerable to such attack, as results presented by Musikas (1985) indicate. His reports of good actinide/lanthanide separation factors for solvent extraction by thio derivatives of HDEHP were later dismissed (Freiser, 1988) as being the result of hydrolysis of the extractant to produce the oxygenated derivative. Because the oxygenated analogs of thiophosphorus ligands extract trivalent lanthanide/actinide cations very strongly, even very low concentrations of these degradation products profoundly compromise the ability of the soft-donor extractant to accomplish the separation.

Thiophosphinic acids like Cyanex 301 are slightly more resistant to hydrolytic degradation than the dialkyldithiophosphates though the oxygenated products of their hydrolysis are as damaging to a successful lanthanide/actinide separation as HDEHP is in the thiophosphate system. This extractant when employed for separations of d-transition metals (e.g. Cd^{2+}) is often used in a de-aerated environment to reduce the impact of degradation of the extractant on separation efficiency. Unfortunately, for separations of radioactive materials, the effect of radiolysis (and the oxygenated by-products of water radiolysis) cannot be eliminated and degradation of the extractant will be problematic in process applications.

Other derivatives of dialkyl dithiophosphinic acids have also been prepared and evaluated as potential actinide/lanthanide separation reagents. Results from Jarvinen *et al.* (1995) indicate moderate separation factors for americium from europium using dithiophosphinic acid extractants (R_2PS_2H) Cyanex 301, dicyclohexyldithiophosphinic acid, and diphenyldithiophosphinic acids. Wang *et al.* (2001) have synthesized several dialkylthiophosphinic acids where 2,4,4-trimethylpentyl group present in Cyanex 301 was replaced with *n*-octyl, 1-methylheptyl, 2-ethylhexyl, heptyl, or hexyl groups. It has been observed that by using 0.5 M solution of the thiophosphinic acids, the pH for 50% extraction ($pH_{1/2}$) of americium and europium from 1 M sodium nitrate is 2.58, 2.63, 2.67, 3.19, and 3.94, 3.99, 4.06, 4.52, respectively, for R = *n*-octyl, 1-methylheptyl, 2-ethylhexyl, or 2,4,4-trimethylpentyl groups. The Am/Eu separation factors for the four extractants are $\sim 1 \times 10^4$. These authors suggest that di(2-ethylhexyl)dithiophosphinic acid is the most promising of these extractants because of its lower $pH_{1/2}$ and higher loading capacity of extraction of americium as compared to Cyanex 301 (Tian *et al.*, 2001). More data on extractions at macro concentrations of the lanthanides, $S_{\mathrm{Eu}}^{\mathrm{Am}}$ mixer–settler or centrifugal contactor runs will be required to substantiate these studies.

In an attempt to lower the $pH_{1/2}$ of this class of extractants, Modolo and Odoj (1999) prepared bis(*p*-chlorophenyl)dithiophosphinic acid. This extractant in a process solvent that includes tri(*n*-butyl)phosphate or trioctylphosphine oxide as a co-extractant is able to selectively extract trivalent actinides from lanthanides with separation factors acceptable for process applications. This extractant is receiving attention for possible process application, as will be discussed in Section 24.4.5b.

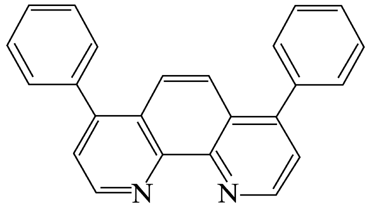
The higher $S_{\mathrm{M}}^{\mathrm{M}'}$ between americium and europium has been suggested by Ionova *et al.* (2001) as being due to the strong coordination of M(III) to soft-donor sulfur atoms of Cyanex 301, covalent effect being significantly higher for Am–S as compared with Eu–S bonds. These authors have further shown that while using a mixture of Cyanex 301 and neutral O-bearing co-extractants, the extraction of M(III) and $S_{\mathrm{Eu}}^{\mathrm{Am}}$ can be correlated with the effective charge on O atom of the neutral organophosphorus extractant molecule. The $S_{\mathrm{Eu}}^{\mathrm{Am}}$ reported are 3200 for Cyanex 301 alone, 4700 for Cyanex 301 and TBP, 9100 for Cyanex 301 and tri-*tert*-butyl phosphate, 16 000 for Cyanex 301 and triphenyl phosphate, 0.45 for Cyanex 301 and TOPO/CMPO, 95 for Cyanex 301 and *N*, *N′*-dimethyl-*N*,*N′*-dibutyltetradecylmalonamide, and 17 000 for Cyanex 301 and *N*, *N′*-di (ethyl-2-hexyl)dimethyl-2,2-butanamide.

Other classes of sulfur donor extractants appear to be more resistant to hydrolysis, and have demonstrated some potentially useful selectivity for

Table 24.9 *Distribution ratios and separation factors for americium/europium extraction by* 4-*benzoyl*-2,4-*dihydro*-5-*methyl*-2-*phenyl*-3*H*-*pyrazol*-3-*thione/toluene* (0.0297 M)/0.1 M *$NaClO_4$ as a function of* 4,7-*diphenyl*-1,10-*phenanthroline* (*synergist*) *from* (*Ensor* et al., 1988).

[DPPHEN]	D_{Am}	S_{Eu}^{Am}
0.00269	25.3	183
0.00215	21.9	196
0.00144	14.8	192
0.00108	10.3	174
0.000718	6.1	156
0.000359	2.7	129

actinides over lanthanides. For example, the mixture of 0.3 M 4-benzoyl-2, 4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (BMPPT)/0.01 M TOPO/benzene extracts (from 0.1 M $LiClO_4$, pH 3) americium preferentially over europium ($S_{\mathrm{Eu}}^{\mathrm{Am}} = 68$) (Smith *et al.*, 1987). The analogous system based on the oxygen-donor analog and TOPO (Chmutova and Kochetkova, 1970) gave stronger extraction but no significant separation of curium from europium. Further substitution of the soft-donor synergist 4,7-diphenyl-1,10-phenanthroline (DPPHEN, Structure x) for TOPO (Ensor *et al.*, 1988), results in even greater selectivity for americium ($S_{\mathrm{Eu}}^{\mathrm{Am}} = 190$, pH 3.7, 0.03 M HBMPPT/0.0027 M DPPHEN). The extracted species is $M(BMPPT)_3(DPPHEN)$ (Table 24.9). This is the only known example of a system that contains soft-donor atoms in both the primary extractant and in the synergist. Choppin *et al.* (1995) have reported on the separation of americium from europium using various combinations of thiothenoyltrifluoroacetone, tri(*n*-butyl)phosphate, tributylphosphine sulfide, and *N*,*N*-dimethyl-*N*,*N*′-dihexyl-3-oxapentanediamide as coextractant ligands in a synergistic extraction system. In this case, the soft-donor ligands show little enhancement of Am/Eu separation factors.



Structure x

24.3.10 Supercritical fluid extraction of actinides

The field of supercritical fluid extraction (SFE) of metal ions has been developed during the past decade. Among the first papers published, those by Wai and co-workers were the most important. In 1991, this group (Laintz *et al.*, 1991) published a paper describing the solubility of fluorinated metal dithiocarbamates in supercritical carbon dioxide (sc-CO_2) wherein they demonstrated that the solubility of the fluorinated dithiocarbamates were two to three orders of magnitude higher than those of the corresponding non-fluorinated compounds. This technique was thus recognized as a promising new extraction method for metal ions from various sources. A year later, Wai and co-workers published a second paper (Laintz *et al.*, 1992) related to the SFE of metal ions from aqueous solutions and solid materials, and in 1993 they demonstrated the possibility of extracting lanthanide (Ln) and actinide (An) ions from solid materials with a fluorinated β-diketone (Lin *et al.*, 1993).

The rationale for the use of SFE of metal ions as an alternative to conventional liquid–liquid extraction (LLE) was mainly to minimize the generation of the secondary organic waste often encountered in LLE processes. Carbon dioxide was chosen as the most appropriate supercritical fluid because: (i) the values of the critical point (Darr and Poliakoff, 1999) were appropriate for a SFE application: $P_c = 72.9$ atm, $T = 304.2$ K, $\rho_c = 0.47$ g mL^{-1}; (ii) CO_2 can be considered as a green solvent for the environment; (iii) (aside from asphyxiation hazards) CO_2 is harmless to workers; (iv) CO_2 is almost inert with respect to radiolysis; (v) CO_2 is inexpensive. Moreover, the high diffusivity of sc-CO_2 means that rapid extraction of the metal ions from their sources can be expected. Since 1991, about 80 reports related to the SFE of metal ions have been published, most of them related to actinides. The most studied actinide ion is U(VI), with about 50 papers. This field was recently reviewed by Darr and Poliakoff (1999) and by Wai (2002). The sections to follow present the most important aspects of the SFE of actinide ions contained within various sources: (i) aqueous solutions, (ii) solid materials, (iii) pure actinide oxides. As most of the information available in the literature is related to U(VI), the examples discussed will predominantly concern this ion.

(a) Experimental setup and SFE procedures

Fig. 24.12 is a schematic of an experimental setup proposed by Tomioka *et al.* (2001a) for the SFE of metal ions from a metal oxide. A similar apparatus has been described by Wai and Laintz (1999). The carbon dioxide passes first through a vessel where it dissolves the contained ligand (solid or liquid). In the second vessel, the sc-CO_2 ligand solution then comes into contact with the actinide oxide to be extracted. Trofimov *et al.* (2001) recently showed that the use of ultrasound increases the solid dissolution rate. After extraction, the metal ion complex can be recovered by reducing both the pressure and temperature of the sc-CO_2 solution, leading to the precipitation of the metal ion complex and of the excess ligand. The CO_2 can subsequently be recycled. To perform this reduction of pressure and temperature, the loaded sc-CO_2 solution passes through a capillary restrictor made of silica or stainless steel. Wai *et al.* (1998) noted some drawbacks to using this technique, such as clogging of the capillary

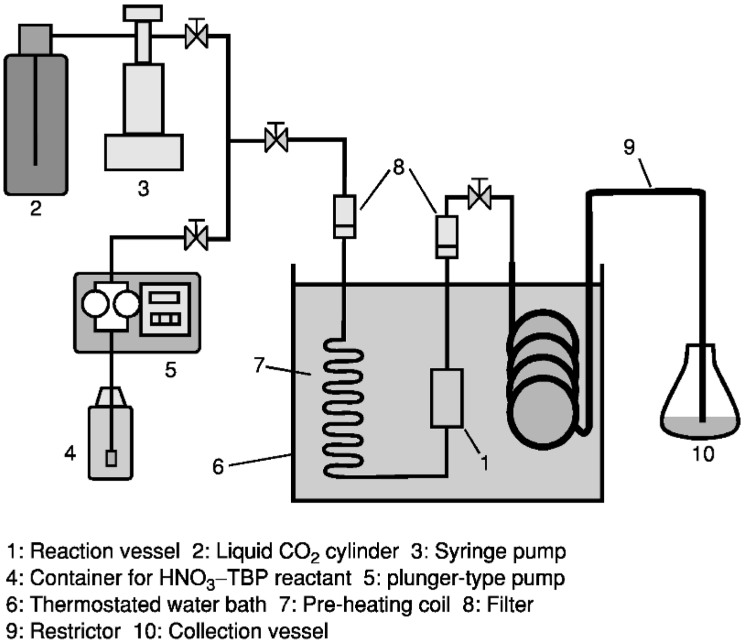


Fig. 24.12 *Apparatus for the dissolution of uranium oxide powder with supercritical CO_2 containing the HNO_3–TBP complex (adapted from Tomioka* et al., 2001*a*).

by the solutes, or breaking of the silica capillary in case of the use of sc-CO_2 modified with methanol. They therefore proposed an improved stripping method to eliminate these drawbacks by passing the loaded sc-CO_2 solution through an acidic aqueous solution while maintaining the pressure and temperature conditions of the SFE. Extraction of metal ions from aqueous solutions can be performed in such an apparatus with minor modifications.

Several systems have been developed to measure the concentration of the metal ion extracted into the sc-CO_2. The most popular uses a UV–visible spectrophotometric cell to measure colored metal ion complexes, as in the case of U(VI) (Furton *et al.*, 1995; Addleman *et al.*, 1998; Sasaki *et al.*, 1998). Recently, Wai and co-workers (Carrott and Wai, 1998; Hunt *et al.*, 1999) proposed sophisticated UV–visible measurement cells, with several light path lengths (38 μm, 733 μm, and 1 cm) coupled with optical fibers, the spectra being measured with a charge–coupled device array UV–visible spectrophotometer. In the case of SFE of U(VI), the same research group also proposed the use of a Raman measurement cell (Addleman *et al.*, 1998) or of a time-resolved laser-induced fluorescence spectrometry cell (TRLIFS) (Addleman *et al.*, 1998, 2000a,b; Addleman and Wai, 1999, 2000). The latter technique permits the measurement of U(VI) complexes under a wide range of concentrations.

The pressure and temperature conditions often chosen for SFE of metal ions are the following: pressure in the range 150–300 atm, temperature in the range 60–120°C. Frequently used conditions are 150 atm and 60°C. SFE of metal ions can be carried out in two modes:

(1) Static mode: The actinide containing sample and the sc-CO_2 fluid are placed in contact and stirred until the actinide distribution equilibrium is obtained. The actinide-loaded sc-CO_2 fluid is then removed from the extraction vessel.
(2) Dynamic mode: The sc-CO_2 fluid containing the extractant is continuously fed to the extraction vessel and the actinide-loaded sc-CO_2 fluid is then stripped online.

(b) SFE properties of actinide ions

(*i*) *Ligands*

Numerous ligands can be used for the SFE of actinide ions, most of which have also been used (or are structurally similar to reagents that have been used) in conventional solvent extraction. The most important ones are as follows.

β-Diketones

A ligand of this type, 2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedione (FOD), was used by Wai and coworkers in the first article related to the SFE of actinide ions (Lin *et al.*, 1993). It was shown that about 99% of 10 μg of uranyl ion contained within uranyl acetate solutions at pH 1.0 or deposited on cellulose-based filter paper from a solution at pH 6.5, can be extracted under the following SFE conditions: 80 μg of FOD, sc-CO_2 containing 5% methanol, wet paper, 60°C; 150 atm. In another article, the same group (Lin *et al.*, 1994) studied the SFE efficiency of several β-diketones for Th(IV) and U(VI); the following ligands were studied: acetylacetone (AA), trifluoroacetylacetone (TAA), hexafluoroacetylacetone (HFA), thenoyltrifluoroacetone (TTA), and FOD. In the absence of methanol in the sc-CO_2 and all other SFE conditions being identical to those mentioned above, the extraction efficiency observed for U(VI) and Th(IV) were the following, respectively: 10 and 12% (AA), 15 and 22% (TAA), 40 and 69% (HFA), 51 and 80% (FOD), and 70 and 82% (TTA). The fluorinated β-diketones are the most effective ligands and among them TTA seems to be the best. Note that Th(IV) is slightly more strongly extracted than U(VI) under these conditions.

Neutral organophosphorous compounds

Organophosphates and phosphine oxides were the most studied neutral organophosphorous compounds for SFE of actinide ions. Work has principally focused on the use of TBP for the extraction of uranyl nitrate (Lin *et al.*, 1994, 1995; Iso *et al.*, 1995, 2000; Meguro *et al.*, 1996, 1997, 1998b, 2002;

Toews *et al.*, 1996; Smart *et al.*, 1997b; Carrott *et al.*, 1998; Sasaki *et al.*, 1998; Addleman *et al.*, 2000a; Addleman and Wai, 2000, 2001; Enokida *et al.*, 2000; Park *et al.*, 2000; Tomioka *et al.*, 2000, 2001a,b, 2002; Clifford *et al.*, 2001; Shamsipur *et al.*, 2001) This was certainly related to the observation of Toews *et al.* (1996) that of the three extractants TBP, tri-*n*-butylphosphine oxide (TBPO) and tri-*n*-octylphosphine oxide (TOPO), TBP was by far the most effective ligand for sc-CO_2 extraction and transport of uranyl nitrate. This is primarily a result of the greater solubility of TBP in sc-CO_2 relative to the phosphine oxides (Lin *et al.*, 1995). Only a few reports concern the TBP-mediated SFE of other actinide ions: Th(IV) (Lin *et al.*, 1995) and Pu(IV) (Iso *et al.*, 2000). SFE of actinide ions (mostly U(VI) and Th(IV) by phosphine oxides has been the subject of a few reports (Lin *et al.*, 1995; Toews *et al.*, 1996; Wai *et al.*, 1999; Addleman *et al.*, 2000a; Shamsipur *et al.*, 2001).

It should be noted that most of the research on the extraction of actinide ions by neutral organophosphorous ligands has been done by Wai (U.S.), Yoshida (Japan) and their coworkers. Some of the results related to the extraction of uranyl nitrate by TBP are presented here; other results related to this system will be presented later in this section. The extracted complex in sc-CO_2 has the same stoichiometry [$UO_2(NO_3)_2(TBP)_2$] as is observed in conventional solvent extraction. The identity of the complex was established by Meguro *et al.* (1996) and confirmed by Wai *et al.* (1999) using the classical slope analysis method. This complex was characterized by UV–visible spectrophotometry (Addleman *et al.*, 1998; Carrott *et al.*, 1998; Sasaki *et al.*, 1998), Raman spectrometry (Addleman *et al.*, 1998), and TRLIFS (Addleman *et al.*, 1998, 2000a,b; Addleman and Wai, 1999, 2000, 2001). TRLIFS was used in particular by Addleman and coworkers to determine the solubility of the U(VI) complex (Addleman *et al.*, 2000a) and the $D_{\mathrm{U(VI)}}$ values (Addleman and Wai, 2001), and for online measurement of the extracted U(VI) (Addleman *et al.*, 2000b). The extraction kinetics of uranyl nitrate by TBP in sc-CO_2 are rapid (Wai *et al.*, 1999) (~45 min) if the U(VI) source consists of aqueous solutions. With solid samples (tissue paper, soil, sand, etc.), the extraction of U(VI) requires more time. An efficient model for interpreting the kinetic aspects of the SFE extraction of uranyl nitrate by TBP in sc-CO_2 in dynamic mode was recently proposed by Clifford *et al.* (2001).

The value of $D_{\mathrm{U(VI)}}$ is 2.0, for extraction by 0.3 mol L^{-1} TBP in sc-CO_2 at 60°C and 15 MPa from an aqueous solution of 3 mol L^{-1} HNO_3 (Iso *et al.*, 2000). Under the same experimental conditions, the distribution ratio for Pu(IV) was found to be 3.1 (Iso *et al.*, 2000). Other thermodynamic aspects of the extraction of uranyl nitrate by TBP are considered below in the discussion of the influence of pressure and temperature on the SFE of metal ions. Uranyl nitrate can be effectively extracted from various sources, such as aqueous solutions, whether acidic or neutral, and solid waste (cellulosic paper, contaminated soil or sand, metallic waste). The solubility of $UO_2(NO_3)_2(TBP)_2$ in sc-CO_2 was found to be the highest of all the metallic complexes studied so far (Meguro *et al.*, 1996):

~0.43 mol L^{-1} at 40°C and 225 atm (Carrott *et al.*, 1998). This moderate solubility warrants consideration of process development for spent nuclear fuel reprocessing. Only a few reports have considered the use of bidentate neutral organophosphorous extractants. This is certainly due to the low solubility of these ligands in sc-CO_2, as shown by Meguro *et al.* (1998a) for dihexyl (*N,N,*-diethylcarbamoyl)methylphosphonate and for the octyl(phenyl)(*N,N*-diisobutyl)carbamoylmethylphosphine oxide (OΦCMPO).

Synergistic mixtures

In 1994, Lin *et al.* (1994) were the first to report the existence of synergistic phenomena for the SFE of U(VI) and Th(IV) ions. For example, with TTA and TBP extractants at 60°C and 150 atm, SFE was carried out in dynamic mode on samples consisting of sand (200 mg) contaminated with 10 μg of U and 10 μg of Th with the following results (U and Th extracted, respectively): TTA (80 μmol) = 72 and 74%; TBP (80 μmol) = 15 and 10%; TTA + TBP (40 μmol + 40 μmol) = 94 and 93%. A net synergistic effect was thus observed for the extraction of both actinide ions. Several papers related to SFE of actinide ions by diketones and neutral organophosphorous compound synergistic mixtures have been published since (Furton *et al.*, 1995; Lin *et al.*, 1998, 2001; Murzin *et al.*, 1998; Addleman *et al.*, 2000a, 2000b; Geertsen *et al.*, 2000).

(*ii*) *Modifiers*

The addition of a modifier can be an effective means of enhancing the extraction efficiency of sc-CO_2 extractant solutions. Methanol is the most widely used modifier. The use of methanol as an sc-CO_2 modifier was often reported when the ligands were β-diketones and their synergistic mixtures, but modifiers are not ordinarily used in the case of TBP alone. The following example illustrates the efficiency of methanol as an sc-CO_2 modifier. Lin *et al.* (1994) studied the SFE of U(VI) and Th(IV) with the β-diketones: AA, TAA, HFA, FOD, and TTA, with neat or 5% methanol-modified sc-CO_2. The following experimental conditions were chosen: 60°C, 150 atm, cellulose-based filter contaminated with 10 μg of U and 10 μg of Th, 80 μmol of ligand, dynamic extraction. The actinide ion extraction yields obtained for neat and 5% methanol-modified sc-CO_2, respectively, were as follows: AA (U = 10 and 45%; Th = 12 and 58%), TAA (U = 15 and 98%; Th = 22 and 95%), HFA (U = 40 and 95%; Th = 69 and 92%), FOD (U = 51 and 98%; Th = 80 and 97%), TTA (U = 70 and 96%; Th = 82 and 91%). The presence of methanol thus induces a net increase in uranium and thorium extraction efficiency, and this is certainly correlated to the increased polarity of the sc-fluid due to the presence of the modifier.

With SFE of solid samples, such as soil, sand or paper, it is also observed (Lin *et al.*, 1993) that a small amount of water must be added to obtain satisfactory metal ion extraction efficiency.

(c) Influence of pressure and temperature on SFE of actinide ions

The SFE efficiency of actinide ion complexes can be tuned by modifying the pressure and temperature conditions as well. To illustrate these properties, consider the TBP SFE of U(VI) and Pu(IV) nitrates from aqueous nitric acid solutions, as studied by Yoshida and coworkers (Iso *et al.*, 2000). At constant temperature and TBP concentration in sc-CO_2, an increase in pressure induces a decrease in $D_{U(VI)}$ and $D_{Pu(IV)}$ correlated with the higher density of the sc-fluid. A simple linear correlation between $D_{U(VI)}$ or $D_{Pu(IV)}$ and ρ is observed in log–log plots:

$$\log D = a \log \rho + b \tag{I}$$

in which a is a proportionality constant related to the solvation characteristics of the metal complexes in sc-CO_2. The slopes a of the relationships were equal to $-(2.7 \pm 0.5)$ for U(VI) and $-(1.6 \pm 0.1)$ for Pu(IV). The differences in D as well as in the slope a between U(VI) and Pu(IV) make it possible to design a SFE scheme to separate uranium from plutonium. In the case of U(VI), for a temperature increase from 313 to 353 K and for a pressure of 40 MPa, $D_{U(VI)}$ decreases by a factor of about 2, as shown by Yoshida and coworkers (Meguro *et al.*, 1997; Iso *et al.*, 2000). Conversely, the same group (Iso *et al.*, 2000) has shown that $D_{Pu(IV)}$ increases with T, and the lower the pressure the greater the temperature effect.

The increase in the pressure of sc-CO_2 that induces an increase in the density of the sc-fluid has a large impact on the solubility of solutes. Chrastil (1982) demonstrated that the solubility S (g L^{-1}) of an organic solute in a sc-fluid is correlated with the density (g L^{-1}) of the sc-fluid by the following empirical relation

$$\ln S = \kappa \ln \rho + C \tag{II}$$

where the value of k is related to the solute–solvent interactions and that of C to the volatility of the solute. Since then, equation (II) has also been found to represent variations of the solubility of metal ion complexes in sc-CO_2. A review of the solubility of chelating agents and their metal complexes has been published by Smart *et al.* (1997a). This equation was also shown to be usable to represent the solubility of actinide ion extractants and their complexes (Meguro *et al.*, 1998b). This is the case in particular for $UO_2(NO_3)_2(TBP)_2$ (Carrott *et al.*, 1998; Addleman *et al.*, 2000a) which, as noted above, is the metallic complex with the highest solubility in sc-CO_2.

(d) Sources of actinide ions for SFE

Several sources of actinide ions can be treated by SFE, including:

(1) Aqueous solutions: Acetate-buffered solution are often used when the extractants are β-diketones (Lin *et al.*, 1994), nitric acid, and nitric acid and alkali nitrate solutions (Lin *et al.*, 1995; Meguro *et al.*, 1996, 1997,

1998b; Smart *et al.*, 1997b; Iso *et al.*, 2000), uranium mine water (Lin *et al.*, 1994).

(2) Solid matrices (surrogates or genuine wastes): Cellulosic filter paper (Lin *et al.*, 1993, 1994; Brauer *et al.*, 1994; Shamsipur *et al.*, 2001; Kumar *et al.*, 2002), sand (Tomioka *et al.*, 2002), soil (Fox *et al.*, 1999), kaolin (Furton *et al.*, 1995), glass wool (Furton *et al.*, 1995), metals (Murzin *et al.*, 1998; Shadrin *et al.*, 1998), asbestos (Murzin *et al.*, 1998), rubber (Murzin *et al.*, 1998), plastics (polyethylene, polyester) (Furton *et al.*, 1995), contaminated with solid actinide compounds, such as nitrates or oxides,

(3) Actinide oxides: This case is particularly important in the light of the potential future applications, and is considered here in greater detail. Wai *et al.* (1997) filed a patent related to the SFE of metal ions directly from their oxides. They proposed as ligands numerous acidic compounds including β-diketones, phosphinic acids, and carboxylic acids. Better performance was seen for fluorinated derivatives. In 2000, Tomioka and coworkers (Enokida *et al.*, 2000; Tomioka *et al.*, 2000) described the dissolution of gadolinium and neodymium ions from their sesquioxides M_2O_3 (M=Gd and Nd) by the complex TBP–HNO_3 dissolved in sc-CO_2. Wai and Waller (2000) also demonstrated the efficiency of the SFE extraction of uranium from UO_3 by TTA or TTA + TBP synergistic mixtures. Several papers related to the dissolution of uranium oxides (UO_2, U_3O_8, and UO_3) by the TBP–HNO_3 complex have been published since then (Enokida *et al.*, 2000; Samsonov *et al.*, 2001; Tomioka *et al.*, 2001a,b; Trofimov *et al.*, 2001). The dissolution of UO_2 was less rapid than those of the two other oxides, but it is possible to increase the dissolution rates of oxides if the HNO_3/TBP molar ratio in sc-CO_2 is greater than 1. In a recent conference paper, Samsonov *et al.* (2002) reported the SFE of actinides from their oxides using TBP–HNO_3; the studied oxides were: ThO_2, UO_2, U_3O_8, and UO_3, NpO_2, and PuO_2. Under the experimental conditions [65°C, 250 atm, TBP–HNO_3 reagent in sc-CO_2, thrice-repeated alternation of static (10 min) and dynamic (15 min) extractions] it was shown that the extraction yields of U oxides were good ($> 85\%$ for the lowest value) while those of the oxides of Th, Np, and Pu were almost nil.

(e) Possible applications

(*i*) *Industrial processes*

(1) Spent nuclear fuel reprocessing: Smart and Clifford (2001) from BNFL (UK) filed an international patent in 2001 in which they claimed that the reprocessing of spent nuclear fuel will be possible using the SFE method. The several steps of the conceptual process flow sheet are the following: (i) oxidize decladding of spent fuel under oxygen at 600°C, (ii) SFE of uranium by treatment of the oxidized fuel with a sc-CO_2 solution containing

an acidic ligand like a β-diketone, (iii) separation of U from the other extracted ions in fractionation columns, and (iv) reduction of the volatile uranium complex by hydrogen to precipitate UO_2. Probably the most interesting reagent for such application is TBP–HNO_3 as noted by the teams of Wai and Yoshida.

(2) Actinide waste decontamination: As noted above, the efficiency of SFE extraction of actinides from miscellaneous solid wastes has been demonstrated. An interesting case was the demonstration by Shadrin *et al.* (1998) of the efficiency of SFE for decontamination (U, Np, Pu, and Am) of 'real-world' contaminated stainless steel. This could be a basis for further industrial developments.

(*ii*) *Analytical applications*

SF-chromatography has been used to develop analytical methods. Examples include the work of Martin-Daguet *et al.* (1997) and Geertsen *et al.* (2000) for the analysis of U(VI).

(f) Conclusions

SFE of actinide ions has been a very active research field since its inception a decade ago. Important nuclear applications may some day be developed, particularly in spent nuclear fuel reprocessing and nuclear waste decontamination. The observation by Wai *et al.* on dissolution of uranium oxides by sc-CO_2 solutions of HNO_3–TBP solutions is noteworthy. The Wipff group is examining the system using the techniques of computational chemistry (Baaden *et al.*, 2002; Schurhammer and Wipff, 2003). However, fundamental understanding of the basic chemistry of actinide interactions in supercritical media lags far behind practical demonstrations. Considerable basic research and development studies are still required, but it is safe to say that the interest in this field is likely to increase in the future.

24.3.11 Actinides in room-temperature ionic liquids (RTILs)

Room temperature ionic liquids (RTILs) were discovered by Hurley and Wier (1951), who found that a mixture of $AlCl_3$ and ethylpyridinium bromide (EPB) in a 2:1 molar ratio melted at $-40°C$ and that this liquid is suitable for the electrodeposition of aluminum metal at room temperature. Research in this area has been pursued with two main objectives: the development of electrolytes for batteries, and the use of RTILs as 'green' liquids for the design of industrial processes for the synthesis of organic compounds. Though continuing research has established that this class of RTILs can indeed be quite toxic, these liquids are considered 'green' compared with traditional organic solvents used in the industry because they have no vapor pressure, hence no gaseous emissions, at least from intact RTIL formulations. However, it should further be noted that many RTIL formulations are based on the use of hydrolytically unstable inorganic anions like PF_6^- (reacts with water to produce HF). For more information on the properties of these materials, see reviews by Hussey (1983) and Welton (1999). The interest in using RTILs to develop separation processes for metals, for example liquid–liquid extraction with hydrophobic RTILs, is quite recent, as noted in a review by Visser *et al.* (2002). This subject became a hot topic in the late 1990s.

The first paper dealing with an actinide in an RTIL, published in 1982 by De Waele *et al.* (1982), examined the electrochemical behavior of uranium(IV) in a Lewis acidic $AlCl_3$ + *N*(*n*-butyl)pyridinium chloride (BPC) RTIL. Since that time, about 20 papers including patents for separation applications related to the chemistry of actinides within RTILs have been published, most of them (16) being related to uranium. In this short review, after a brief presentation of RTILs, the main chemical properties of actinides in RTILs will be described and the possible uses of RTILs for actinide separation presented.

(a) A brief description of RTILs

RTILs (Carpio *et al.*, 1979; Hussey, 1983; Visser *et al.*, 2002) are salts made of organic cations, such as: (i) *N*-alkyl quaternary ammonium, R_4N^+, (ii) *N*-alkyl pyridinium, (iii) *N*-alkylisoquinolinium, (iv) 1-*N*-alkyl-3-methylimidazolium, (v) *N*-alkyl quaternary phosphonium, R_4P^+, associated with various anions, e.g. halides (Cl^-, Br^-), haloaluminates (chloro or bromo), chlorocuprate ($CuCl_2^-$), tetraalkylborides (R_4B^-), NO_3^-, $CF_3CO_2^-$, BF_4^-, PF_6^-, and $N(SO_2CF_3)_2^-$. With the anions BF_4^-, PF_6^-, $N(SO_2CF_3)_2^-$, the RTILs are most often hydrophobic and can be used, for example, for the development of liquid–liquid extraction separation processes (Visser *et al.*, 2002). Nevertheless, most of the work related to actinides concerns RTILs of $AlCl_3$ and *N*-alkylpyridinium or *N*-alkylmethylimidazolium chlorides (called APC and AMIC, respectively). Both classes are highly sensitive to moisture. Recent work concerning the use of RTILs for nuclear fuel reprocessing is based on an RTIL made of *N*-alkylmethylimidazolium nitrate (Thied *et al.*, 1999). RTILs with nitrate anions were mentioned for the first time by Lane (1953).

The physical properties, such as the density, viscosity, or electric conductivity of RTILs consisting of mixtures of $AlCl_3$ and APC or AMIC have been the subject of numerous measurements (Carpio *et al.*, 1979; Hussey, 1983; Fannin *et al.*, 1984). The density of these melts exceeds 1 kg dm^{-3}; although most of them are quite viscous, their conductivity is suitable for electrochemical applications. The chemistry of these melts is dominated by the Lewis chloro-acidity. Depending on the molar ratio (M_r) of $AlCl_3$ versus APC or AMIC, the chloro-acidity (which can be expressed as pCl^- with low and high pCl^- for basic and acidic melts, respectively) of the melts varies. For $M_r = 1$, > 1, and < 1, the melts are neutral, acidic, and basic, respectively. The main reactions between aluminum chloride and the chloride ion occurring in these melts that control pCl^- are the following:

$$AlCl_3 + Cl^- \rightleftarrows AlCl_4^- \tag{24.23}$$

$$AlCl_4^- + AlCl_3 \rightleftarrows Al_2Cl_7^- \tag{24.24}$$

For these melts, pCl^- can vary between ~0 and 15 for highly basic and highly acidic melts, respectively, as shown by Schoebrechts and Gilbert (1985) for RTILs containing mixtures of $AlCl_3$ and *n*-butylpyridinium chloride. If oxygen-bearing compounds such as water are present in these melts, aluminum oxochloro complexes, e.g. $AlOCl_3^{2-}$, are formed that can influence the chemistry of the other metallic solutes. An ^{17}O NMR study of water in these melts was carried out by Zawodzinski and Osteryoung (1987a,b). One of the main advantages of these RTILs is the large electrochemical window available. For example, for melts made of mixtures of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride (EMIC), Gray *et al.* (1995) noted the following values for the electrochemical window (ΔV):

(i) neutral melt: $\Delta V = 4.7$ V, between the anodic $4\,AlCl_4^- \rightleftharpoons 2Al_2Cl_7^- + Cl_2 + 2\,e^-$ and cathodic $Na^+ + e^- \rightleftharpoons Na$ or ($EMI^+ + ne^- \rightarrow$ unknown coompound) reactions,

(ii) acidic melt: $\Delta V = 2.5$ V, between the anodic $4\,AlCl_4^- \rightleftharpoons 2Al_2Cl_7^- + Cl_2 + 2\,e^-$ and cathodic $4\,Al_2Cl_7^- + 3\,e^- \rightleftharpoons Al + 7AlCl_4^-$ reactions,

(iii) basic melt: $\Delta V = 3.3$ V, between the anodic $2\ Cl^- \rightleftharpoons Cl_2 + 2\,e^-$ and cathodic $Na^+ + e^- \rightleftharpoons Na$ (or $EMI^+ + ne^- \rightarrow$ unknown compound) reactions.

(b) Basic actinide properties in RTILs

Almost all studies of actinide chemistry in RTILs have been done in materials obtained by mixing $AlCl_3$ with APC or AMIC. The only exception is the work reported by Mohammed (1987) who also studied the properties of uranium within RTILs made of mixtures of $AlBr_3$ and EMI bromide. Most of the published work (16 papers) concerns uranium. Neptunium and plutonium were the subjects of only one and three papers, respectively. No work related to other actinides was found in the literature.

(c) Uranium chemistry in RTILs made of mixtures of $AlCl_3$ and APC or AMIC

The chemistry of uranium within these melts has been studied using electrochemical and spectrochemical methods. The most detailed spectrometric study by Costa and coworkers (Hopkins *et al.*, 2000, 2001) concerned the U(VI) chloro complex, $UO_2Cl_4^{2-}$, in basic ($AlCl_3$ + EMIC) RTIL, carried out by

UV–visible–NIR, Raman, and one-photon and two-photon excitation spectroscopy, and by luminescence lifetime measurements. As will appear from the references in the next sections, many research groups have been involved in the study of the properties of actinides in RTILs. A brief summary of the properties of U in basic or acidic ($AlCl_3$ + EMIC) RTILs, used as an example of this type of RTIL, is presented below.

(*i*) *Basic* (*$AlCl_3$ + EMIC*) *RTILs*

Uranium can exist in these basic ($AlCl_3$ + EMIC) RTILs as U(iii), U(iv), and U(vi). U(v) was not stable in these basic melts as noted by Dai *et al.* (1997b). The chemical forms for the stable uranium solutes are the following: UCl_6^{3-} for U(iii), UCl_6^{2-} for U(iv), and $UO_2Cl_4^{2-}$ for U(vi). These species have been characterized mainly by UV–visible–NIR spectroscopy. In the case of U(vi) species, Dai *et al.* (1997a) observed that it is certainly stabilized in the medium by establishing a hydrogen bond with the H born by the carbon in position 2 on the heterocycle ring of the EMI^+ cation.

The diffusion coefficients of U(iii) and U(iv) chloro complexes have been determined electrochemically and both values were found to be similar (1.61 and 1.85×10^{-7} cm^2 s^{-1}, respectively) and compatible with the 1:6 stoichiometry between U(iii) or U(iv) ions and the Cl^- ligand within the complexes. The electrochemical reaction $UCl_6^{2-} + e^- \rightleftharpoons UCl_6^{3-}$ was found to be reversible. Conversely, no reduction of U(iv) to U(iii) was observed in basic RTILs made of mixtures of $AlCl_3$ and BPC, as shown by Heerman *et al.* (1985). This difference is a result of the reduction potential of BP^+ being higher than that of EMI^+. Thus, BP^+ can oxidize U(iii) to U(iv). The U(vi)/U(iv) electrochemical conversion in [$AlCl_3$ + EMIC] RTILs is irreversible. Moreover, no reduction of U(iii) to U metal was observed.

(*ii*) *Acidic* (*$AlCl_3$ + EMIC*) *RTILs*

Owing to the large decrease of the concentration of Cl^- in the acidic ($AlCl_3$ + EMIC) RTILs compared with the basic melts, the chloro complexes of U(iii), U(iv), U(vi) are destabilized. Note that U(vi) is not chemically stable in these media. It is converted to U(v) species, the ultimate complex being UCl_6^-, after reduction and loss of oxide ions (Anderson *et al.*, 1999). The UCl_6^- complex was also observed by Sinha (1986) in ($AlCl_3$ + BPC) RTIL. It should be noted that U(v) was found to be stable in these RTILs. Moreover, if oxide ions are present in these RTILs, mixed oxo-chloro complexes can be formed. The chemistry of these RTILs is thus more complex than for the basic melts. After extensive electrochemical and spectrochemical work, Costa *et al.* (2000) proposed a general scheme (Fig. 24.13) for the inter-conversion of U(vi), U(v), U(iv), and U(iii) species by chemical and electrochemical equilibria in acidic ($AlCl_3$ + EMIC) RTILs.

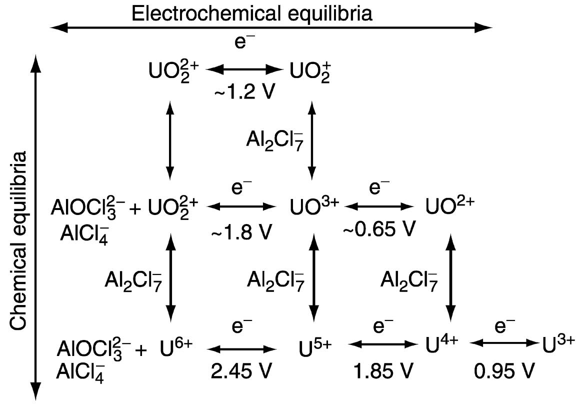


Fig. 24.13 *Mechanism for the inter-conversion of the different chemical forms of uranium within acidic RTILs* (*Costa* et al., 2000) (*note that the* Cl^- *ligands bound to the U ions are not shown for clarity*).

(d) Neptunium chemistry in basic and acidic ($AlCl_3$ + BPC) RTILs

Schoebrechts and Gilbert (1985) published the only paper on neptunium chemistry in ionic liquids. In acidic as well as in basic RTILs, the electrochemical reduction of Np(IV) to Np(III) is quasi-reversible on a glassy carbon electrode. UV–visible and Raman spectra indicated that Np(IV) and Np(III) both exist as hexachloro complexes in basic media. For acidic melts, these complexes are destabilized and Np(III) was found to lose more Cl^- ligands than Np(IV). These results are close to those observed for U in ($AlCl_3$ + EMIC) RTILs mentioned above.

(e) Plutonium chemistry in basic and acidic ($AlCl_3$ + EMIC) RTILs

Costa *et al.* (2000) published the only fundamental paper related to plutonium chemistry in basic and acidic ($AlCl_3$ + EMIC) RTILs. In basic RTIL, the reversible redox couple Pu(IV)/Pu(III) was observed at +0.37 V [the reference electrode being an aluminum metal wire in a 40/60 basic ($AlCl_3$ + EMIC) RTIL]. For acidic melts, the electrochemical behavior of plutonium resembles that described above for uranium, with the involvement of the plutonium oxidation states 6+, 5+, 5+, and 3+, and the existence of chloro and oxochloro complexes (Fig. 24.13). Further work is required for a more precise understanding of the chemistry of plutonium in these RTILs.

(f) Possible separation techniques for actinides using RTILs

The potential interest of using RTILs in the industrial processing of actinide nuclear materials is being tested by a team led by Costa at Los Alamos National Laboratory (USA) which studied plutonium processing (Costa *et al.*, 2000;

Harmon *et al.*, 2001). Another team in UK led by Seddon supported by British Nuclear Fuels Plc, proposes the use of RTILs for the reprocessing of commercial spent nuclear fuels and the treatment of nuclear wastes. In recent years, this team filed several patents in this area (Fields *et al.*, 1998, 1999; Thied *et al.*, 1999, 2001). Several techniques that could be used in processing nuclear materials within RTILs are briefly described in the following sections.

(*i*) *Dissolution*

Dissolution of solid actinide compounds in RTILs has been established. UO_3 readily dissolves in basic ($AlCl_3$ + BPC, Heerman *et al.*, 1985; $AlCl_3$ + EMIC) RTILs (Anderson, 1990; Anderson *et al.*, 1991). As shown by the patent of Fields *et al.* (1998), UO_2 dissolves in RTIL made of nitrates of BP^+ or EMI^+. This requires the presence of an oxidant to convert U(IV) (from UO_2) into soluble U(VI). Suitable oxidants include HNO_3, H_2SO_4, and $[NO][BF_4]$. These nitrate-based RTILs are the main new media proposed by BNFL for nuclear spent fuel reprocessing: in their patent, Thied *et al.* (2001) have shown that uranium and plutonium *metals* can be dissolved by anodic electrochemical oxidation in BMI nitrate (for U at room temperature) and EMIC (for Pu at 90°C).

(*ii*) *Precipitation*

U(VI) can be precipitated from an RTIL of BMI nitrate in the form of a crystalline compound (Bradley *et al.*, 2002) with the formula $[\{(UO_2)(NO_3)_2\}_2(C_2O_4)][BMI]_2$. The source of the oxalate anion that induces the precipitation of U(VI) can be acetone, being oxidized to oxalate by the medium.

(*iii*) *Electrodeposition of metals*

Thied *et al.* (2001) claimed the feasibility of electrorefining uranium in molten hexylethylimidazolium (HEI) chloride at 70°C using a uranium metal rod anode and a copper cathode. During the experiment described, for a total of 236 Coulombs passed in the electrochemical cell, 193 mg of uranium metal was dissolved from the anode as U(III) species in the melt and 18.7 mg of uranium was deposited on the copper cathode. Solid material was found at the bottom of the cell, indicating that deposited uranium does not adhere well to copper. An identical experiment was performed for plutonium, but no plutonium deposit was observed on the cathode.

More work is necessary in the domain of electrodeposition of actinide metals from RTILs. The experience accumulated in the field of electrodeposition of metals could be used to select suitable systems. RTILs made of AMI^+ cations are preferable owing to the low potential required for the reduction of AMI^+. For example, in melts made of neutral ($AlCl_3$ + EMIC), the electrodeposition of lithium and sodium metals can be performed if the solutes HCl (Gray *et al.*, 1995) or SO_2Cl_2 (Fuller *et al.*, 1995) are present in the melts. Tsuda *et al.* (2001, 2002) also studied the electrodeposition of lanthanum metal or Al–La alloy from ($AlCl_3$ + EMIC) RTIL.

(*iv*) *Liquid–liquid extraction*

Liquid–liquid extraction of metal ions is possible with hydrophobic RTILs based on the use of the anions: BF_4^-, PF_6^-, and $N(SO_2CF_3)_2^-$. The first work was published by Dai *et al.* (1999) who showed that Sr(II) can be very efficiently extracted from aqueous solutions by a crown ether dissolved in RTILs made of AMI^+ cations and the anions PF_6^- or $N(SO_2CF_3)_2^-$. Subsequent investigations (Jensen *et al.*, 2002b, 2003) have established that the elevated distribution ratios and resistance to back extraction exhibited by this system are at least in part a result of extraction occurring by a cation exchange mechanism in which the AMI^+ cation is transferred (irreversibly) to the aqueous phase. Since then, Rogers and his co-workers published several important papers in this field (Visser *et al.*, 2000a,b, 2001a,b) including a review paper (Visser *et al.*, 2002).

A few reports address features of the partitioning of actinides into RTILs (Davis, 2002; Visser and Rogers, 2002; Visser *et al.*, 2003). This system likewise is impacted by the problem of undesirable partitioning of the hydrophobic cation to the aqueous and irreversibility of the phase transfer reaction (Jensen *et al.*, 2003). Much additional work is required before this simple solvent-substitution approach to improving actinide separations with RTILs can be established.

(g) Conclusions

The chemistry of the actinides in RTILs is still in its infancy. Due to the recent impetus given by several research teams in the U.S. and UK, growing interest can be expected worldwide in this field owing, in particular, to the interesting practical applications that could be designed for the nuclear industry. Issues related to biphasic instability, generation of HF, the expense and toxicity of the RTILs may prove a significant obstacle to any efforts for an early implementation of these compounds in actinide process chemistry.

24.3.12 Pyrochemical processes

Pyrochemical processing involves the conduct of dry chemical reactions at high temperature in which the reactions occur in solid, liquid, and gas phases. Oxidation–reduction, volatilization (of halide or metal), slagging (melt refining, molten salt extraction, carbide slagging), liquid metal (melt refining, liquid metal extraction, liquation, precipitation), and electrolytic processes are the most common types.

Molten salts – or fused salts – lead to operating conditions that are constraining: high temperatures are required and corrosion effects are common, making identification of appropriate containers quite difficult. However, metallurgists use molten salts for electrolytic production of some metallic products, notably for refining very electropositive elements and strong reducing agent such as alkali metals. Potassium and sodium metals were first prepared in 1807 by using melt electrolysis of respectively potash and soda (Davy, 1808). Today melt electrolysis (alkali chloride) remains the only process for production of metallic sodium or lithium. Molten salt refining is also appropriate for aluminum, which is obtained by electrolytic decomposition of aluminum oxide in molten cryolite (Hall–Héroult process) (Grojtheim *et al.*, 1982).

Essential to the examples above, molten salts also have some properties which make them attractive for nuclear applications: (i) they are less subject to radiolytic degradation than aqueous media due to their ionic liquid structure; (ii) criticality concerns and problems are reduced due to the absence of neutron moderating elements and organic solvents. These properties in particular enable the processing of materials producing high radiation loadings, for example, high concentrations of fissile materials like spent nuclear fuels after a short cooling interval. In addition, it is possible to reduce the number of chemical conversion steps compared to those needed for aqueous processes. The first significant attempts at actinide metal production in molten salts started with the Manhattan Project in the 1940s (Rhodes, 1986). Significantly, Kolodney (1982) confirmed that uranium and plutonium could be electrodeposited from molten chlorides. The literature on U and Pu electrorefining in molten salts has been reviewed by Willit *et al.* (1992). Basic chemistry and technologies developed in Russia have been described by Bychkov and Skiba (1999).

Today, molten alkali and alkaline earth chlorides have been most extensively studied for plutonium conversion and separation. Three processes are in use throughout the world at significant scale-up (Moser and Navratil, 1983): (i) direct oxide reduction (DOR) process which consists of PuO_2 reduction by calcium in Ca-based chloride salt; (ii) molten salt extraction (MSE) process for ^{241}Am removal from weapon-grade plutonium by $MgCl_2$ in alkali chloride salt; (iii) electrorefining (ER) process for high plutonium purification using molten alkali and/or alkaline earth chloride electrolyte.

Pyroprocessing has also been proposed and developed for reducing the cost of fuel fabrication and fuel reprocessing (Motta, 1956). Between 1964 and 1969, a rudimentary process without molten salts – melt refining – was first demonstrated in Idaho Falls to recycle metallic fuel from the second experimental breeder reactor (EBR-II) (Trice and Chellew, 1961; Stevenson, 1987).

At the same time in the former USSR, emerged a concept of vibropacked fuel fabrication for fast reactors and pyroelectrochemical reprocessing based on electrolysis of oxide fuel in molten alkali chlorides. After being applied to UOX fuel, the Dimitrovgrad Dry Process (DDP) process has been adapted today for

MOX fuel reprocessing and weapon-grade plutonium conversion into plutonium oxide for civilian use in Russian fast reactors (Bychkov *et al.*, 1995; Skiba and Ivanov, 1995).

Due to the low burn-ups that have been achieved with EBR-II and for safety considerations, the interest in metal fuels declined in the U.S. for the next 15 years while ceramic fuel development, mainly oxides, increased (Burris, 1986). Consequently, molten salt process development slowed in the U.S. In the mid-1980s, interest of molten salts was renewed by the integral fast reactor concept proposed by Argonne National Laboratory (Till and Chang, 1988; Chang, 1989; Hannum, 1997). A combination of the electrometallurgical technology (EMT) and a set of molten salt/liquid alloy extractions was selected for overall actinide management purposes in the IFR fuel cycle (metallic alloy of U, Pu, and Zr) (Burris *et al.*, 1987). EMT consists of electrorefining the reactor fuel in LiCl–KCl melt at 500°C in an inert atmosphere: (i) the fuel in metallic form is dissolved at the anode, (ii) uranium, plutonium, and other transuranium elements are selectively deposited on solid or liquid cathode (e.g. cadmium), (iii) cladding material and fission products are left at the anode and/or in the electrolyte. In parallel, a pyrometallurgical process for the recovery of the transuranium elements from irradiated oxide fuels was initiated as a means of providing a source of plutonium for the start-up of additional IFRs (Pierce, 1991).

After the IFR program was stopped in 1994, EMT development was sufficiently advanced to be proposed for new applications: DOE spent nuclear fuel reconditioning (Laidler, 1994). A demonstration campaign (1996–1999) on spent EBR-II fuel in Idaho Falls used EMT for converting the fuel to a safe configuration by eliminating the sodium seal and recovering high enriched uranium for interim storage.

EMT is now being considered around the world for various fuel cycle concepts. Japan calls for the development of: (i) a global fuel cycle combining oxide fuel in pressurized water reactors (PWR) with transmutation of actinides as metal fuel in fast neutron reactors and (ii) a ^{15}N-enriched nitride fuel cycle involving molten salt reprocessing for ^{15}N management. For both projects, spent fuel reprocessing should take place in a LiCl–KCl melt using previous separation techniques: DOR process (lithium substituting calcium), ER process on solid or liquid cathode, and MSE process (Inoue *et al.*, 1991; Arai and Yamashita, 1997; Takano *et al.*, 1998).

Researchers in the U.S. recently have proposed a baseline process combining aqueous and pyrochemical processes in the framework of the preparation of a technology development roadmap for the accelerator transmutation of waste (ATW) Technology (ATW Separations, 1999). The process begins with an aqueous 'UREX' process that would produce from light water reactor (LWR) spent fuel a pure U stream for waste, technetium, and iodine streams for target fabrication and a transuranium elements–fission product oxide stream. Using pyroprocessing, this oxide stream would be treated for converting TRU elements to a metallic form suitable for fabrication of ATW fuel (based on Zr).

The pyroprocessing should involve two steps: (i) DOR process with Li in LiCl melt to reduce the actinide oxides to the metallic form and (ii) EMT in LiCl–KCl melt to separate transuranium elements from the remaining fission products. The baseline option for ATW irradiated fuel processing would rest on a chloride volatility process for zirconium separation coupled to an electrowinning process in LiCl–KCl for TRU and fission product separation.

Since the mid-1990s, countries of the European Community (Great Britain, France, Spain, Italy), the European Institute for Transuranium Elements (Karlsruhe, Germany), and the Czech Republic have launched research programs for the development of molten salt chemistry and technology for various applications (Partitioning & Transmutation, future fuel cycles). At present, these programs only involve work at the laboratory scale on fundamental aspects or small pilot projects.

Finally, a fused medium in which fuel and reprocessing are strongly connected concerns molten fluorides. In the past, molten fluorides have been developed as fuel and coolant in molten salt reactor systems. The development was largely carried out at Oak Ridge National Laboratory in the 1960s for the molten salt breeder reactor concept, using molten LiF–BeF_2 solutions. Today molten salt reactor development has been stopped, though some countries continue isolated investigations (e.g. Czech Republic or Russia).

(a) Chemistry of actinides in major salts – general considerations

As noted above, all the significant pyrochemical technology developments for plutonium conversion and for oxide, metal, or nitride fuel reprocessing call essentially for halide systems: molten chlorides of alkaline and alkaline earth metals, molten fluorides of different cation compositions. Other salt systems, based on oxy-anion salts, have been proposed as backup process or for exotic fuel processing. The most common salts of alkali metals are nitrates, sulfates, molybdates, and tungstates.

Both fundamental and technological progress was reported at the beginning of the 1990s. In this section, after a presentation of the main chemical properties of actinides in molten salts, the principles of separation techniques will be described and main ongoing work on pyroreprocessing in the nuclear industry will be presented. For more detailed information, the reader is referred to the literature cited herein. Molten salt chemistry of actinides has been reviewed previously by Martinot (1991).

(b) Molten chlorides

(*i*) *Thorium*

Anhydrous $ThCl_4$ is colorless and is prepared, among other techniques, by reacting a mixture of $CCl_4 + Cl_2$ gases on ThO_2 at 600°C (Cuthbert, 1958). Dissolved in a KCl melt, thorium exists in the tetravalent oxidation state.

The existence of Th(II) has been reported (Smirnov and Ivanovskii, 1957), but this conclusion also has been disputed (Martinot, 1991). Apparent standard potentials of Th(IV)/Th(0) (relative to the Cl_2/Cl^-, mole fraction couple) are –2.52, –2.50, and –2.47 V at 673, 723, and 773 K, respectively, in LiCl–KCl eutectic (Martinot *et al.*, 1977) and $-3.109 + 6.3810^{-4}T$ (923–973 K) (in volts) in NaCl–KCl eutectic (Srinivasan and Flengas, 1964). Activity coefficient at infinite dilution in LiCl–KCl and NaCl–KCl, solubility product of ThO_2 in LiCl–KCl and NaCl–KCl, potential–pO^{2-} diagram in LiCl–KCl with $[Th(IV)] = 10^{-2}$ M are given by Martinot (1986, 1991).

(*ii*) *Protactinium*

Anhydrous $PaCl_4$ is prepared from PaO_2 by reacting with CCl_4 at 300°C (Stein, 1964) while $PaCl_5$ is obtained from Pa_2O_5 reactions with $SOCl_2$ at 400°C (Brown and Jones, 1966; Hendricks *et al.*, 1971). Pa(V) is reduced in chloride melts to Pa(IV). Apparent standard potential of Pa(IV)/Pa(0) (referred to Cl_2/Cl^-, mole fraction) are –2.35, –2.32, and –2.29 V at 673, 723, and 773 K, respectively, in LiCl–KCl eutectic (Martinot *et al.*, 1980). Activity coefficient at infinite dilution, solubility product of PaO_2 and potential–pO^{2-} diagram in LiCl–KCl with $[Pa(IV)] = 10^{-2}$ M are given by Martinot and Fuger (1986, 1991).

(*iii*) *Uranium*

A great deal of work has been done in the past in binary melts (NaCl–KCl, LiCl–KCl, NaCl–CsCl), in NaCl–KCl–$BaCl_2$, NaCl–KCl–$MgCl_2$, LiCl–NaCl–$CaCl_2$–$BaCl_2$, and the results have been reviewed (Martinot, 1991; Willit *et al.*, 1992; Bychkov and Skiba, 1999). Some results in LiCl–KCl have been published as well (Roy *et al.*, 1996; Sakamura *et al.*, 1998; Shirai *et al.*, 1998). The reader is referred to these papers for more detailed information. Only values related to melts in use in the current EMT development are reported hereafter. It essentially concerns three alkali chloride eutectics: NaCl–KCl, NaCl–2CsCl, and 3LiCl–2KCl.

Uranium in NaCl–KCl

The first EMF measurements, referred to Ag/AgCl (5 mol%) or Cl_2/Cl^- electrodes, have been made from 700 to 850°C (Flengas, 1961; Smirnov and Skiba, 1963). These authors reported only the U(III)/U(0) and U(IV)/U(III) couples. Martinot and coworkers gave the temperature dependence of the several apparent standard potentials (referred to Cl_2/Cl^- electrode). At 700°C (Martinot and Ligot, 1989; Martinot, 1991), $E°[U(III)/U(0)] = -2.49$ V, $E°[U(IV)/U(III)] = -1.33$ V, and $E°[U(V)/UO_2] = -0.80$ V. A recent review (Bychkov and Skiba, 1999) reports 'formal electrode potential' at 727°C (referred to Cl_2/Cl^- electrode): $E°[U(III)/U(0)] = -2.19$ V, $E°[U(IV)/U(III)] = -1.39$ V, and $E°[U(VI)/UO_2] = -0.40$ V. Willit *et al.* (1992) report that the formal potential incorporates both standard potential and ratio of activity coefficients of the oxidized and reduced species.

Activity coefficients for U(IV) and U(III) are available at various temperatures (Flengas, 1961; Martinot *et al.*, 1975; Martinot, 1991). Diffusion coefficients for U(IV) and U(III) at 700°C have been determined (Willit *et al.*, 1992). Martinot and Ligot (1989) and Martinot (1991) also report the temperature dependence of the solubility product of UO_2; a potential–pO^{2-} diagram has been calculated for $[U(V)] = [U(IV)] = [U(III)] = 10^{-2}$ M. These authors claim that U(VI) does not exist at equilibrium and that the stability area of U(V) is very wide in comparison with the other chloride melts.

Uranium in NaCl–2CsCl

Investigations in the eutectic have been made in the framework of the DDP process development. Few data are available in the open literature. Formal electrode potentials (referred to Cl_2/Cl^- electrode) are given at 727°C: $E°[U(III)/U(0)] = -2.39$ V, $E°[U(IV)/U(0)] = -1.45$ V, and $E°[U(VI)/UO_2] = -0.65$ V (Bychkov and Skiba, 1999).

Uranium in 3LiCl–2KCl

U(III), U(IV), and U(VI) have been identified spectrophotometrically in LiCl–KCl melt (Gruen *et al.*, 1960). At present, the existence of U(V) is no longer considered in dispute (Martinot, 1991). As for the NaCl–KCl eutectic, historic background and basic data have been reported in previous reviews (Martinot, 1991; Willit *et al.,* 1992; Bychkov and Skiba, 1999). Several apparent standard potentials (referred to Cl_2/Cl^-, molar fraction) are available from Martinot (1991): at 450°C, $E°[U(III)/U(0)] = -2.59$ V, $E°[U(IV)/U(III)] = -1.49$ V, $E°[U(VI)/U(V)] = -0.84$ V, and $E°[U(VI)/UO_2] = -0.81$ V. Data from Russian studies are summarized at 500°C by Bychkov and Skiba (1999): $E°[U(III)/U(0)] = -2.31$ V, $E°[U(IV)/U(III)] = -1.40$ V, and $E°[U(VI)/UO_2] = -0.50$ V, all referred to Cl_2/Cl^-. Recent results on the U(III)/U(0) couple (Roy *et al.*, 1996; Sakamura *et al.*, 1998) give at 450°C $E° = -1.287$ V vs Ag/AgCl (–2.498 V vs Cl_2/Cl^-), which is consistent with other reports.

Activity coefficients at infinite dilution for U(IV) and U(III) are given as a function of temperature (Martinot, 1975, 1991). New calculations have been made recently by Roy *et al.* (1996) and by Betchel and Storvick (1999). Roy and coworkers indicate non-ideal solution behavior for U(III) (activity coefficient is 3.1×10^{-3} at 450°C). Diffusion coefficients for U(IV), U(III) and U(VI) have been determined by Caligara *et al.* (1968) for the range of temperature 400–550°C; other studies of U(III) and U(IV) have been reviewed by Willit *et al.* (1992). $D_{U(III)}$ is typically between 4.1 and 10.3×10^{-3} $cm^2 s^{-1}$. Using the values of UO_2 solubility product (Martinot and Fuger, 1986), Martinot (1991) has calculated potential–pO^{2-} diagram at 450°C (Fig. 24.14). The stability area of U(V) is rather narrow in comparison with NaCl–KCl eutectic.

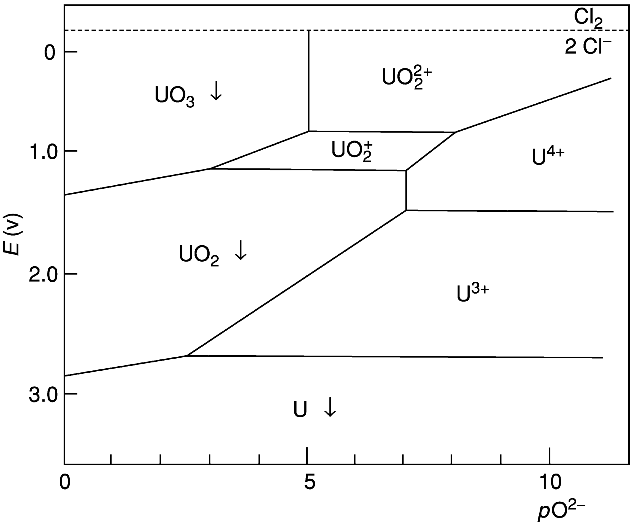


Fig. 24.14 *Potential–*pO^{2-} *diagram for* [*U*(*iv*)] = [*U*(*iii*)] = [*U*(*iv*)] = [*U*(*v*)] = 10^{-2} M *in* 3*LiCl–2KCl at* 450°C (*Martinot*, 1991).

(*iv*) Neptunium

Neptunium has been the subject of fewer investigations than uranium. Its chemical behavior has been most extensively studied in alkali chloride melts. In the eutectic (3LiCl–2KCl), the 3+, 4+, and 5+ oxidation states have been identified spectrophotometrically (Gruen *et al.*, 1960). Np(iv), Np(iii), and Np(v) are stable species while Np(vi) does not exist as a stable species. Np(vi) is reduced by chloride ions to Np(v) (Martinot, 1991). Standard potentials for Np(iii)/Np(0), Np(iv)/Np(iii), and Np(v)/NpO_2 have been measured (vs Cl_2/Cl^-, molar fraction) at various temperatures by Martinot and coworkers (Martinot *et al.*, 1967; Martinot and Duyckaerts, 1969a,b). At 450°C, the standard potentials are: $E°$[Np(iii)/Np(0)] = –2.41 V, $E°$[Np(iv)/Np(iii)] = –0.70 V, and $E°$[Np(v)/NpO_2] = –0.32 V (Martinot, 1991). Bychkov and Skiba (1999) report formal potentials (vs Cl_2/Cl^-, molar fraction) at 500°C: $E°$[Np(iii)/Np (0)] = –2.315 V, $E°$[Np(iv)/Np(iii)] = –1.51 V, and $E°$[Np(v)/NpO_2] = –0.32 V (450°C). The latest reports from Roy and coworkers (Roy *et al.*, 1996; Sakamura *et al.*, 1998) give for Np(iii)/Np(0) $E° = -1.487$ V vs Ag/AgCl (i.e. –2.698V vs Cl_2/Cl^-). Discrepancies in the results could possibly be explained by the variety of experimental arrangements.

Activity coefficient of Np(iii) and diffusion coefficients of Np(iii), Np(iv), and Np(v) are available in the literature (Martinot, 1975, 1986, 1991). $D_{Np(III)}$ is equal to $(4.6 \pm 0.2) \times 10^{-6}$ $cm^2\,s^{-1}$ at 400°C. The solubility product of NpO_2 has also been measured as a function of temperature by Martinot and

Fuger (1986). Potential–$p\text{O}^{2-}$ diagram has been calculated for [Np(v)] = [Np(iv)] = [Np(iii)] = 10^{-2} M at 450°C (Martinot, 1986, 1991).

(*v*) *Plutonium*

The electrochemistry of plutonium in molten chlorides was studied early driven by the belief that electrorefining could be a method of purification of plutonium notably for military applications (Brodsky and Carleson, 1962; Mullins and Leary, 1965). Willit *et al.* (1992) have published a useful review on the technological aspects. The melts investigated include LiCl–KCl, NaCl–KCl, $BaCl_2$–KCl, $BaCl_2$–$CaCl_2$–LiCl—NaCl, and NaCl–$CaCl_2$. The most stable oxidation state of plutonium in alkali chloride melts is the trivalent state. Chronopotentiometric and potentiometric studies carried out in the 1960s and 1970s to understand the mechanism of Pu(iii) reduction (Campbell and Leary, 1966; Nissen, 1966; Martinot, 1991; Bychkov and Skiba, 1999) have been recently repeated (Roy *et al.*, 1996; Sakamura *et al.*, 1998, 2001; Shirai *et al.*, 1998, 2001). Campbell and Leary (1966) measured the standard potential of Pu(iii)/Pu in 3LiCl–2KCl as a function of temperature using a Ag/AgCl reference electrode. Recent results with the same kind of reference electrode agree with the previous value within the uncertainties of the Ag/AgCl electrode potentials due certainly to the membrane potential: $E°$[Pu(iii)/Pu(0)] = –2.204 + 0.000845T (vs Ag/AgCl, molar fraction, AgCl 1 wt%) (Sakamura *et al.*, 2001). When adjusted to the Cl_2/Cl^- reference, the standard potential should be –2.775 V at 500°C (Roy *et al.*, 1996). Bychkov and Skiba (1999) reports a similar result (–2.82 V) while Martinot (1991) gave a more positive potential.

The activity coefficient of Pu(iii) in 3LiCl–2KCl is between 1.0×10^{-3} and 4.1×10^{-3} from 400 to 500°C (Roy *et al.*, 1996). Diffusion coefficient $D_{\text{Pu(III)}}$ is equal to 12×10^{-6} $\text{cm}^2\ \text{s}^{-1}$ (Nissen, 1966; Willit *et al.*, 1992). These data are similar to those of UCl_3. The Pu(iv)/Pu(iii) couple has been investigated (Martinot and Duyckaerts, 1970, 1973; Landresse and Duyckaerts, 1974; Bychkov and Skiba, 1999). In common alkali chloride melts, the standard potential of the Pu(iv)/Pu(iii) couple is very close to that of Cl_2/Cl^-. For example, in 3LiCl–KCl at 500°C, $E°$[Pu(iv)/Pu(iii)] = +0.01 V, in NaCl–KCl at 727°C $E°$[Pu(iv)/Pu(iii)] = +0.09 V, in NaCl–2CsCl at 600°C, $E°$[Pu(iv)/Pu(iii)] = –0.05 V (Bychkov and Skiba, 1999).

In the presence of a chlorine–oxygen gas mixtures, oxygen-free trivalent and tetravalent forms of plutonium disappear while oxygenated ions of Pu(v) and Pu(vi) appear (Martinot, 1991; Bychkov and Skiba, 1999). The potential–$p\text{O}^{2-}$ diagram in 3LiCl–2KCl at 450°C is available from Martinot and coworkers (Martinot and Duyckaerts, 1973; Martinot, 1991) but the authors indicate that it must be considered as a tentative diagram due to large uncertainties in solubility products of plutonium oxides. The NaCl–2CsCl eutectic has been well investigated and temperature dependencies of standard potentials of Pu(vi)/PuO_2 and Pu(v)/PuO_2 couples are known. A potential–$p\text{O}^{2-}$

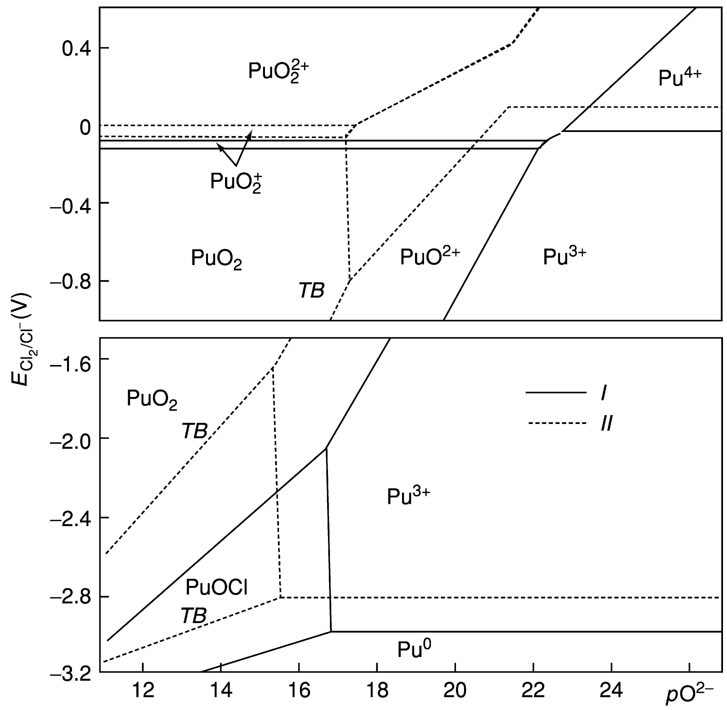


Fig. 24.15 *Potential–p*O^{2-} *diagram for* [Pu(IV)] = [Pu(III)] = [PuO_2^+] = [PuO_2^{2+}] = [PuO^{2+}] = 10^{-3} M *in NaCl–2CsCl at* 600°C (*solid line*) *and* 800°C (*dashed line*). *Insoluble species are indicated with the TB notation.* (*Vavilov* et al., 1985).

diagram (Fig. 24.15) has been calculated for the medium NaCl–2CsCl (Vavilov *et al.*, 1985).

(*vi*) *Americium*

The existence of both trivalent and divalent americium in alkali chloride melts has been claimed. Initially, similarity in the spectrum of $AmCl_3$ dissolved in 3LiCl–KCl at 450°C obtained by Gruen *et al.* (1960) and the spectrum of Am(III) in concentrated HCl establish the existence of Am(III). Later, chronopotentiometric studies by Martinot *et al.* (1973) in the same eutectic confirmed the existence of the Am(III)/Am(0) couple. Leary and Mullins (1973) argued the existence of Am(II) in NaCl–KCl eutectic, while Kolesnikov *et al.* (1976), using measurements of polarization of various cathodes in $AmCl_3$–NaCl–KCl melts ($AmCl_3$ 1.1 wt%) at 700°C, just showed the wave of discharging of Am(III) to the metal. More recently, based on cyclic voltammetry at 450°C in 3LiCl–2KCl, Grimmett *et al.* (1994) proposed that deposition of Am proceeds in two steps: reduction of Am(III) to Am(II) and then Am(II) into Am metal. The two oxidation states have been confirmed by Lambertin *et al.* (2000).

Standard potentials vs Cl_2/Cl^- for Am(III)/Am(II) and Am(II)/Am(0) in 3LiCl–2KCl between 450 and 500°C reported by several authors (Bychkov and Skiba, 1999; Fusselman *et al.*, 1999; Lambertin *et al.*, 2001) are internally consistent. At 450°C, $E°$[Am(III)/Am(II)] = –2.83 V, $E°$[Am(II)/Am(0)] = –2.852 V (Fusselman *et al.*, 1999). The existence and solubility products of AmO^+, AmOCl, and Am_2O_3 in 3LiCl–2KCl have been determined by potentiometric titration and cyclic voltammetry; a potential–pO^{2-} diagram has been calculated at 470°C for [Am(III)] = [Am(II)] = 10^{-2} M (Lambertin *et al.*, 2000). Lambertin also reports disproportionation of divalent americium in 3LiCl–2KCl can be induced by addition of fluoride anion.

(*vii*) *Curium and transcurium elements*

There have been few studies on the chemistry of curium in chloride melts. Trivalent curium has been identified in 3LiCl–2KCl and NaCl–KCl (Martinot *et al.*, 1975; Kolesnikov *et al.*, 1976). In NaCl–KCl at 750°C, Kolesnikov and coworkers showed, as for americium, that the potential of discharging Cm(III) to Cm(0) is close to the potential of deposition of the alkali metal (difference 0.25–0.3 V) and claimed use of a liquid cathode for alloying americium or curium during recovery by electrolysis. Attempts have been carried out with a zinc cathode (Kolesnikov *et al.*, 1976). In their investigations on the lowest oxidation states of lanthanides and actinides, Kulyukhin *et al.* (1997) show that californium, einsteinium, and fermium in LiCl–$NdCl_2$–$NdCl_3$ melt can be reduced only to the 2+ oxidation state. This is also true for americium.

(c) Molten fluorides

The chemical development carried out in support of the molten salt breeder reactor (MSBR) at Oak Ridge National Laboratory (ORNL) has produced a quantitative description of the chemistry and thermodynamics of actinide and fission-product fluorides in molten LiF–BeF_2 solutions (Baes, 1966). The molten-salt technology was based on the concept of a high-temperature, thermal-neutron breeder reactor that operated on the ^{233}U–^{232}Th fuel cycle with ^7LiF–BeF_2–ThF_4–UF_4 (71.7–16–12–0.3 mol%) as reference fuel (Hightower, 1975). In that case, the nature of the fuel logically implies on-site reprocessing involving molten phases to minimize the number of conversion steps and to have low reprocessing costs. The processes that have been developed are described in numerous reports from ORNL. The chemistry of the actinides in molten fluorides has been reviewed (Martinot, 1991). We refer the reader to this comprehensive review as a source for quantitative data – in particular for solubility products, apparent standard potentials, and activity coefficients – of the actinides in molten fluorides. The basic chemical properties of actinides in MSBR melt and the principles of molten salt reactor processing are briefly described in the following sections.

(*i*) *Thorium and protactinium*

In LiF–BeF_2 (67–33 mol%), LiF–BeF_2–ThF_4 (72–16–12 mol%), and LiF–NaF–KF (46.5–11.5–42 mol%) melts, only the tetravalent oxidation state is observed for thorium. Coordination complexes are formed depending on the excess of free fluoride ions in the melt. The activity coefficient for ThF_4 has been measured as a function of the LiF mole fraction in various LiF–BeF_2–ThF_4 melts (Baes, 1974). In the MSBR fuel cycle, ^{233}Pa is formed as a result of neutron capture by ^{232}Th. In such a medium, tetravalent and pentavalent protactinium are potentially coexisting species. By controlling the pO^{2-} and the redox potential of the melt (i.e. U(IV)/U(III) ratio, if the MSBR operating conditions this ratio is ~100), it is possible to have protactinium only in the tetravalent oxidation state (Ross *et al.*, 1973; Tallent and Ferris, 1974).

(*ii*) *Uranium and plutonium*

Trivalent and tetravalent uranium are stable in MSBR melt. Apparent standard potentials have been experimentally measured in LiF–BeF_2 (67–33 mol%) as a function of temperature (Martinot, 1975). The chemistry of uranium has been largely investigated and equilibrium constants of interest have been determined in MSBR melt (Baes, 1969; Long and Blankenship, 1969; Toth and Gilpatrick, 1972) to control the redox potential of the fuel and undesirable reactions (e.g. corrosion). By fixing the ratio of U(IV)/U(III) to about 100, only the trivalent oxidation state is stable. Quantitative data (apparent standard potential of Pu(III)/Pu(0), solubility of PuF_3 and PuO_2) are available in LiF–BeF_2 (67–33 mol%) and LiF–BeF_2–UF_4 (70–10–20 mol%) (Baes, 1969; Toth and Gilpatrick, 1972).

(d) Processing requirements

If a thorium–uranium reactor is to operate as a breeder, ^{233}Pa must be isolated from the region of high neutron flux during its decay to ^{233}U. Also, the fission products must be removed in order to minimize neutron absorptions. The rare earths and zirconium are the principal fission products that must be removed. It also is necessary to remove the excess uranium that is produced to maintain the proper redox potential of the fuel salt and to maintain oxide and corrosion product concentrations at acceptable levels (Long and Blankenship, 1969).

(e) Molten-salt reactor processing

The reference flow sheet has been described (Bell and McNeese, 1971; Hightower, 1975) and was based upon a fluorination-reductive extraction and a metal-transfer process. The fuel salt containing 0.3 mol% of UF_4 and approximately 0.0035 mol% of PaF_4 is withdrawn from the reactor on a 10-day cycle. Uranium is first removed as volatile UF_6 in a continuous fluorinator. The U-free salt is then fed to an extraction column where protactinium, zirconium, and the remaining uranium are extracted into a bismuth stream containing a reductant.

Subsequently, the bismuth stream is hydrofluorinated in the presence of a second salt stream, which results in transfer of the extracted materials to the salt. Reductant is added to recovered bismuth, and the resulting metal stream is recycled to the extraction column. The secondary salt stream is circulated through a hydrofluorinator, a fluorinator, and a protactinium decay tank. The fluorinator is used to maintain an acceptably low uranium concentration in the protactinium decay tank. The salt is withdrawn from the decay tank periodically to remove zirconium and other fission products that accumulate in the tank. The salt is held for a sufficient period before final discard to allow ^{233}Pa to decay to ^{233}U, which is recovered from the salt by batch fluorination.

Salt leaving the protactinium extraction column is essentially free of uranium and protactinium but contains the rare earths. It is fed to the metal transfer process (McNeese, 1971). This process for removal of rare earths and separating them from thorium is based upon the selective extraction of rare earths from bismuth into LiCl (Ferris *et al.*, 1970, 1972). Rare earths and thorium are extracted into bismuth containing elemental lithium reductant (0.2 at.%) and the rare earths are selectively removed from the bismuth by contact with LiCl. Divalent and trivalent rare earths are removed separately from the LiCl by extraction into Bi–Li streams containing 50 and 5 at.% Li, respectively. The bismuth stream used for the isolation of protactinium is actually fed to the recirculating bismuth stream in the rare earth removal system.

Uranium is returned to the fuel salt in a fuel reconstitution step before the salt is sent back to the reactor. The uranium addition is performed by absorbing the UF_6 stream coming from the fluorinators into a recycle salt stream containing dissolved UF_4. UF_6 reacts with UF_4 to give non-volatile UF_5, which is reduced by hydrogen gas into UF_4. At last a purification step is necessary to remove traces of bismuth before the salt is returned to the reactor.

(f) Molten oxy-anion salts

(*i*) *Molten molybdates*

Investigations of molten molybdates focus on recrystallization of uranium and plutonium oxides (Bychkov and Skiba, 1999). A MoO_3–Na_2MoO_4 melt could be a potential candidate. Ustinov (1995) studied various phase diagrams of binary and ternary systems: UO_2–MoO_3, PuO_2–MoO_3, UO_3–MoO_3, CeO_2–MoO_3, ZrO_2–MoO_3, BaO–MoO_3, RuO_2–MoO_3, UO_2–MoO_3–Na_2MoO_4, PuO_2–MoO_3–Na_2MoO_4 in the temperature range 1000–1200°C. Practically all the oxides are dissolved in molten MoO_3 except for RuO_2. The solubility of the oxides of fission products in MoO_3 is higher than those of oxides of uranium and plutonium. On the other hand, oxides of uranium and plutonium have a low solubility in Na_2MoO_4. The solubility of molybdates of U and Pu increases with the temperature. From the experimental phase diagrams, various recrystallization methods are proposed for the production of: (i) UO_2, (ii) PuO_2, (iii) homogeneous solid solution of $(U–Pu)O_2$, and (iv) uranium molybdates.

(*ii*) *Molten tungstates*

Molten tungstates, $M_2WO_4–M_2W_2O_7$ where $M = Li$, Na, K, and Cs have some interesting physical properties: (i) high thermal stability, (ii) low volatility, (iii) relatively low melting points, and (iv) high values of decomposition voltage (Afonichkin and Komarov, 1995). Common working temperatures are in the range 700–900°C and an inert atmosphere is required (Afonichkin *et al.*, 2001). Nevertheless, there have been few experiments on actinides. Afonichkin and coworkers investigated the electrodeposition of uranium oxide from $Na_2WO_4–UO_2WO_4$ and $Na_2WO_4–Na_2W_2O_7–UO_2WO_4$ melts. In the binary melt, an ionic model has been proposed to explain the dissolution of uranium oxide and the formation of UO_2, UO_{2+x}, U_4O_{9-y}, and U_3O_8 phases on the cathode (Afonichkin *et al.*, 2001):

$$U_3O_8 + 2Na_2WO_4 + \frac{1}{2}O_2 \rightleftarrows Na_2[UO_2(WO_4)_2] + Na_2U_2O_7 \tag{24.25}$$

$$Na_2[UO_2(WO_4)_2] \rightleftarrows 2Na^+ + [UO_2(WO_4)_2]^{2-} \tag{24.26}$$

$$[UO_2(WO_4)_2]^{2-} \rightleftarrows UO_2^{2+} + 2WO_4^{2-} \tag{24.27}$$

$$2UO_2^{2+} + 2WO_4^{2-} \rightleftarrows U_2O_5^{2+} + W_2O_7^{2-} \tag{24.28}$$

and, in concentrated UO_2WO_4 solutions,

$$UO_2^{2+} + U_2O_5^{2+} + 2WO_4^{2-} \rightleftarrows U_3O_8^{2+} + W_2O_7^{2-} \tag{24.29}$$

Electrolysis:

$$UO_2^{2+} + 2e^- \rightleftarrows UO_2 \tag{24.30}$$

$$U_3O_8^{2+} + 2e^- \rightleftarrows U_3O_8 \tag{24.31}$$

$$(1-2x)UO_2^{2+} + xU_2O_5^{2+} + 2(1-x)e^- \rightleftarrows UO_{2+x} \tag{24.32}$$

$$2(1+y)UO_2^{2+} + (1-y)U_2O_5^{2+} + 2(3+y)e^- \rightleftarrows U_4O_{9-y} \tag{24.33}$$

If the ternary system allows a lower melting point, the resulting addition of $Na_2W_2O_7$ in the melt decreases the potential of the melt decomposition. However, it has been shown that the transition from the binary to the ternary melt has minimal effect on the oxygen coefficient and on the main parameters of electrolysis. Current efficiency does not exceed 65% of theoretical value (Afonichkin and Komarov, 1995; Afonichkin *et al.*, 2001), indicating chemical interactions of the cathodic product with the electrolyte. With increasing temperature and $W_2O_7^{2-}$ concentration, the current efficiency decreases.

(*iii*) *Nitrates and sulfates*

Several authors (Morgan *et al.*, 1980; Martinot, 1991; Bychkov and Skiba, 1999) have prepared comprehensive reviews of pyroprocessing of actinides in nitrate and sulfate media. Such media create awkward operating conditions since nitrate melts are particularly hazardous and processes in molten sulfates involve corrosive gaseous phases. A distinctive feature of the molten alkali nitrate melts (300–450°C) is the ability to dissolve uranium oxide while PuO_2 remains insoluble. In molten sulfates (450–650°C), both uranium and plutonium oxides can be dissolved using gaseous sulfur oxides or vapor of sulfuric acid (Brambilla, 1984; Bychkov and Skiba, 1999). Uranium oxide could be recovered by electrolysis though PuO_2 is precipitated by decomposition of its sulfate at high temperature (Brambilla, 1984; Bychkov and Skiba, 1999).

(g) Separation techniques: principles, performances, and limitations

(*i*) *Oxide–oxide processes*

Since the 1960s, Research Institute of Atomic Reactors (RIAR, Dimitrovgrad), has been developing fabrication and reprocessing processes for oxide fast reactor fuel (Bychkov *et al.*, 1995; Skiba and Ivanov, 1995). It combines vibropacking fabrication of fuel rods and pyroelectrochemical technology of spent fuel in molten alkali chlorides. Original studies conducted at Hanford within the framework of the Salt Cycle Process development (for UO_2–PuO_2 fuel reprocessing) involved LiCl–KCl melts (Benedict *et al.*, 1963). Changing the melt composition and the electrolysis atmosphere allowed production of various oxides. For instance, highly enriched UO_2 was dissolved in equimolar LiCl–KCl with chlorine sparging and UO_2Cl_2 was then electroreduced at 550–800°C to UO_2 on the cathode, leaving plutonium and fission products in the melt. If one wanted a PuO_2–UO_2 solid solution, electrolysis was done in the same melt at 475–675°C under chlorine–oxygen gaseous mixture. If it was only necessary to recover plutonium, dissolution was performed in 2.5:1 LiCl–KCl melt and plutonium was precipitated as dioxide with chlorine–oxygen sparging. Since that time, RIAR has developed a similar process, named Dimitrovgrad dry process (DDP), at the semi-industrial scale, for spent UO_2 or MOX fuel reprocessing, in two other alkali melts: NaCl–2CsCl or NaCl–KCl–UO_2Cl_2 (Bychkov and Skiba, 1999).

(*ii*) *Basis of the DDP*

Dissolution

First, spent oxide fuel is dissolved in the melt by a strong oxidizing agent, chlorine gas at 650–700°C. Actinides are present either as chlorides or oxychlorides (see Section 24.3.12b). Uranium and plutonium behaviors can be explained by the following chemical reactions and equilibria:

$$UO_2 + Cl_2 \rightleftarrows UO_2Cl_{2\,\mathrm{melt}} \qquad (24.34)$$

$$PuO_2 + Cl_2 \rightleftarrows PuO_2Cl_{2\,\mathrm{melt}} \qquad (24.35)$$

$$PuO_2Cl_2 \rightleftarrows PuO_2Cl_{\mathrm{melt}} + \frac{1}{2}Cl_2 \qquad (24.36)$$

$$PuO_2Cl_2 + Cl_2 \rightleftarrows PuCl_{4\,\mathrm{melt}} + O_2 \qquad (24.37)$$

$$PuCl_4 \rightleftarrows PuCl_{3\,\mathrm{melt}} + \frac{1}{2}Cl_2 \qquad (24.38)$$

U(VI) present as uranyl species UO_2^{2+} is stable; treating the melt with chlorine–oxygen gaseous mixture will stabilize the highest oxidation states of plutonium, respectively PuO_2^+ and PuO_2^{2+}. The temperature dependence of equilibrium constants for plutonium species in NaCl–2CsCl is known for various partial pressures of chlorine gas (Vavilov *et al.*, 1985).

Uranium and plutonium recovery

The recovery of uranium and plutonium as oxides at high temperature (> 400°C) works because UO_2 and PuO_2 conduct electricity and can be electrodeposited at a cathode like a metal. According to the formal potentials listed in Table 24.10, UO_2 and PuO_2 are reduced at more positive potentials than all the fission products, except for noble metals (Bychkov and Skiba, 1999; Bychkov *et al.*, 2000). If plutonium recovery is not necessary, UO_2Cl_2 is electroreduced to UO_2 at the pyrolytic carbon cathode, leaving plutonium and the majority of fission products in the melt. Recovery efficiency is 99.0–99.5% (Bychkov and Skiba, 1999). At the anode, chloride ions are oxidized to chlorine gas.

Table 24.10 *Formal electrode potentials of actinides and fission products* (*vs* Cl_2/Cl^-, *molar fraction*) *in NaCl–2CsCl eutectic at* 600°C (*in* volts) (*Bychkov and Skiba*, 1999).

Sm(II)/Sm	–3.58	Pu(III)/Pu	–2.83	U(VI)/UO_2	–0.65
Eu(II)/Eu	–3.39	U(III)/U	–2.39	Pd(II)/Pd	–0.48
Ce(III)/Ce	–3.08	Zr(IV)/Zr	–2.17	Rh(III)/Rh	–0.44
		Fe(II)/Fe	–1.48	Ru(III)/Ru (510°C)	–0.413
		U(IV)/U(III)	–1.45	Np(V)/NpO_2	–
		Mo(III)/Mo	–0.97	Pu(IV)/Pu(III)	–0.05
		Ag(I)/Ag	–0.932	Pu(VI)/PuO_2	+0.12

If both uranium and plutonium recovery is desired, electrolysis must be carried out while sparging the melt with an oxygen–chlorine gaseous mixture (Bychkov and Skiba, 1999). The cathodic products are quasi-homogeneous (U, Pu)O_2 with two-phase composition: solid solution of PuO_2 in UO_2 crystals and solid solution of UO_2 in PuO_2 crystals. UO_2 deposition rate is pre-set by current density while PuO_2 deposition rate is limited by the diffusion of plutonyl ions to the cathode (Bychkov *et al.*, 2000). If it should be necessary to recover only PuO_2, dissolution is performed in NaCl–KCl and plutonium oxide is precipitated by oxygen gas (Bychkov and Skiba, 1999).

Behavior of minor actinides

(Np, Am, and Cm). After the dissolution step, neptunium is present in the melt as NpO_2^+. As a result, neptunium is electroreduced to NpO_2 and is co-deposited with uranium oxide (see Table 24.11). The behavior of americium and curium is not similar to that of neptunium; they remain as soluble species in the melt like other soluble fission products (alkaline elements, alkaline earth elements, and rare earth elements) (Kormilitzyn *et al.*, 1999).

Separation of americium and curium from the soluble fission products by carbonate precipitation has been proposed. Sodium carbonate is added to the spent melt (NaCl–2CsCl or NaCl–KCl) for fractional precipitation of americium and curium, probably as sesquioxides M_2O_3 (M = Am and Cm). Similar results were obtained for both media in terms of the possible separation of minor actinides and rare-earth elements (hereafter REE) (Kormilitzyn *et al.*, 1999, Fig. 24.16). Unfortunately, americium precipitates between lanthanide(III) and lanthanide(II), which makes it difficult to separate Am from REE. Even if a small part of the americium sesquioxide could be recovered by filtration at high temperature, the remaining americium precipitates as mixed oxide with REE. If the separation of americium from REE is not necessary, the melt can be purified by adding phosphate to precipitate americium (and curium) and fission products. Fission products in the trivalent oxidation state precipitate as insoluble double phosphates $Na_3M(PO_4)_2$, while many fission products in the divalent

Table 24.11 *Gibbs energies of formation of selected oxides at* 1700 K *compiled by Mullins* et al. (1960) *from* (*Glassner*, 1957) kJ (g atom O)$^{-1}$ (*Recalculated from values in* kcal (g atom O)$^{-1}$).

La_2O_3	–452	Pu_2O_3	–402	InO	–105
Ce_2O_3	–452	UO_2	–397	Sb_2O_3	–96
Nd_2O_3	–444	ZrO_2	–385	K_2O	–84
Y_2O_3	–439	MgO	–376	TcO_2	–67
SrO	–422	NbO	–268	Rh_2O	–8
		FeO	–151	Rb_2O	–8
		MoO_2	–134	RuO_2	0
				TeO_2	0

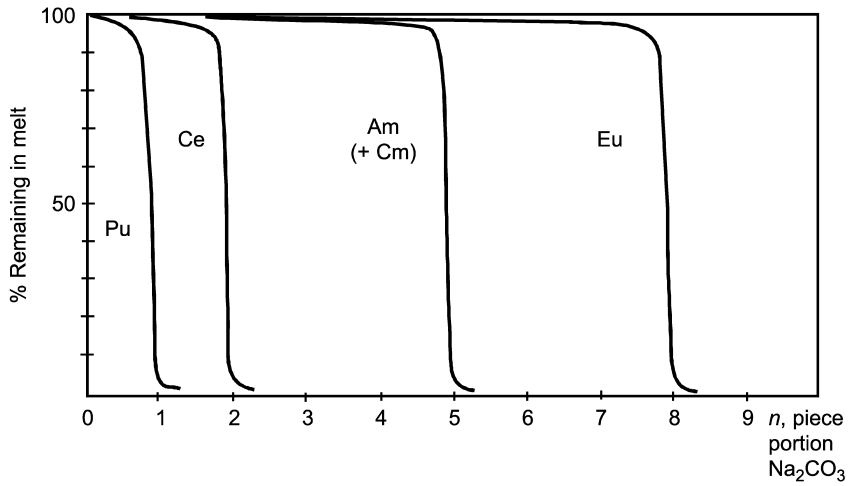


Fig. 24.16 *Relative contents for Pu, Am, Ce, Eu in NaCl–2CsCl melt during fractional carbonate precipitation coming just after electrolysis step* (*Kormilitzyn* et al., 1999).

oxidation state, including alkaline earth elements, also precipitate (Kormilitzyn *et al.*, 1999).

(h) Applications, separation efficiency in the DDP

A chlorinator–electrolyzer has been designed that will accommodate a volume of 40 L. It can reprocess a loading of about 30 kg of material. All the internal surfaces that come into contact with the salt and gaseous phases (anode-crucible, cathode, gas tube) are crafted of pyrolitic graphite. After pyroelectrochemical treatment, the cathodic deposits are crushed, purified from salts by distillation, dried, and classified for vibropac fabrication of fuel rods (Bychkov and Skiba, 1999). Since the 1970s about 3 metric tons of UO_2, 100 kg of PuO_2, and 1600 kg of $(U–Pu)O_2$ have been produced in molten alkali chlorides for BOR60, BN350, and BN600 reactors. From 1968 to 1973, 5.8 kg of spent UO_2 coming from VK-50 and BOR60 reactors were reprocessed while spent MOX fuel reprocessing began in the 1990s with 4.1 kg from BN350 (burn-up 4.7%) and 3.5 kg from BOR60 (burn-up 21–24%) (Bychkov and Skiba, 1999). For example, reprocessing of MOX fuel from BOR60 involved: (i) dissolution of the fuel in LiCl–4.53NaCl–4.88KCl–0.66CsCl; (ii) electrolysis to remove part of UO_2 free from Pu; (iii) PuO_2 precipitation; (iv) additional electrolysis for removing residual uranium as UO_2, and (v) melt purification by phosphates.

Mass balances give information on the behavior of actinides and fission products. It has been found that (Bychkov and Skiba, 1999; Bychkov *et al.*, 2000): (i) Zr, Nb, Ru, Rh, Pd, and Ag were located in the first UO_2 deposit; (ii) U/Pu separation factor in the first electrolysis is 120–140; (iii) most of the

Np is distributed between the two UO_2 deposits; (iv) Am is present in UO_2 deposits (~3.5 wt%), in PuO_2 precipitate (~18 wt%) and in phosphates (~73 wt%); (v) practically all the Cm is in phosphates though it has also been detected in the second UO_2 deposit; (vi) representatives of REE (Ce and Eu) are concentrated in phosphates, and (vii) Cs, Rb, and partially Sr remain in melt.

If a (U, Pu)O_2 deposit is desired, it will be necessary to perform a preliminary electrolysis for the removal of Ru, noble metals and Zr, before carrying out the main electrolysis under a chlorine–oxygen atmosphere. In tests on simulated materials in NaCl–2CsCl, the separation factors observed were: ~ 1000 for Cs, >100 for REE, ~1 for Ru and Zr without preliminary electrolysis, and ~10 with preliminary electrolysis (Kormilitzyn *et al.*, 1999).

DDP is currently used for oxide fuel reprocessing and for producing three oxides: UO_2, PuO_2, and (U–Pu)O_2. The latter one is mainly dedicated to MOX fuel fabrication for BOR-60 reactor. Research programs are now focused on conversion of weapon-grade plutonium into MOX fuel, development of a process for complete recycle of Pu, Np, Am and Cm (*D*ry reprocessing, *O*xide fuel, *V*ibro-compact, *I*ntegral, *T*ransmutation of *A*ctinides, DOVITA program) (Bychkov and Skiba, 1999).

(i) Metal–metal processes

(*i*) *Melt refining* (*or oxide slagging process*)

Early pyrometallurgical processes which have been developed for minimizing the cost of recycling were rudimentary. One example is the melt refining process, which was proposed to reprocess the metallic uranium fuel alloy used in the core of the second experimental breeder reactor (EBR-II) (Motta, 1956; Burris *et al.*, 1964). The fuel was an enriched uranium alloy (~52 wt% ^{235}U) containing 5 wt % *fissium* (mixture of molybdenum, ruthenium, rhodium, palladium, zirconium, and niobium) with sodium used as a thermal bond (Burris *et al.*, 1964; Steunenberg *et al.*, 1970). Melt refining is also named oxide slagging or oxide drossing. Fission products were removed by combining volatilization and selective oxidation.

After the mechanical removal of cladding and sodium bonds, the separation process consisted simply in melting the fuel at 1300–1400°C in a lime-stabilized zirconia crucible. Volatile fission products that are condensable, such as iodine and cesium, were trapped on alumina–silica fibers while gaseous fission products (krypton, xenon) were stored to allow decay of 5.3 day ^{133}Xe before being released into the atmosphere. Elements more electropositive than zirconium (see Table 24.11: alkali metals, alkaline earth, and rare earth elements) reacted with the zirconia to form an insoluble oxide slag. The other fission products (noble metals comprising the *fissium*) and the actinides remained with the uranium in the metallic form to be recycled. At this stage, the uranium recovery yield ranged from 90 to 95 wt% (Trice and Chellew, 1961; Burris *et al.*, 1964).

The melt refining process leaves a residue or skull (mixture of oxides and unpoured metal) at the bottom of the crucible, which represented about 5–10% of the loading. An auxiliary process had been proposed to recover uranium from the skull. After preliminary oxidation of the skull under oxygen–argon mixture at 700°C, the resulting oxides were dissolved into a chloride flux. Contact with liquid zinc between 700 and 800°C allowed the removal of noble metals (Ru, Mo, Rh, Pd) and Ag. Uranium was then extracted from the chloride flux by using Mg–Zn alloy (magnesium being the reducing agent and zinc the alloying agent). Combining this process with the melt refining increased the uranium recovery yield to about 99.5 wt%. The fission product removals that had been achieved (rare earths: 90%, Ru: 80%, Mo: 90%, Pd: >99%, Zr: 75%, Ba, and Sr: >99%) were sufficient to maintain the desired concentrations of the *fissium* alloying elements in the EBR-II fuel (Burris *et al.*, 1964). The complementary process, named the skull reclamation process, has been studied only at the laboratory scale (Burris *et al.*, 1964; Steunenberg *et al.*, 1970).

Oxide slagging was also investigated for plutonium reactor fuels, for example with the proposed LAMPRE fuel (Los Alamos Molten Plutonium Reactor Experiment, 10 wt% Fe–Pu alloy) (Mullins *et al.*, 1960). Tests on synthetic spent plutonium fuel have been performed in magnesia and zirconia crucibles. But this approach was rapidly abandoned because of numerous drawbacks: high temperature, slow reaction rates, and the creation of a plutonium-bearing residue.

(j) Melt refining under molten salts (or halide slagging processes)

In the halide slagging process, in particular chloride slagging, the active fission products were rapidly removed from the molten fuel as a result of chemical reactions occurring at the interface between two liquid phases. Moreover, the plutonium transfer was less than 1 wt%. The process consisted of contacting the molten fuel at 600–700°C with molten alkali chloride salts containing plutonium chloride or magnesium chloride as an oxidant. Used slags were $PuCl_3$–NaCl, $MgCl_2$–LiCl—KCl, or $MgCl_2$–NaCl–KCl (Leary *et al.*, 1958; Mullins *et al.*, 1960). Gibbs energies of formation of selected halides are shown in Table 24.12.

Results were in agreement with thermodynamic predictions: electropositive fission products (alkali and alkaline earth elements, rare earths) were oxidized and dissolved in the chloride slag. But, as in every melt refining process, the noble metal fission products were not removed from the spent fuel. Mullins *et al.* (1960) gave for $MgCl_2$–NaCl–KCl at 700°C the percentage transferred into the salt phase for the following elements: Pu 0.92, Fe 0.04, Zr < 0.04, Mo < 0.15, Ru < 0.20, Ce 98, La 100, Mg 26. In these experiments, the $MgCl_2$ exceeded by 10% the stoichiometric quantity needed to remove the rare earths. A similar process has been tested on (10–20 wt% plutonium)–uranium alloys with $BaCl_2$–$CaCl_2$ and $MgCl_2$ as oxidant (Glassner, 1957). The effect of the slag

Table 24.12 *Gibbs energies of formation*[a] *of selected chlorides at* 775 K. *Compiled by Ackerman* (1991) *from Pankratz* (1984) kJ (g atom Cl)$^{-1}$.

CsCl	–367.4	$CeCl_3$	–287.0	UCl_3	–231.0
KCl	–362.8	$NdCl_3$	–284.1	$ZrCl_4$	–195.0
$SrCl_2$	–354.4	YCl_3	–272.4	$CdCl_2$	–135.1
LiCl	–345.2	$AmCl_3$	–268[b]	$FeCl_2$	–122.3
NaCl	–339.3	$CmCl_3$	–268[b]	$MoCl_2$	–70.3
$LaCl_3$	–293.7	$PuCl_3$	–261.1[b]	$TcCl_3$	–46
$PrCl_3$	–288.7	$NpCl_3$	–242.7[b]		

[a] Recalculated from values in kcal (g atom Cl)$^{-1}$.

[b] Estimated values.

composition is minor. The criteria for slag selection must be melting point and high stability of halide components (alkali or alkaline earth elements).

(k) Molten metal-salt extraction processes

By combining liquid metal (or alloy) solvent with molten salts and using oxidation–reduction reactions, it is possible to accomplish separations that could not be achievable by melt refining. The elements are distributed in the two-phase solvent system and the distribution coefficients depend on the nature of the oxidizing and reducing agents and on the activities of the reacting species in solution. In general, chlorides are preferred because of their lower volatility, their compatibility with many containers, and favorable solubility relationships. Such separation techniques in various biphasic systems have been proposed in the past by several American laboratories: Brookhaven National Laboratory investigated Bi/$MgCl_2$–NaCl–KCl to reprocess bismuth–uranium fuel (Bennett *et al.*, 1964); the Hanford Works studied the actinide distribution in Al/$AlCl_3$–KCl (Dwyer, 1956); the Ames Laboratory examined the same in Zn/LiCl–KCl (Moore and Lyon, 1959); Los Alamos National Laboratory tested Hg/RbCl–LiCl–$FeCl_2$ for the reprocessing of LAMPRE fuel (Chiotti and Parry, 1962); Argonne National Laboratory proposed various applications in $MgCl_2$-based salt with Cu–Mg or Zn–Mg alloy. One of them is the Argonne salt transport process for the reprocessing of LMFBR fuels (Steunenberg *et al.*, 1970).

(*i*) *Argonne salt transport process*

The partitioning of element M between magnesium alloy and $MgCl_2$-based salt can be expressed by:

$$\mathrm{M(alloy)} + \tfrac{1}{2}n\mathrm{MgCl_2(salt)} \rightleftharpoons \mathrm{MCl}_n\mathrm{(salt)} + \tfrac{1}{2}n\mathrm{Mg\ (alloy)} \qquad (24.39)$$

If K_a is the equilibrium constant, a_i and γ_i respectively the activity and the activity coefficient of the reactants, the distribution ratio D_M for a metal M (ratio of mole fraction of MCl_n in salt to atom fraction of M in alloy) will be expressed by:

$$\begin{aligned}\log D_M = (-\Delta G^\circ/2.3RT) + (-\tfrac{1}{2}n\log a_{Mg} + \log\gamma_M)\\ - (-\tfrac{1}{2}n\log a_{MgCl_2} + \log\gamma_{MCl_n})\end{aligned} \tag{24.40}$$

where $\Delta G^\circ = -\mathrm{RT}\ln K_a = \Delta G_f^\circ(MCl_n, T) - \frac{1}{2}n\Delta G_f^\circ(MgCl_2, T)$. The first term in brackets in equation (24.40) depends on temperature via the Gibbs energy of formation of MCl_n and $MgCl_2$. The second term depends on temperature and composition of the alloy while the third depends on temperature and composition of salt. Importance of these terms on D_M decreases from left to right when salt with $MgCl_2$ is used as the oxidizing agent (Bowersox and Leary, 1960).

The halides of the noble-metal fission products and the metals used for cladding (like Fe), have a less negative Gibbs energy of formation (see Table 24.12) the first term dominates the distribution ratio and they should be easily separated from actinides by remaining in the alloy. For actinides and rare earth elements, the two following terms cannot be ignored. Johnson (1974) has explained their effect on distribution coefficients.

Distribution ratios of actinides and rare earth elements between molten $MgCl_2$ and Mg-alloy (Mg–Zn, Mg–Cu) have been measured over a wide range of magnesium content (Knighton and Steunenberg, 1965; Knighton, 1969). They are at a minimum when a Zn–Mg alloy is used (Mg content is about 10 wt%). A similar effect is not observed when Cu–Mg alloy is used. These two alloys have been proposed by Argonne National Laboratory to separate uranium and plutonium from fission products. Salt transport separation is based on the selective transfer of uranium and plutonium from a donor alloy to an acceptor alloy via a saline phase (see Fig. 24.17):

$$\mathrm{Pu(donor\ alloy)} + \tfrac{3}{2}\mathrm{MgCl_2(salt)} \rightarrow \mathrm{PuCl_3(salt)} + \tfrac{3}{2}\mathrm{Mg\ (donor\ alloy)} \tag{24.41}$$

$$\mathrm{PuCl_3(salt)} + \tfrac{3}{2}\mathrm{Mg(acceptor\ alloy)} \rightarrow \mathrm{Pu(acceptor\ alloy)} + \tfrac{3}{2}\mathrm{MgCl_2(salt)} \tag{24.42}$$

When uranium and plutonium are salt-transported from the donor alloy to the acceptor alloy, noble fission product metals remain in the donor alloy and rare earth fission product are stabilized in the salt phase. Using 50 mol% $MgCl_2$–30 mol% NaCl–20 mol% KCl and Mg–44 at% Cu alloy at 650°C, the separation factor for Ce from Pu is about 1000.

Typical phase compositions for plutonium recovery and purification are: for the donor alloy, Cu–33wt% Mg; for the salt, 50 mol% $MgCl_2$–30 mol% NaCl–20 mol% KCl; for the acceptor alloy, Zn–5 wt% Mg. The solubility of the transported material in the donor alloy must be high enough to have a significant transfer rate. For example, the solubility of uranium at 600°C in Cu–33 wt% Mg alloy is very low (50 ppm) while it can reach 3.8 wt% in

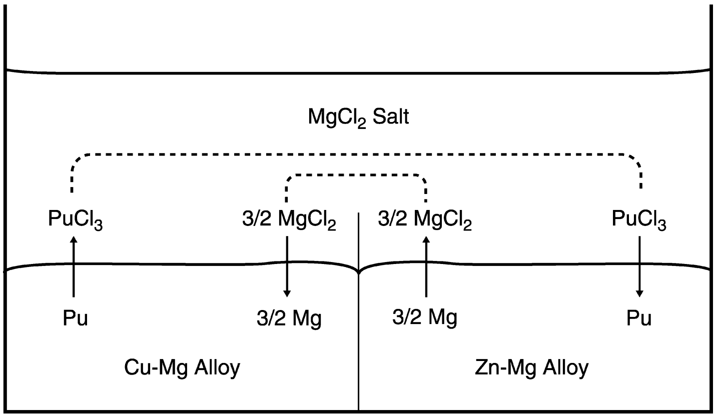


Fig. 24.17 *Scheme of salt transport process for plutonium* (*Steunenberg* et al., 1970).

Cu–6.5 wt% Mg alloy (Steunenberg *et al.*, 1970). Salt transport process has been developed at the laboratory scale, but no full scale application has yet been developed, though it was proposed in the mid-1990s in a conceptual flow sheet for recovering actinides from LWR fuels (Pierce *et al.*, 1993; Johnson *et al.*, 1994) (see Section 24.3.12n).

(*ii*) *Other applications of molten salt-metal extraction*

Development of this separation technique in molten fluorides has been carried out largely at Oak Ridge National Laboratory, in support of the molten salt breeder reactor (MSBR) concept for the reprocessing of fuel based on molten LiF–BeF$_2$ solutions (see Section 24.3.12**c**). In chlorides, molten salt-metal extraction has been proposed for enhanced recovery of actinides from spent salt generated during electrorefining of metallic fuel (see Section 24.3.12.l). It has also been developed as one process stage for actinide recovery from HLLW coming from PUREX (see Section 24.3.12m(i)).

(l) Electrorefining

Early work on electrorefining from molten salts was done to prepare either high-purity metallic uranium or plutonium separately. It began with investigations on uranium at small scale (Driggs and Lilliendahl, 1930; Marzano and Noland, 1953), at larger scale (Anonymous, 1951; Chauvin *et al.*, 1962, 1964), then with plutonium. A significant application is the recovery and purification of plutonium developed at Los Alamos National Laboratory (Mullins *et al.*, 1962) and used at Rocky Flats, Hanford and in various countries (Moser and Navratil, 1983). There has been little research and development related to the application of electrorefining techniques to the recovery and purification of spent fuels.

Investigations on irradiated uranium (Chauvin *et al.*, 1964) and on Los Alamos Molten Plutonium Reactor Experiment (LAMPRE) fuel (Leary *et al.*, 1958) have been carried out.

Interest in electrorefining was revived with the proposed advanced fast reactor concept called the integral fast reactor (IFR) (Burris, 1986; Till and Chang, 1988; Chang, 1989; Hannum, 1997) whose primary feature was an integral fuel cycle in which the core and blanket materials after discharging are to be processed and refabricated in an onsite facility. The fuel cycle was based on electrorefining with a molten salt electrolyte ($LiCl–KCl–UCl_3/PuCl_3$) at 500°C in an inert atmosphere. An abundant literature has appeared on the chemistry and technology of IFR (see in particular Burris *et al.*, 1987; Willit *et al.*, 1992; Hannum, 1997; Anonymous, 2000). In the discussion below, the following features of this system will be presented: (i) a brief description of the main steps of the pyro-process; (ii) the chemical basis for partitioning of actinides and fission products between metallic (solid or liquid) and salt phases; and (iii) the separation efficiencies obtained at laboratory scale and in the only engineering scale application (EBR-II spent fuel treatment demonstration) completed to date.

(*i*) *Reprocessing in the IFR fuel cycle*

After discharging the spent core fuel (alloy of U, Pu, and Zr) in its stainless cladding, the fuel is chopped and placed in an anode basket. The anode basket containing the chopped fuel is put into an electrorefiner containing molten LiCl–KCl electrolyte and a liquid cadmium pool under inert atmosphere. $CdCl_2$ is added in the electrolyte to oxidize electropositive fission-product metals (alkali, alkaline earths, and a large fraction of the rare earth metals) to their chlorides (see Table 24.12). The amount of oxidizing agent to be added is adjusted to maintain 2 mol% actinide chlorides in the salt phase. The basket is made anodic and the following sequence occurs: (i) nearly pure uranium is electro-transported to a solid mandrel cathode and (ii) transuranium elements and some uranium are transferred by electro-transport to a liquid cadmium cathode. Noble metal fission products remain in an unoxidized form and are removed from the basket with the cladding hulls, although some portion falls into the cadmium pool at the bottom of the electrolyzer. Electropositive fission products remain in the salt and build-up during the successive reprocessing batches and progressively modify the electrochemical and physical properties of the electrolyte. Periodic treatment is thus required to remove them and recycle the electrolyte.

The molten metal-salt extraction (using Li–Cd alloys) has been proposed for reduction and removal of transuranium elements (TRUs) from the electrolyte salt and for TRU reoxidation back into the salt to start the next electrorefining campaign. Moreover, the use of UCl_3 as oxidant makes it possible to avoid the introduction of cadmium in the electrorefiner and thus the lower cadmium pool can be eliminated. This approach avoids the deposition of cadmium and makes easier the removal of solids that accumulate at the bottom of the electrolyzer.

Both types of cathode products are processed to distill off adhering salt and cadmium (in case a liquid cadmium cathode is used). Such a process produces three waste streams: fission product gases, metal waste stream that contains cladding hulls, and noble metal fission products, and salt waste stream (alkali, alkaline earth fission products). The treatment, the immobilization, and the disposal of these wastes are challenging, but their discussion is not within the scope of this chapter. These features have largely evolved during the laboratory-scale and engineering-scale developments depending on the applications. The lone large-scale feedback is the demonstration campaign on the treatment of spent metal fuel from the EBR-II fast reactor commenced in 1996 at the Argonne-West site in Idaho. Processes and results obtained are discussed in reference Anonymous (2000).

(*ii*) *Chemical basis of electro-transport in LiCl–KCl*

Johnson (1988) and Ackerman and coworkers (Ackerman, 1991, Tomczuk *et al.*, 1992; Ackerman and Johnson, 1993) have described the chemistry that controls the electro-transport in LiCl–KCl electrolyte on solid or liquid cathode. The transfer of the element of interest (for example U or Pu) is done by electrolyzing (electrochemical oxidation) this element into the salt (electrolyte) at the anode and electrodepositing it as metal at the cathode. The element must be initially present in the electrolyte before starting electrolysis. Dissolution is facilitated by addition of a chemical oxidizing agent (i.e. a chemical agent whose the chloride is less stable than the chloride of the element one wishes to electro-transport). For uranium electro-transport, the oxidizing agent can be $\mathrm{CdCl_2}$ (see Table 24.12).

In the electrorefiner, the salt is well stirred and is in contact with both metal (electrode) phases. When a predetermined number of moles of metal (of given composition) are removed from the anode to the cathode, the compositions of both electrodes and the salt change until the salt is in equilibrium. For both elements M and M′, the following equilibrium exists at each electrode:

$$n1(\mathrm{MCl}_{n2}) + n2(\mathrm{M}')_{\mathrm{alloy}} \rightleftarrows n1(\mathrm{M})_{\mathrm{alloy}} + n2(\mathrm{M}'\mathrm{Cl}_{n1})\mathrm{salt} \tag{24.43}$$

Equilibrium constant K_a can be expressed using mole fraction x_i and activity coefficient γ_i of M and M′ in metal phase(s) and salt by:

$$\begin{aligned} K_\mathrm{a}(T) = {} & [(\gamma\mathrm{M})^{n1}(\gamma\mathrm{M}'\mathrm{Cl}_{n1})^{n2}]/[(\gamma\mathrm{M}')^{n2}(\gamma\mathrm{MCl}_{n2})^{n1}]\cdot \\ & [(\mathrm{xM})^{n1}(\mathrm{xM}'\mathrm{Cl}_{n1})^{n2}]/[(\mathrm{xM}')^{n2}(\mathrm{xMCl}_{n2})^{n1}] \end{aligned} \tag{24.44}$$

where $\Delta G^\circ(T) = -RT\ln K_\mathrm{a}(T) = n_2\Delta G^\circ_\mathrm{f}(\mathrm{MCl}_{n1}, T) - n_1\Delta G^\circ_\mathrm{f}(\mathrm{M}'\mathrm{Cl}_{n2}, T)$. By writing donor alloy = anode and acceptor alloy = cathode (Johnson, 1988), the equations are similar to those written for salt transport description (see Section 24.3.12.**k**). The metal (electrode) phases need not to be in equilibrium with each other in the classical sense which would mean that activity of each metal would be the same in all phases (Anonymous, 1951; Tomczuk *et al.*, 1992; Ackerman and Johnson, 1993).

Concentrations in the salt phase at equilibrium depend on activity coefficients in metal phases (solid or liquid) and salt. As the salt is diluted, the activity coefficients of MCl_{n2} and $M'Cl_{n1}$ are assumed to be constant. However, activity coefficients of M and M′ in metal phases can vary greatly when changing the metal phase and they can be greatly reduced by the formation of intermetallic compounds. For instance, the plutonium activity is reduced in cadmium by formation of $PuCd_6$ (Johnson *et al.*, 1965). A similar decrease for rare earth activity coefficients is observed with Cd (Johnson and Yonco, 1970). Uranium does not form intermetallic compounds with cadmium at the electrorefining temperature (500°C) (Martin *et al.*, 1961).

A reduction in the activity coefficient of an element (e.g. Pu) is equivalent to a reduction in the stability of the corresponding chloride. In presence of cadmium, plutonium behaves as its trichloride was about 3.3 kJ $(\text{equiv.})^{-1}$ more stable than uranium trichloride whereas it is 30.1 kJ $(\text{equiv.})^{-1}$more stable in absence of cadmium (Ackerman, 1991, see Table 24.12). This result also implies that the difference between the reduction potential of Pu(III)/Pu(0) and U(III)/U(0) is less negative at the liquid cadmium cathode than at the solid cathode. Sakamura *et al.* (1999) have summarized the reduction potential of actinide and rare earth elements in LiCl–KCl salt when the nature of the cathode change (see Fig. 24.18). These data are compiled from the literature (Martin *et al.*, 1961; Lebedev *et al.*, 1968, 1969; Krumpelt *et al.*, 1974; Ackerman and Johnson, 1993; Kurata *et al.*, 1996; Kinoshita *et al.*, 1999).

The removal of pure uranium on a solid mandrel electrode is possible because the reduction potential of U(III)/U(0) is far from those of the other actinides (see Fig. 24.18). The range of $PuCl_3/UCl_3$ ratios in the electrolyte within which pure uranium can be removed at a solid cathode has been determined by Tomczuk *et al.* (1992). At a liquid cadmium cathode, the reduction potentials of actinides are very similar and such a cathode should be suitable for recovery of all actinides together. However, the potentials are too close to those of rare earth elements to be suitable for an actinide/rare earth separation. The gap between actinides and rare earth elements is increased if bismuth is substituted for cadmium. This change could enable an actinide/RE separation (see Section 24.3.12 m(i)). The principal drawback of bismuth as an electrode material (compared to cadmium) is that it is not distillable and therefore difficult to purify.

(*iii*) *Separation efficiencies in EBR-II demonstration campaign* (2000)

From 1996 to 1999, a hot demonstration was conducted in the Fuel Conditioning Facility at Idaho Falls where 100 spent driver assemblies (410 kg of highly enriched uranium alloyed with ~10 wt% Zr, plus stainless steel cladding) and

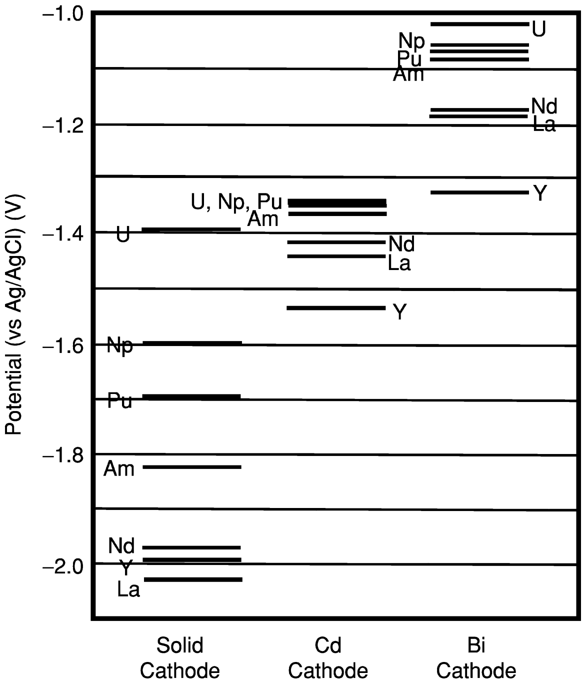


Fig. 24.18 *Reduction potential of actinide and rare earth elements at solid cathode, liquid cadmium cathode, and liquid bismuth cathode in LiCl–KCl eutectic salt at* 500°C, $x_{M\ in\ salt} = x_{M\ in\ Cd} = x_{M\ in\ Bi} = 0.001$. (*Figure created from information in Sakamura* et al., 1999.)

25 spent blanket assemblies (1200 kg of depleted-uranium with stainless steel cladding) from the Experimental Breeder Reactor-II have been treated by the electro metallurgical technology (EMT) developed by Argonne National Laboratory. The metallic fuel was separated into three components: metallic uranium, a metallic waste form from the anode, and a highly radioactive salt mixture. The global process involved the following steps: (i) chopping the fuel elements; (ii) electrorefining; (iii) removing entrained salt (about 20 wt%) from uranium deposits and consolidating dendritic deposits in a cathode processor; (iv) casting into ingots the uranium metal from the cathode; (v) casting into ingots the metal residue from the anode; and (vi) mixing, heating, and pressing the salt electrolyte with zeolite to form a ceramic waste.

The core of the process is the electrorefining step in LiCl–KCl melt at 500°C: the metallic fuel is selectively dissolved at the anode while nearly pure uranium metal is deposited at the cathode, leaving fission products, fuel cladding material, plutonium, and other transuranium elements partially at the anode and partially in the molten salt. In addition, the process neutralizes the reactive components (e.g. sodium-bonds) of the fuel. The distribution of actinides

(U, Np, and Pu) and some fission products in each flux has been calculated from material balance given by Mariani and coworkers (Anonymous, 2000; Mariani *et al.*, 2000) for spent driver fuel treatment (Table 24.13).

Two electrorefiners have been designed and developed. The first, Mark-IV, was used for driver elements and contained a cadmium pool. This pool was not used as cathode but acted as neutron absorber and corrosion-resistant barrier. $CdCl_2$ was added into the electrolyte to oxidize some of the U and other active metals before starting electrotransport. The anode assembly (four baskets) could hold about 8 kg of uranium. An overall anode batch size of 16 kg was achieved by using dual anode assemblies with a single cathode. Steel scrapers were placed near the cathode to control the growth of the uranium dendritic deposit and to allow the removal of the deposit through the cathode port. During the demonstration campaign, Mark-IV was used to treat 12 driver assemblies at an average rate of 24 kg of uranium per month over a 3-month period.

The second electrorefiner, Mark-V, cadmium free, was used for blanket elements (large quantities of depleted uranium). The throughput has been increased by using anode–cathode modules (ACMs) with a capacity of 37 kg per ACM. The overall anode batch size was about 150 kg when four ACMs are used. Each ACM would be able to produce about 87–100 kg of uranium per month. During the demonstration campaign, Mark-V was used to treat 4.3 blanket assemblies at an average rate of 206 kg of U per month over one month.

(m) Oxide–metal processes

A pyrometallurgical partitioning technology for the recovery of uranium and transuranium elements from high-level liquid waste (HLLW) has been developed by the Japanese Central Research Institute of Electric Power Industry (CRIEPI) (Inoue *et al.*, 1991), as described below.

(*i*) *Recovery of actinides from denitrated HLLW*

The process begins with a denitration step in which dehydration by heating converts all the elements in water to insoluble oxides (except for alkali metals which are removed by rinsing with water). The resulted oxides are chlorinated in molten LiCl–KCl eutectic melt. Kurata *et al.* (2000) argue that Cr, Fe, Zr, Mo, and Te are separated during the chlorination step. This is followed by a set of reductive extraction steps.

(*ii*) *Reductive extraction of noble metals*

The purpose of the first reductive extraction is to remove as much of the noble metals as possible while carrying less than 0.1% of each actinide into the reductive extraction product. Extraction step is performed by adding Cd–Li alloy. Laboratory-scale tests show that the amounts of neptunium, plutonium,

Table 24.13 *Actinide and fission product distribution (in %) in EBR-II spent driver fuel treatment.*

	U	*Pu*	*Np*	*Na*	*Ce*	*Cs*	*Ru*	*Sb*	*Tc*
cladding hulls[a]	2.4	11.6	8.5	8.1	10.5	7.8	100	100	99
uranium ingot for interim storage	91.9	0.3	2.1	<0.05	0	0	0	0	0.3
dross from cathode processor	1.3	0	0	0	0	0	0	0	0
remaining in electrorefiner salt[b]	3.6	87.8	88.0	88.4	89.5	91.5	0	0	0
remaining in electrorefiner hold-up, cadmium pool and plenum sections	0.8	0.3	1.4	3.5	0	0.7	0	0	0.7
total output	100	100	100	100	100	100	100	100	100

[a] To be converted to metal waste form.

[b] To be converted to ceramic waste form.

and americium extracted in cadmium alloy is less than 0.1% while a larger fraction of uranium is transferred to the alloy. The zirconium removal from the salt ranges from 50 to 95% (Fusselman *et al.*, 1997).

(*iii*) *Reductive extraction of actinides and rare earth elements*

The purpose of the second reductive extraction is to separate the actinides from alkaline earth elements with a recovery yield of each actinide higher than 99.9%. Uranium, transuranium elements are reduced by adding Cd–Li and transferred into Cd alloy, leaving alkaline earth elements in the salt phase. Laboratory-scale experiments indicate that the removal of U, Np, Pu, and Am from the melt is more than 99.9% but most of the rare earth elements are also reduced and so not separated from the actinides (Fusselman *et al.*, 1997).

(*iv*) *Separation of actinides from rare earth elements*

The cadmium phase coming from the second extraction step serves as an anode in an electrorefining step. The goal is to extract the actinides and rare earths from the cadmium alloy for recycling it and to deposit uranium onto the cathode as solid metal (Fusselman *et al.*, 1997, see also Section 24.3.12k). The salt coming from the electrorefining step is then introduced in a multistage extraction step for separating the transuranium elements (TRUs) from rare earths (REs). Distribution coefficients for actinides and rare earths in LiCl–KCl/Li–Cd system have been measured by numerous workers (Sakata *et al.*, 1991; Koyama *et al.*, 1992; Ackerman and Settle, 1993; Hijikata *et al.*, 1993; Sakamura *et al.*, 1994). The LiCl–KCl/Li–Bi system has been investigated by Kurata *et al.* (1995).

Liquid bismuth is used instead of cadmium because the LiCl–KCl/Li–Bi system provides better TRU/RE separation factors than the LiCl–KCl/Li–Cd system (see Table 24.14). Separation factors obtained in laboratory-scale tests performed as described in Fig. 24.19 at 500°C are constant at each extraction stage and are in good agreement with those given in the literature, except for uranium and zirconium whose separation factors vary and are higher than expected. This result could be explained by transfer of a part of uranium and zirconium to the salt phase as soluble oxygenated species due to traces of oxygen in the salt (Uozumi *et al.*, 2001).

(*v*) *Actinide electrorecovery*

Contrary to extraction in the LiCl–KCl/Cd system wherein the actinides can be recovered from the final metallic product (An–Cd alloy) by cadmium distillation, in the LiCl–KCl/Bi system bismuth is not easily distillable, as was noted above. It is therefore necessary to carry out a complementary oxidation–reduction step to separate actinides from bismuth and to recover them as metal.

Table 24.14 *Some separation factors of TRUs and trivalent REs relative to uranium* (*Kurata* et al., 1995).

Element	*LiCl–KCl/Bi at* 773 K, *Kurata* et al. (1995)	*LiCl–KCl/Cd at* 773 K, *Ackerman and Settle* (1993)	*LiCl–KCl/Cd at* 773 K, *Koyama* et al. (1992)	*LiCl–KCl/Cd at* 773 K, *Hijikata* et al. (1993)	*LiCl–KCl/Cd at* 723 K, *Sakamura* et al. (1994)
U	1	–	1	1	1
Np	1.1×10^1	–	2.2	2.1	2.9
Pu	1.3×10^{1}[a]	1.9	1.9	–	3.6
Am	–	2.9	3.1	–	1.1[b]
Cm	–	–	3.5	–	–
Pr	9.22×10^2	4.3×10^1	–	–	–
Nd	9.33×10^2	4.4×10^1	3.9×10^1	4.9×10^1	6.4×10^1
Ce	8.34×10^2	4.9×10^1	–	5.2×10^1	–
La	2.53×10^3	1.3×10^2	–	1.26×10^2	–

[a] Estimated from γ_{Pu} in Bi.

[b] At $\log D_U = 0$.

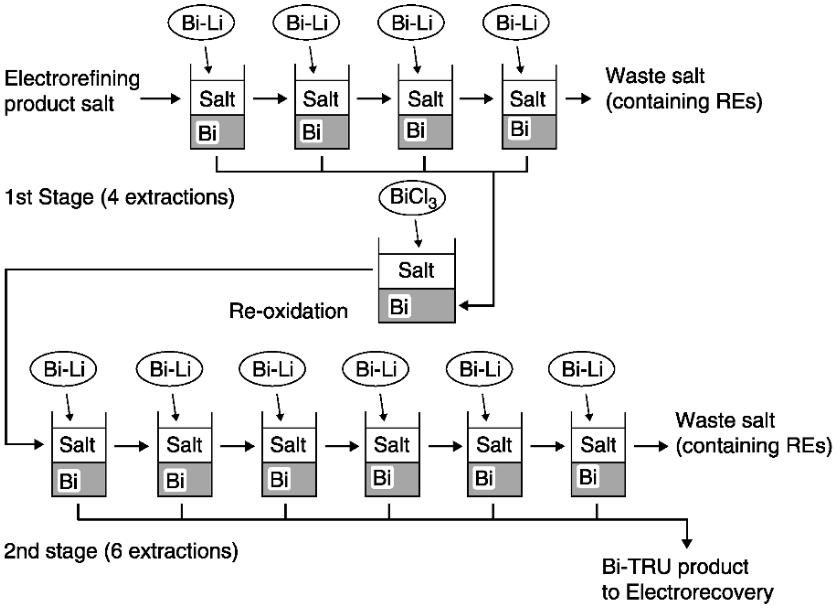


Fig. 24.19 *Schematic flow sheet tested for TRUs/REs separation.* (*Figure created from information in Uozumi* et al., 2001).

An electrolytic recovery in which actinides are stripped from bismuth used as anode and collected on a cathode has been proposed (Uozumi *et al.*, 2001). All the actinides are well stripped (97% for U and more than 99% for TRUs) from Bi. During the electrodeposition, 91–93% of each actinide – U, Np, and Pu – whose lowest stable oxidation state is 3+, are collected on a tantalum cathode. Americium exhibits a more complex behavior because of its two possible oxidation states (3+ and 2+). The recovery of americium is limited by the reproportionation reaction $2\mathrm{Am(III)} + \mathrm{Am(0)} \rightleftharpoons 3\mathrm{Am(II)}$ (see Section 24.3.12b) and only 25% of the total is recovered. Reuse of the americium-bearing salt in the previous step has been proposed to avoid sending it to waste.

Laboratory-scale demonstration tests show that, by combining electrorefining and reductive extraction as described above, less than 0.1% of uranium and individual TRUs are transferred to waste salt. The weight ratio between TRUs and REs in the final product is 2.01 (larger than 1.0, the minimal value required ratio for transmutation strategies).

(n) Recovery of actinides from LWR fuels

Argonne National Laboratory has developed (and is still developing) oxide pyroprocessing compatible with the pyrochemical processes for metal fuels. One purpose is to recover actinides from spent light water reactor fuels to introduce them into an integral fast reactor fuel cycle. Basically the process for oxide fuel involves the reduction of the oxides to metallic form, followed by either: (i) a combination of the salt transport and halide slagging for separation of fission products and the separation of the uranium from the transuranic elements (see Section 24.12k, (Pierce *et al.*, 1993; Johnson *et al.*, 1994) or (ii) the standard electrorefining process (see Section 24.3.12l) for the same purpose (Pierce, 1991; Laidler, 1994). Typically, the reducing agent is calcium or lithium.

(*i*) *Calcium reduction*

In the 1960s, the production of plutonium metal by direct calcium reduction of plutonium dioxide (direct oxide reduction or DOR process) was investigated. These efforts were reviewed by Moser and Navratil (1983). First attempts showed that molten salts were necessary for dissolving the CaO produced and for allowing plutonium metal consolidation. The first used salt was $CaCl_2$ at 800°C but the binary melt $CaCl_2$–CaF_2 with lower working temperature is efficient for minimizing corrosion and product contamination. Calcium reduction has been adapted for LWR fuel reduction when salt transport is used. The oxide fuel is reduced by a Ca–Mg–Cu alloy in contact with $CaCl_2$–CaF_2. Calcium plays the role of reducing agent while Mg–Cu alloy is the donor alloy for salt transport as described in Section 24.3.12k. Most of the reduced uranium and noble metals are insoluble in Mg–Cu alloy and thus precipitate while TRUs and trivalent REs are solubilized in the alloy. Alkali metals, alkaline earth elements, Sm, Eu, Se, Te, Br, and I remain in the salt phase (Pierce *et al.*, 1993; Johnson *et al.*, 1994).

Reduction experiments at laboratory scale have been carried out on high-fired UO_2, powders of PuO_2 and NpO_2, several representative fission product oxides, and simulated fuel pellets with non-radioactive fission products. Reduction yields obtained for the actinides are more than 99%. Neptunium coprecipitates with uranium (Pierce *et al.*, 1993; Johnson *et al.*, 1994). The salt is electrochemically treated for CaO decomposition and calcium regeneration. Oxygen is liberated at the carbon anode as CO and CO_2 and the calcium that is produced is dissolved in a liquid cathode of recycled Mg–Cu alloy. The feasibility of the electrochemical regeneration of the spent salt has been established at the laboratory scale. Current efficiency of 70% is reached when Mg–Cu alloy is used as cathode, but the current density of about 170 mA cm^{-2} is low for a full-scale process (Pierce *et al.*, 1993).

(*ii*) *Lithium reduction*

Reduction by lithium in chloride melts has been proposed when the objective of the process is electrorefining in LiCl–KCl melt (Johnson *et al.*, 1994; Laidler, 1994). In such reduction no metallic solvent is required and the temperature is lower so that common construction materials can be used. The reduction produces lithium oxide in the salt. Lithium is a less effective reducing agent than calcium, thus the progress of the reduction depends greatly on the activity of Li_2O (i.e. its concentration in the salt) (Johnson *et al.*, 1994). Moreover, it is necessary to maintain Li_2O dissolved in salt to avoid physical interactions between the reduced oxides and Li_2O. Reductions on UO_2 in various chloride melts between 500 and 750°C showed that reductions were complete, but Li_2O solubility was exceeded when low-temperature melts were used (Johnson *et al.*, 1994). Pure LiCl, whose the melting point is 602°C, has been chosen as the medium for the reduction and Li_2O solubility has been measured in the range 600–750°C (Johnson *et al.*, 1994; Usami *et al.*, 2002). Johnson *et al.* (1994) gives 8.7 wt% at 650°C and 11.9 wt% at 750°C.

Experiments on mock fuel with TRU oxides in LiCl at 650, 700, and 750°C have shown poor reduction efficiencies for TRUs. The reduction efficiency decreases with increasing temperature. For instance, the amount of plutonium remaining in salt varies from 0.004 to 37.7% in the range 500–750°C while the americium remaining in the salt varies from 0.06 to 29.6%. To prevent this, LiCl–KCl (60–40 wt%) melt has been proposed as the medium for reduction at lower temperature (500°C) (Johnson *et al.*, 1994). It has been claimed that PuO_2 is completely reduced by lithium at 650°C in LiCl with no intermediate product formation, even if Li_2O concentration is just below the solubility limit (Usami *et al.*, 2002). In reduction tests performed at 500°C, alkaline earth elements and europium are in the salt presumably as chlorides while the other REs probably remain as precipitated sesquioxides in the salt phase (Pierce *et al.*, 1993). Laboratory-scale (50 to 100 g of simulated fuel) and engineering-scale (3.7 to 5.2 kg of simulated fuel) experiments are currently performed to determine and to master the parameters for process scale-up, taking into account the electrorefiners developed at Argonne National Laboratory (Karell *et al.*, 2001). As was the case in calcium reduction, the spent reduction salt is decomposed electrochemically to recover the salt and the lithium metal. Laboratory-scale experiments showed that platinum is a suitable oxygen-evolving electrode that can be operated at high current densities (2 to 3 A cm^{-2}). Current efficiencies are reported at 50–80% (Karell *et al.*, 2001).

(o) Nitride–nitride process

In the early 1990s, the Japan Atomic Energy Research Institute (JAERI) proposed a double strata fuel cycle concept for partitioning–transmutation strategies in which the minor actinides from the commercial fuel cycle go into a second-stratum transmutation ('actinide-burner') cycle. Dense fuel is preferable in the second-stratum and nitride fuel is regarded as the reference fuel (metallic fuel remaining an alternative) by JAERI (Mukaiyama *et al.*, 1995; Ogawa *et al.*, 1995). Having a high electrical conductivity, the molten salt electrolytic process developed for metallic fuel (see Section 24.3.12l) can be applicable to mononitride fuel (Arai *et al.*, 1995).

(*i*) *Dissolution step*

The actinide nitrides are anodically dissolved in molten LiCl–KCl eutectic at 773 K as follows:

$$UN + 3Cl^- \rightleftarrows 3e^- + UCl_3 + \tfrac{1}{2}N_2 \tag{24.45}$$

Actinides and most of fission products (except for zirconium) behave almost the same as in metallic fuel (Arai *et al.*, 1995; Kobayashi *et al.*, 1999). According to the above chemical reaction, nitrogen escapes from salt bath as N_2 gas so that such dissolution should facilitate the recycling of ^{15}N-enriched nitrogen, which would have to be used in nitride fuel to minimize the generation of ^{14}C (Ogawa *et al.*, 1995). The release of nitrogen has been studied during NdN dissolution by chemical oxidation (with $CdCl_2$). About 90% of the nitrogen is evolved as N_2 gas (Arai *et al.*, 1999; Kobayashi *et al.*, 1999).

The feasibility of the anodic dissolution has been demonstrated at the laboratory scale for UN (Kobayashi *et al.*, 1995), for NpN and PuN (Arai *et al.*, 1999; Shirai *et al.*, 2000). During the dissolution, a by-product (UNCl) can be formed at the anode. The stability diagram of the U–N–Cl system has been determined. This by-product can be decomposed by heating to high temperatures (Ogawa *et al.*, 1997). The chemistry of AnN in molten LiCl–KCl is still in its infancy and several unknowns remain: (i) the effect of partial pressure of released N_2 on the redox potential of AnN/An(III); (ii) the formation of AnNCl, and (iii) the behavior of transplutonium elements.

(*ii*) *Actinide nitride recovery*

Fission products and actinides are dissolved in the bath as chlorides. The actinides can be recovered as nitrides by either direct or indirect methods (Ogawa *et al.*, 1997):

(i) the actinide chlorides are directly converted to actinide nitrides in molten LiCl–KCl by using Li_3N (Lithium Nitride Extraction of actinides (LINEX process),

(ii) the actinide chlorides are first electro-reduced as actinide metals on a liquid cadmium cathode and then they are converted to nitrides in the liquid cadmium (with either N_2 gas or Li_3N).

The LINEX process is based on the comparable stability of mononitrides of actinides and lanthanides. As the Gibbs energies of formation of the lanthanide trichlorides are more negative than those of the actinide trichlorides (see Table 24.12), the actinide nitrides should be preferentially formed and the following equilibrium should be displaced to the right:

$$AnCl_3 + Li_3N \rightleftarrows AnN + 3LiCl \tag{24.46}$$

In LiCl–KCl eutectic, the equilibrium constant must be expressed by taking into account the chemical activities of the various species. First attempts of nitridation by Li_3N have been performed on a $LiCl–UCl_3–NdCl_3$ mixture where preferential nitridation of UCl_3 has been observed (Ogawa *et al.*, 1997).

Nitridation in liquid cadmium has been tried on 2 wt%U–1 wt%Gd–1 wt% Ce–Cd mixtures with N_2 gas over the temperature range of 773–873 K (Akabori *et al.*, 1997). Uranium was preferentially nitrided to form U_2N_3, while almost all of Ce remained in the liquid Cd phase as $CeCd_{11}$. Gadolinium behavior is more complex and a small portion of Gd is precipitated (nitride or metallic forms). Nitridation in liquid cadmium appears efficient for light lanthanides (La–Nd).

24.4 APPLICATIONS OF SEPARATIONS IN ACTINIDE SCIENCE AND TECHNOLOGY

24.4.1 A question of scale and more – analytical separations and hydrometallurgical processing

Previous sections of this chapter have dealt with actinide separations emphasizing the basics of actinide solution chemistry in aqueous/organic media and molten salt/metallic phases, historical background, and emerging techniques that may figure prominently in future developments of actinide separations options. In this section, the focus will be on applications of the most extensively developed methods for analysis and industrial-scale processes.

(a) Separation techniques for actinide speciation in the environment

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 (generally below 10^{-8} M and often far less), conventional techniques (e.g. spectrophotometry) are not useful, except for the unique case of curium, which can be determined at extremely low concentrations through its fluorescence emissions (discussed in Chapter 9). For most laboratories, separation chemistry combined with radiometric or mass spectrometric analysis are the most appropriate techniques for such speciation at these low concentrations. The key challenge is to determine the oxidation state using procedures that do not alter this oxidation state during the measurement. Time of analysis and efficient separation procedures are clearly the most important aspect of separation for this purpose. Several complementary separation methods can (and should) be applied to insure accuracy. Some examples of actinide oxidation state speciation methods based on sorption or solvent extraction are:

- LaF_3 coprecipitation in which a lanthanide fluoride carries An(III) and An(IV), leaving An(V) or An(VI) in the solution phase, a technique that traces its roots to the dawn of discovery of transuranium actinides. Care must be exercised during the application of this technique, as excess fluoride can promote reduction during the precipitation process (Choppin and Nash, 1996). Samples must be acidified as well, thus risking the chance of oxidation state change during analysis.
- Silica gel (SiO_2) selectively sorbs An(IV) and An(VI) from basic media leaving An(V) in solution (Inoue and Tochiyama, 1977).
- $CaCO_3$ selective sorbs An(V) and An(IV), leaving An(VI) in solution as the tris carbonato complex (Kobashi *et al.*, 1988).
- Thenoyltrifluoroacetone (TTA, 0.5 M in xylene) selectively extracts An(IV) from 0.25 to 1.0 M acid. The same extractant can then be used to extract An (VI) from acetate buffer at pH 4 (Bertrand and Choppin, 1982). Photolysis of this solution can be used to produce comparatively pure samples of Pu(V) in neutral solutions (Saito *et al.*, 1985).
- The β-diketone 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 (Saito and Choppin, 1983).

Filtration of the sample should always be conducted prior to conducting the analysis to determine whether some portion of the material is being transported as colloidal material. Most of the analytical procedures require that the ambient conditions of the solution be altered. It has been suggested that acidification of the sample may be undesirable, as redox-active metals like Pu can undergo oxidation state change with a change in pH. However, there are situations under which acidification might be desirable, for example when appreciable concentration of organic complexing agents are present. In these cases, acidification can reduce the stability of the actinide complex, releasing the cation, and improving the accuracy of the analysis. The guiding principle in conducting such analyses is to never rely on a single observation by one technique to establish actinide oxidation state speciation in natural water samples. Multiple methods should be applied in tandem and some of the methods applied should include alteration of the solution conditions.

As discussed more extensively in Chapter 30, quantitative analysis of actinide concentrations in environmental or bioassay samples by standard methods requires extensive treatment to promote the release of the radionuclides from the complex matrix. For such quantitative analysis, preserving the ambient condition of the sample is a less important consideration than assuring complete recovery of the sample and applying internal standards to trace yields of the separation processes. Analyses of such samples have required up to 24 h processing time. Standard ion exchange and solvent extraction 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 (Horwitz *et al.*, 1995). These extraction chromatographic materials are based on well-known solvent extraction methods, as follows:

- TRU® resin for selective sorption of An(III), An(IV), An(VI), Ln(III). The extractant is 0.75 M CMPO in TBP.
- TEVA® resin for sorption of An(IV). The extractant is $(C_{10}H_{21})_2(C_8H_{17})(CH_3)N^+$ (Aliquat 336, neat i.e. without diluent present).
- U/Teva® resin for sorption of U(VI), An(VI). The extractant is $(C_5H_{11}O)_2(C_5H_{11})P{=}O$ DP[PP], neat.

An example of an element-specific separation scheme of actinides using TRU® resin is as follows:

- load sample from 2 M HNO_3, rinse off non-TRUs with 1.0 M HNO_3 then 9 M HCl,
- elute Am^{3+} with 4 M HCl,
- elute Pu^{4+} with 4 M HCl/0.1 M hydroquinone,
- elute Th^{4+} with 2 M HCl,
- elute Np^{4+} with 1 M HCl/0.03 M oxalate,
- elute UO_2^{2+} with 0.1 M $NH_4HC_2O_4$,
- analyze fractions radiometrically.

Analytical methods of this sort are seeing increasing application for bioassay. In addition, instrumental analysis methods suitable for quantitation of lanthanides (Nash and Jensen, 2000) would be suitable for application to samples containing actinides at higher concentrations, but there are few examples of these techniques having been applied for actinide analysis.

24.4.2 Hydrometallurgy – industrial scale separations of actinides

The production of electricity by nuclear fission is, at present, nearly 366 gigawatts electric (GW_e), generated from 438 operating nuclear reactors. The spent fuel from power production reactors contains moderate amounts of transuranium (TRU) actinides and fission products in addition to the still slightly enriched uranium. As we noted previously, there are three choices for the management of the spent fuel: (a) recycle to recover valuable components; (b) direct geologic disposal as waste, or (c) long-term monitoring after stabilization for surface or near-surface storage. At present, both byproduct recycle and ‘short-term’ monitoring are being practiced worldwide. After more than 30 years of continuous investigation, no repositories have been fully licensed to receive commercial reactor fuels. Yet safe disposal of either spent fuel or the high-level waste (HLW) generated during reprocessing of spent fuel is a matter of great environmental concern (Baetsle, 1992). The question of waste disposal has become the largest single issue standing in the way of further development of this otherwise environmentally friendly technology. Furthermore, a recent analysis projecting how fission-based nuclear power could favorably impact greenhouse gas emissions emphasizes the need for breeding additional fuel to satisfy a projected long-term shortage (Hoffert *et al.*, 2002). Satisfying this demand can only be accomplished by closing the loop of the fuel cycle by reprocessing spent fuel.

Though the pyrometallurgical processes described in Section 24.3.12 may ultimately prove the most efficient method for actinide recycle and transmutation, the nearly 60 years of industrial-scale experience that has been accumulated worldwide on aqueous-based processing of nuclear fuels clearly qualify these methods as the best approach to actinide recycle during at least the next 20 years. In this section, the ongoing research seeking new approaches to hydrometallurgical processing of nuclear fuels will be outlined.

(a) Statement of the problem

At present, half of the world's spent nuclear fuel is produced in a 'once-through cycle'. The other half is reprocessed to recycle uranium and plutonium. A deep geological repository is still considered the best option for the sequestration of either spent fuel or high-level waste by-products of reprocessing from the environment. Without actinide partitioning and transmutation, radioactivity levels in a repository will remain above natural backgrounds for several hundred thousand to several million years. How to accomplish long-term surveillance of a geologic repository to make reliable predictions on the projected lifetime of the engineered and natural barriers beyond a period of 10000 years (which time exceeds, that of all human history) and, above all, public acceptance of such repositories are key questions that impact the future of nuclear power.

The option of partitioning actinides from HLW represents an opportunity to reduce the uncertainties associated with geologic disposal. Partitioning followed by geologic disposal of the transplutonium actinides and long-lived fission products can reduce the volume of materials requiring this most expensive form of sequestration, allowing less expensive near-surface burial of shorter-lived fission products. Homogeneous feed streams for waste form production (for example, containing only actinides) would enable the use of waste forms specifically designed to accommodate the class of waste being sequestered (as opposed to demanding that one waste form be compatible with the largest part of the periodic table of species present in wastes). The long-term stability of such tailored waste forms would be easier to assure based on analogies with natural systems.

Table 24.15 *Long-lived actinides in HLW solution and their half-lives.*

Nuclide	^{237}Np	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Am	^{243}Am	^{246}Cm
$t_{½}$ (yr)	2.144×10^{6}	87.74	24 411	8550	432.2	7370	4760

Exercise of the partitioning and transmutation (P&T) option seeks to convert all long-lived nuclides into short-lived radioactive (or stable) species. Successful application of this approach to radioactive waste management could substantially reduce the requirement for geologic repository capacity. The trade-offs are that a P&T approach to radioactive waste management could increase opportunities for Pu proliferation and will increase the *volumes* of some categories of high-level, intermediate-level, and low-level wastes. However, even if the cost of P&T exceeds the gain in energy from actinide incineration, the added safety margin for the repository could justify the expense. The important actinides from a waste management perspective are given in Table 24.15.

It should be noted that there are different degrees of difficulty associated with different processing options. Spent fuel freshly discharged from the reactor (or allowed only a short cool-down interval) is the most demanding because of the radiation, thermal heat, and diversity of materials to be separated. Long-term storage of these materials prior to reprocessing reduces these problems, as heat and the most intense radiation decline at a moderate rate. In plants designed to recycle purified materials that have not been irradiated (for example, decommissioned weapons), the radiation effects are significantly diminished and heat loads are minimal thus the processes are less damaging to materials and reagents. The aqueous processing of waste materials may approach either situation depending on the source. For tank wastes like those found in the DOE complex in the U.S., their long-term storage implies that most of the fission product radioactivity has decayed and heat loads are significantly reduced (though not eliminated). But for such materials, chemical diversity remains and challenging solid–liquid separations are needed prior to any processing.

24.4.3 Actinide production processes with considerable industrial experience

There are several coprecipitation and solvent extraction procedures that have been utilized to separate and recover actinides from different solutions including the dissolver solutions (resulting from dissolution of the spent fuel). Among the coprecipitation reagents, lanthanum fluoride and bismuth phosphate were widely used in the earlier times. As has been noted previously, bismuth phosphate has been used for plant-scale separation of Pu from dissolver solutions. Among the solvent extraction processes, REDOX, BUTEX, TLA, and PUREX processes have been demonstrated to the production scale, mainly for the separation of uranium and plutonium. A brief description of these processes, and why they cannot be used for the recovery of minor actinides from high level waste or TRU waste solutions will be discussed below.

(a) Bismuth phosphate process

Bismuth phosphate is a highly specific carrier for Pu in the trivalent and tetravalent oxidation states. Pu(IV) is more efficiently carried on $BiPO_4$ than Pu(III). For separating Pu from dissolver solutions, free of UO_2^{2+} and with high D_f from the fission products, $BiPO_4$ precipitation from moderate HNO_3 solutions containing sulfuric acid can be used. Under such conditions, UO_2^{2+} is sufficiently complexed by sulfate ion to prevent precipitation of uranyl phosphate (Perlman, 1946; Lawroski, 1955; Thompson and Seaborg, 1956; Hill and Cooper, 1958; Stoller and Richards, 1961; Wick, 1967; Cleveland, 1970; Schulz and Benedict, 1972). Pu can be redissolved in ~10 M HNO_3. A few cycles of $BiPO_4$ precipitation and dissolution followed by a final LaF_3 precipitation considerably increases the concentration of Pu in the solution and final recovery can be accomplished by plutonium peroxide and then oxalate precipitations.

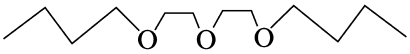
For large-scale isolation of plutonium at the Hanford site, the $BiPO_4$ process was employed by adding sodium nitrite in the dissolver solution to adjust the valency of plutonium to the 4+ state, while neptunium remains in the 5+ and uranium in the 6+ state. Plutonium is co-precipitated with $BiPO_4$, leaving behind all the actinides and fission products. $BiPO_4$ product precipitate is dissolved in ~10 M nitric acid and plutonium oxidized to 6+ state by strong oxidizing agents like $K_2Cr_2O_7$, $KMnO_4$, or sodium bismuthate. PuO_2^{2+} remains in the filtrate. It can then be reduced to Pu(IV) with Fe^{2+}. This cycle can be repeated several times. The flow sheet developed at Hanford gave an overall D_f of 10^7. This process was employed during the Manhattan Project because it was the only separation technology reliable enough to be scaled up quickly to meet wartime production demands. The inability to operate the process continuously (separations are made batch-wise) and its rejection of the still-useful enriched uranium caused the discontinuation of its application in favor of the solvent extraction processes, which overcame both of these limitations.

(b) REDOX process

This process, developed at the Argonne National Laboratory, utilizes methyl (isobutyl)ketone (hexone) as the extractant and dissolver solution as the aqueous phase. Plutonium is oxidized to the hexavalent state with $Na_2Cr_2O_7$. High nitrate salt concentrations are generated by addition of $Al(NO_3)_3$ under acid-deficient conditions. PuO_2^{2+} and UO_2^{2+} are extracted into the organic phase, leaving behind most of the fission products, corrosion products, and trivalent actinides in the raffinate (Anonymous, 1951; Merrill and Stevenson, 1955; Stoller and Richards, 1961). Uranium and plutonium are stripped from the hexone phase by water containing small amounts of $Na_2Cr_2O_7$ (to maintain oxidizing conditions). This cycle is repeated two or three times to get a high D_f from the fission products. Finally, the feed solution containing uranium, plutonium, $Al(NO_3)_3$, acid, and $Na_2Cr_2O_7$ in the required quantity (for feed adjustment and keeping metal ions as PuO_2^{2+} and UO_2^{2+}) are contacted with the hexone solution. From the loaded organic phase, plutonium is stripped by an aqueous solution of $Al(NO_3)_3$ and ferrous sulfamate, which reduces Pu(VI) to Pu(III). Uranium is subsequently stripped with water. To obtain uranium and plutonium in high purity and with high D_f from the fission products, the entire cycle is repeated several times. The ability to run this process as a continuous operation and to recover uranium marked a major improvement for production efficiency over the $BiPO_4$ process. However, the process generated enormous volumes of moderately difficult wastes containing mixed fission products and minor actinides, and demanded procedures to accommodate the toxicity and flammability of the extractant. At Hanford, the process-generated aqueous wastes were made basic and stored in underground tanks. The Al_2O_3 that was generated as a by-product of this process complicates current efforts to remediate tank wastes.

(c) BUTEX process

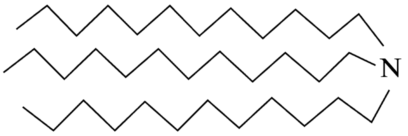
This process, developed in the UK, utilizes the triether dibutylcarbitol, 'Butex' ($C_4H_9O–(C_2H_4O)_2–C_4H_9$; Structure y) as the main extracting agent. The primary advantage of this process as compared with REDOX is that it is possible to extract uranium and plutonium from HNO_3 solutions without the addition of a salting out agent (Howells *et al.*, 1958). The extraction order for actinides and a few fission products is $UO_2^{2+} > PuO_2^{2+} > Pu^{4+} > U^{4+} > Zr^{4+} > Ce^{4+} > Ru(NO)^{3+}$. Like the REDOX and $BiPO_4$ processes, BUTEX rejected neptunium and the transplutonium actinides to the waste stream. Because of several limitations including the high viscosity and density of the extractant, and the formation of crystalline uranyl nitrate–Butex compounds, this process was discontinued as more efficient processes emerged.



Structure y

(d) TLA process

Trilaurylamine (TLA, Structure z) is a highly specific extractant for Pu(IV) while the extration of U(VI) is very low. Thus the TLA process was suggested for a second-stage plutonium recovery process (Auchapt *et al.*, 1968). A solution of 7–20% TLA in diethylbenzene has been used to extract Pu from 1.25–3 M HNO_3. Plutonium was stripped with 3–4 M acetic acid (Coleman, 1964). From a solution formed as zircaloy-clad fuel element is dissolved in nitric acid, plutonium extraction has been shown to be highly effective by using 10% TLA in *t*-butylbenzene (Haeffner *et al.*, 1965; Hultgren, 1967). With certain modifications, the TLA process has generated a $D_{\mathrm{f\,Pu}}$ of 1.75×10^7 from uranium and of 8×10^7 from β and γ activities.



Structure z

(e) PUREX process

The PUREX (originally Plutonium Uranium Extraction but also found in the literature as Plutonium Uranium Recovery by Extraction or Plutonium Uranium Reduction Extraction) process used TBP dissolved in an inert aliphatic diluent as the extractant for uranium and plutonium from dissolver solution (Anonymous, 1951, 1955; McKay, 1956; Cooper and Walling, 1958; Mathieson and Nicholson, 1968; Koch *et al.*, 1977). Normally a solution of 20–30% TBP in *n*-dodecane, odorless kerosene, or another normal (or branched) paraffinic hydrocarbon (or mixture of hydrocarbons) is used as the diluent. This process was first developed at the Oak Ridge National Laboratory (Flanary, 1954). It has been employed at the industrial scale for nearly 50 years and remains the cornerstone of nuclear fuel reprocessing for both defense and power reactor fuels around the world. One of the major advantages of this process is that it selectively extracts $Pu(NO_3)_4$ and $UO_2(NO_3)_2$ from dissolved spent nuclear fuels from solutions of moderate nitric acid concentrations (2–3 M), requires no addition of any salts, and is plagued by few co-extracted impurities.

Both Pu(IV) and Pu(VI) are readily extracted into the organic phase, whereas Pu(III) extraction is comparable to that of americium (see Fig. 24.6). In the hexavalent state, the order of distribution ratio is U(VI) > Np(VI) > Pu(VI). Neptunium, normally maintained in the pentavalent oxidation state in PUREX processing, is extracted even less than the trivalent actinides. Neptunium redox chemistry in nitric acid solutions generally causes some more extractable neptunium species to be present, hence there is often 'leakage' of neptunium into undesirable process streams in a PUREX plant (Drake, 1990), as will be discussed further in Section 24.4.4f. As the detailed description of the PUREX flow sheet is given elsewhere, only the practical steps involved with this process are listed here:

(1) Feed preparation – fuel is decladded and dissolved, nitric acid concentration is adjusted to 2–3 M and plutonium valency is adjusted to 4+, most commonly with H_2O_2 or HNO_2.
(2) Co-decontamination cycle – U(VI) and Pu(IV) are co-extracted into the TBP phase leaving behind the fission products, trivalent actinides, and Np(V) in the aqueous raffinate.

(3) Partition cycle – Pu(IV) is reduced to Pu(III) using ferrous sulfamate, U(IV), or hydroxylamine, resulting in Pu(III) being stripped into the aqueous phase while uranium remains in the TBP phase; U(VI) is subsequently stripped with very dilute nitric acid solution; final cleanup of remaining traces of U(VI) occurs during extractant reconditioning with Na_2CO_3.

(4) A second uranium and plutonium extraction cycle follows step (3) for both the aqueous phases separately after feed adjustments to improve recovery.

(5) Final purification of plutonium is done in modern PUREX plants using additional TBP solvent extraction steps. Historically, pure plutonium has been prepared using anion exchange chromatography, as follows: the feed is adjusted to 7.1 M HNO_3 and the plutonium anionic species $Pu(NO_3)_6^{2-}$ is adsorbed strongly onto the column; remaining contaminants like U, Zr–Nb, Ru, and Fe are not adsorbed; after adequate washings, plutonium is eluted from the anion exchange resin with 0.5 M nitric acid.

The improved PUREX (IMPUREX) process operated at temperatures higher than 50°C suggests several advantages such as prevention of plutonium accumulation in the extractors, improvement in fission products and neptunium separations, etc. (Schmeider and Petrich, 1989) and is worth considering.

All of the processes mentioned above, particularly PUREX, have been operated on a production scale. However, none of these processes can be used to separate and recover trivalent actinides or Np(V) neither from HLW solutions nor from various TRU containing waste solutions, which are often moderately concentrated nitric acid solutions (2–4 M). TBP can be employed to extract trivalent actinides (as was indicated in the work of Sekine, 1965, discussed in Section 24.3.4), but only with the reduction of acidity of the aqueous stream and addition of salting out agents. Diluting the HLW solutions, decreasing the acidity by denitration, or partial neutralization to obtain dilute acid salt solutions will increase the volumes of by-product wastes and increase the difficulty of their disposal. If the so-called minor actinides are to be transmuted, there clearly is a need for developing full-fledged processes for recovery of these minor actinides from HLW and TRU wastes.

(f) THOREX process

In the 1960s and 1970s, great interest developed in the thorium fuel cycle as a supplement to limited uranium reserves. The slightly harder neutron spectrum of heavy water and gas-cooled/graphite-moderated reactors make such reactors reasonable centerpieces of a uranium–thorium breeder reactor cycle, though it has been shown that thorium can be used practically in any type of existing reactor. For example, Stewart *et al.* (1971) have described a thorium–uranium breeder fuel cycle designed around the now-decommissioned Fort St. Vrain gas-cooled reactor. Molten salt reactors have a similar favorable neutron spectrum for this fuel cycle. These initiatives have been virtually brought to a halt for various reasons, except in India, where research has continued with its exploration of the thorium–uranium fuel cycle (Lung and Gremm, 1998).

The initial ^{233}U to operate this fuel cycle must be produced in a ^{235}U-fueled reactor, or with an initial ^{235}U or ^{239}Pu charge surrounded by a ^{232}Th breeding blanket. Two fundamental limitations of the U–Th fuel cycle are the creation of ^{228}Th ($t_{1/2} = 1.912$ years, 5.42 MeV α) and ^{232}U ($t_{1/2} = 68.9$ years, 5.32 MeV α) and their daughters as by-products, and the creation of ^{233}Pa ($t_{1/2} = 27$ days, 0.3 MeV γ, 0.6 MeV β^-) as parent of the desired ^{233}U product. The build-up of isotopic contaminants during successive irradiations of recycled ^{233}U–Th fuels can greatly affect the handling procedures used in fuel-element refabrication. Reactor-fuel elements containing ^{233}U may be fabricated semi-remotely provided that complete fabrication can be accomplished in 2 weeks or less. If ^{233}U contains more than 200 ppm ^{232}U, or if refabrication of fuel elements requires longer than 2 weeks, a shielded refabrication facility is necessary. Thorium fuels must be allowed to decay for 12 years if unshielded refabrication procedures are to be used (Arnold, 1962; Schlosser and Behrens, 1967). The fuel cycle has been advocated as non-proliferating on the basis of the presence of ^{232}U isotope and the energetic γ activity of its ^{208}Tl and ^{212}Bi daughters (Ragheb and Maynard, 1980). Another significant advantage of this fuel cycle is the reduced production of long-lived transuranium actinides.

Several approaches to fuel dissolution have been developed for this fuel cycle dependent in part on the reactor type used to breed ^{233}U. The oxide fuel and the breeding blanket used for gas-cooled reactor fuels are imbedded in a graphite matrix. In this cycle, the spent fuel is crushed and the carbon typically burned out prior to fuel reprocessing.

Stainless steel cladding from water-moderated reactors is easily dissolved with 4–6 M H_2SO_4 (Sulfex process) or 5 M HNO_3–2M HCl (Darex process) in low-carbon nickel alloy or titanium equipment, respectively. Uranium losses to the decladding solutions are readily recovered from the Darex decladding solutions in the acid THOREX extraction process. The ThO_2–UO_2 core can be dissolved in 13 M HNO_3–0.04 M NaF–0.1 M $Al(NO_3)_3$. Uranium and thorium can be recovered from graphite-based fuels by: (a) disintegration and leaching with 90% HNO_3; (b) grinding and leaching with 70% HNO_3; or (c) combustion followed by dissolution in fluoride-catalyzed HNO_3 (Blanco *et al.*, 1962). Irradiated Al-clad Th metal slugs are dissolved in HNO_3 containing Hg^{2+} and F^- as catalysts (Bruce, 1957).

The separation of thorium from uranium is most typically accomplished using the same basic chemistry that drives the PUREX process, i.e. extraction of Th(IV) and U(VI) from nitric acid solutions into TBP solutions with aliphatic hydrocarbon diluents. The use of an acid-deficient feed (0.15 M) induces high decontamination while injection of HNO_3 at the fourth extraction stage provides high salting strength and insures quantitative uranium and thorium extraction. Because thorium is extracted by TBP less effectively than Pu(IV) or

U(VI), the introduction of $Al(NO_3)_3$ (Oliver, 1958) or $Be(NO_3)_2$ (Farrell *et al.*, 1962) as salting out reagent has been demonstrated.

In the acid THOREX process, three solvent extraction cycles are used. In the first cycle, uranium and thorium are extracted away from most fission products by 30% TBP from 5 M HNO_3. Both are stripped into a dilute acid phase. In the second cycle, acid conditions are controlled for selective extraction of uranium while thorium remains in the aqueous raffinate. The extracted uranium is further purified by solvent extraction or ion exchange while the thorium is concentrated and stored for recycle.

The processing of short-cooled thorium metal results in the collection of a first cycle extraction column raffinate that contains 20–30% of the mass 233 as ^{233}Pa. Ultimate recovery of ^{233}U requires storage of the raffinate for decay of ^{233}Pa. During a THOREX pilot plant short-cooled scouting run, an estimated 27 g of ^{233}Pa was collected and stored as extraction column raffinate. A one-cycle solvent extraction flow sheet was used to separate ^{233}U from fission products and other contaminants contained in the raffinate. ^{233}U was extracted into 6% TBP in Amsco 125–82 and subsequently stripped into dilute HNO_3 (McDuffee and Yarbro, 1957, 1958).

Five thorium processing campaigns were conducted at the Savannah River Plant. Two different flow sheets were used and a total of about 240 metric tons of thorium and 580 kg of uranium was processed. In the first two campaigns on thorium oxide, uranium was recovered with a dilute 3.5% TBP flow sheet and the thorium was sent to waste. ^{232}U concentrations in these two campaigns were 40–50 ppm and 200 ppm. In the third campaign, thorium metal and thorium oxide were processed. ThO_2 was processed in the final two THOREX campaigns. The three THOREX campaigns used 30% TBP to recover both uranium and thorium. Irradiation conditions were set to produce a concentration of 4–7 ppm ^{232}U. Dissolving rates for thorium metal exceeded 4 metric tons per day and with thorium sent to waste, solvent extraction rates increased, and posed no limits. When Th oxide feed was used dissolving and THOREX solvent extraction rates were $\approx$1 metric ton per day. Satisfactory flow sheets were developed, losses were acceptable, and decontamination from fission products and Pa were adequate. Th–DBP precipitates did appear in the second Th cycle during the first THOREX campaign (Orth, 1978). Rainey and Moore (1962) demonstrated a laboratory-scale THOREX separation in which good decontamination factors were obtained, and U and Th losses were less than 0.01 and 0.3%. Watson and Rainey (1979a,b) have demonstrated a THOREX computer code.

When the fuel being irradiated contains appreciable amount of ^{238}U, the plutonium thus formed requires that a combination of the THOREX and PUREX processes must be applied. The THOREX process is technologically less advanced and principally hindered by the much lower distribution coefficient of Th nitrate relative to uranium and plutonium. To drive thorium into the

TBP phase, a strong salting agent is required. Aluminum nitrate is replaced by nitric acid to reduce the amount of radioactive waste. However, high acid concentrations are counter-effective in achieving high fission product decontamination. Therefore, several flow sheet variants with acid and acid-deficient feed solutions, respectively, have been investigated (Merz and Zimmer, 1984). To achieve high decontamination factors, a dual cycle THOREX process was developed. This process uses an acid feed solution in the first cycle and an acid-deficient feed in the second cycle. An immediate separation of thorium and uranium appears advisable in view of both fuel cycle strategy and process feasibility.

To test the separation of thorium, uranium, and plutonium from each other, Grant *et al.* (1980) developed a modified THOREX solvent extraction flow sheet using 30% TBP. Not surprisingly, the inclusion of plutonium in the fuel cycle increases complexity. The first and second stages are used as a decontamination cycle to remove most of the fission products from the actinides. After intermediate concentration and adjustment of plutonium valency [to Pu(III)], the next three stages comprise the primary separation system and are used to recover Pu(III), Th, and ^{233}U separately.

Finally, several alternative extractants and even extractant types have also been suggested as a means of separating ^{233}U from irradiated thorium. To overcome the comparatively weak extraction of Th by TBP, Siddall (1958, 1963b) suggests that diamyl(amyl)phosphonate (DAAP) should be considered as a replacement for TBP in Th processing. The separation factor between thorium and zirconium is at least ten times greater with DAAP than with TBP. A high degree of complexing of DAAP by thorium occurs even in dilute HNO_3. This extractant is also less prone to third phase formation.

The extraction behavior of 1 M solutions of tri-2-ethylhexyl phosphate (TEHP), di-2-ethylhexyl isobutyramide (D2EHIBA), and di-*n*-hexyl hexanamide (DHHA) in *n*-dodecane towards U(VI), Th(IV), and Pa(V) in the presence of 220 g L^{-1} of thorium from nitric acid medium also has been studied (Pathak *et al.*, 2000). Separation factors for U(VI) over Th(IV) consistently varied in the order: D2EHIBA > DHHA > TEHP > TBP under most conditions. The quantitative extraction of ^{233}U from a synthetic mixture containing ^{233}U(10^{-5} M), ^{233}Pa (10^{-11} M), and thorium (220 g L^{-1}) at 1 M HNO_3 using a 1 M solution of D2EHIBA in *n*-dodecane is achieved in three stages.

Detailed studies on the processing of irradiated thorium using an amine solvent at pilot plant scale have been reported (Awwal, 1971). In this process, the ^{233}U and thorium are coextracted with 0.1 M methyldidecylamine from a feed solution of 5.8 g Th L^{-1} having 2.5×10^{-3} M H_2SO_4. The extracted thorium is selectively stripped with 1M H_2SO_4 and ^{233}U is stripped with 0.5 M HNO_3. The final product is purified by anion exchange. The decontamination factor from fission products for ^{233}U and thorium are 3.2×10^4, 3.8×10^4, respectively, for the single cycle solvent extraction process. The separation factor of ^{233}U from thorium is 2×10^4.

24.4.4 Actinide production processes at the design and pilot stages

During the last two decades, concerted and mission-oriented research conducted around the world has identified a number of promising extractant systems for actinide separations using solvent extraction, extraction chromatography, supported liquid membrane, magnetically assisted chemical separations, or pyro-reprocessing. The pyrometallurgical options have been discussed in Section 24.3.12. Plant-scale demonstrations are yet to occur, partly because of materials/corrosion issues. Most aspects of separations in the IFR project have been demonstrated at the pilot scale. In the following discussion, the performance of the new extraction systems that have been developed for actinide partitioning will be compared. Many of the new extractant systems under development are based on bifunctional (or multifunctional) reagents, whose unique nature will become apparent in the discussion to follow. The chemical features of many of these systems have been considered above (see Section 24.3.4b). The emphasis in this section will be more on the status of process development. The reader is referred to the cited literature for detailed information on the chemistry of the extraction systems.

(a) Dihexyl-*N*,*N*-diethylcarbamoylmethylphosphonate (DHDECMP or CMP)

Navratil and coworkers (Martella and Navratil, 1979; Navratil and Thompson, 1979) conducted a preliminary feasibility study for separation of actinides from synthetic acidified waste solutions likely to be produced during nuclear fuel fabrication and reprocessing. The initial solution contained large quantities of Na_2CO_3, Na_3PO_4, NaCl, Na_2SO_4, and the actinides, plutonium, americium, and uranium. A first contact with 30% TBP/*n*-dodecane removed more than 99.99% of uranium and most of the plutonium. The aqueous raffinate was then contacted with 20–30% CMP/CCl_4 which removed more than 99.91% of americium and all the residual plutonium and other actinides.

Rapko and Lumetta (1994) have reported the extraction of U(VI), Pu(IV), Am (III), and important competing metal ions (e.g. Fe(III), Zr(IV), Bi(III)) from HNO_3 solutions using a mixture of CMP (0.75 M) and TBP (1.05 M) in an aliphatic diluent [normal paraffinic hydrocarbon (NPH) or isoparaffinic hydrocarbon (ISOPAR)]. Above 2M HNO_3, this organic phase splits into heavy and light fractions (third phase formation) even in the presence of ~ 1 M TBP. Adjustment to about 2.0 M $NaNO_3$ is indicated as necessary to prevent third phase formation. At about 2 M (HNO_3, NO_3^-) in the absence of any aqueous complexing agent, a distribution ratio D_{Am} of about 5 is reasonably good. Though 0.1 M HF has no effect on D_{Am}, 0.05 M oxalic acid decreases D_{Am} to about 1. Salting out with $NaNO_3$ increased this value. D_{Pu} at radiotracer concentrations and D_U at 0.05 M (~12 g L^{-1} total uranium) have been reported. D_{Am} decreases in the presence of such moderate concentrations of uranium, presumably as a result of the tying up of the free extractant by the macroscopic quantities of uranium present. Degradation products and acidic impurities in the CMP extractant can inhibit stripping of plutonium and uranium. The increased volume of wastes in all categories that would result from the introduction of a salting-out reagent required to maintain extraction efficiency and phase compatibility is a significant drawback to the application of this class of reagents.

(b) Octyl(phenyl)-*N*,*N*-di-isobutylcarbamoylmethylphosphine oxide (OϕDiBCMPO or CMPO)

To overcome the comparative weakness of the CMP-class extractants, structurally similar extractants containing the phosphine oxide functional group were prepared. Compounds with different substituents at the phosphoryl group and the amide nitrogen have been synthesized (Kalina *et al.*, 1981a; Chmutova *et al.*, 1983) and studied for extraction of transplutonium metal ions. Alterations have also been made at the bridge between the P=O and C=O groups (Rapko, 1995). Two detailed papers describe the synthesis and purification (Gatrone *et al.*, 1987) and the spectral properties of the carbamoylmethylphosphine oxides (Gatrone and Rickert, 1987). The extraction behavior of mainly trivalent actinides, lanthanides, and a few other metal ions has been studied with all the reagents synthesized in this class. Actinide extraction properties and phase compatibility varied significantly with the nature of the alkyl substituents on the carbamoylmethylphosphine oxide core. Of the compounds investigated, OΦCMPO was found to possess the best combination of properties for actinide extraction in a PUREX-compatible diluent system. The CMPO-type compounds have received the greatest attention of all potential actinide partitioning reagents developed over the past 20 years and as a result represent the best-understood hydrometallurgical reagents for total actinide partitioning from wastes.

Numerous investigations have attempted to demonstrate quantitative phase transfer of americium from HNO_3 or HCl solutions by CMPO into diluents like diethylbenzene, CCl_4, C_2Cl_4, and paraffinic hydrocarbons (Horwitz *et al.*, 1981, 1983, 1986; Kalina *et al.*, 1981a; Horwitz and Kalina, 1984). Extraction of Eu(III) from HNO_3 or HCl with CMPO alone or a mixture of CMPO and TBP in mesitylene or *n*-dodecane has been reported (Liansheng *et al.*, 1990) as has the extraction of neptunium and plutonium (Kolarik and Horwitz, 1988; Mincher, 1989; Nagasaki *et al.*, 1992) and Pm, U, Pu, Am, Zr, Ru, Fe, and Pd (Mathur *et al.*, 1992b) from HNO_3 into a mixture of CMPO and TBP in *n*-dodecane. Basic studies of CMPO have reported its activity coefficients (Diamond *et al.*, 1986), complexes formed with trivalent actinides and lanthanides (Mincher, 1992), electrochemistry of Ce(III) nitrate complex (Jiang *et al.*, 1994), and numerical modeling to predict operations in the TRUEX process (Regalbuto *et al.*, 1992; Vandegrift *et al.*, 1993; Vandegrift and Regalbuto, 1995) and for co-extraction of Tc(VII) with U(VI) (Takeuchi *et al.*, 1995).

The now well-known TRUEX process for the recovery of all the actinides from various types of highly acidic nuclear waste solutions is based on CMPO as the principal extractant. The TRUEX process solvent is 0.2–0.25 M CMPO + 1.0–1.4 M TBP in paraffinic hydrocarbon (linear or branched, though the process has been demonstrated in chlorinated diluents as well) (Vandegrift *et al.*, 1984; Horwitz *et al.*, 1985; Schulz and Horwitz, 1988; Horwitz and Schulz, 1990; Mathur and Nash, 1998; Suresh *et al.*, 2001). TBP hinders third-phase formation, contributes to better acid dependencies for D_{Am}, improves phase compatibility, and reduces hydrolytic and radiolytic degradation of CMPO. The basic actinide solvent extraction chemistry of TRUEX has been discussed in Sections 24.3.4b and 24.3.5. The ability to efficiently extract trivalent, tetravalent, and hexavalent actinides from solutions of moderate acid concentration and with good selectivity over *most* fission products (except lanthanides) is a key feature of this extractant. From an engineering perspective, the more-or-less constant D values of Pu(IV), U(VI), and Am(III) between about 1 and 6 M HNO_3 is important, as it allows efficient extraction of actinides from wastes or dissolved fuels with little or no need to adjust the acidity of the feed solution. This particular feature of TRUEX distinguishes this extraction system from other methods for TRU isolation. A sufficient volume of process-relevant thermodynamic data on CMPO extraction chemistry has been developed to support the existence of a computational model, the generic TRUEX model (GTM) that can be used to predict system performance over a wide range of conditions (Regalbuto *et al.*, 1992; Vandegrift *et al.*, 1993; Vandegrift and Regalbuto, 1995).

Russian chemists have independently developed a TRU extraction process based on a somewhat simpler (thus, less expensive) derivative of CMPO (diphenyl-*N*,*N*-di-*n*-butyl CMPO, DΦDBuCMPO) employing a fluoroether diluent (Fluoropol-732) (Myasoedov *et al.*, 1993). This process behaves similarly to the TRUEX process in terms of its efficiency for actinide extraction, shows little tendency toward third-phase formation, and avoids the interferences caused by degradation of TBP. It has been tested in centrifugal contactors and found to recover actinides with greater than 99.5% efficiency. The corrosive nature of aqueous effluents derived from degraded solvent (i.e. containing HF) is a potential drawback for this process.

Continuing exploration of this extractant has suggested a *un*iversal solvent *ex*traction (UNEX) process for the separation of cesium, strontium, and the actinides from nitric acid solutions and from actual acidic radioactive waste solutions (Law *et al.*, 2001, 2002; Romanovskiy *et al.*, 2001a,b, 2002; Herbst *et al.*, 2002, 2003; Romanovskiy, 2002a,b; Todd *et al.*, 2003). The composition of the UNEX solvent is 0.08 M chlorinated cobalt dicarbollide, 0.5 vol.% polyethylene glycol-400 (PEG-400) and 0.02 M DΦDBuCMPO in a phenyltrifluoromethyl sulfone (FS-13) diluent. Cobalt dicarbollide $[Co(B_9C_2H_8Cl_3)_2^-]$ is a lipophilic substitution-inert Co(III) complex that exhibits significant affinity for Cs^+. Using the Idaho National Engineering and Environmental Laboratory

(INEEL) tank waste, removal efficiencies of 99.4, 99.995, and 99.96% for ^{137}Cs, ^{90}Sr, and the actinides, respectively, have been demonstrated. Possible limitations of the process include corrosive products of diluent degradation (e.g. HF), difficult back extraction due to the requirement of very low acidity for low D_{Am}, and possibly complex solvent cleanup prior to recycle of the extractant (Horwitz and Schulz, 1999).

(*i*) *TRUEX demonstrations with HLW and simulants*

Decontamination of four types of actinide-bearing wastes (or waste simulants) from the Hanford site, plutonium finishing plant (PFP), complexant concentrate (CC), neutralized cladding removal waste (NCRW), and single-shell tank (SST) waste have been the subject of either bench-scale experiments or pilot-scale demonstrations using TRUEX with results as follows:

- The removal of americium and plutonium from the plutonium finishing plant (PFP) aqueous acidic waste [HNO_3/$Al(NO_3)_3$ at 3 M total nitrate with 0.09 M HF, 0–0.2 M U, 10^{-5} to 10^{-4} M Pu, 10^{-6} to 10^{-5} M Am, less than 6×10^{-4} M Be, Cr, Ni, Zn, Pb] was accomplished using the TRUEX solvent (0.25 M CMPO, 0.75 M TBP in C_2Cl_4). The first two highly successful counter-current runs with actual PFP waste employed a cross-flow microfilter unit to remove finely divided solids and 4 cm diameter centrifugal contactor equipment for the solvent extraction of TRU elements. Duplicate runs were completed with 10 L of the clarified waste in about 40 min. The α-activity of the aqueous raffinate was 1–2 *n*Ci · g^{-1} and a TRU D_f of 10^4 was obtained. A generic flow sheet of the TRUEX process for the removal of americium and plutonium from PFP waste is given in Fig. 24.20. A larger-scale demonstration using a 20-stage centrifugal contactor configuration achieved α-decontamination factors up to 6.5×10^4 (Chamberlain *et al.*, 1997).
- The CC waste is alkaline and contains high concentrations of Na^+, NO_3^-, NO_2^-, $Al(OH)_4^-$, CO_3^{2-}, organic complexants (EDTA, HEDTA, citric acid, and their radiolytic and hydrolytic degradation products), and moderate concentrations of Cs^+ and Sr^{2+}. After acidification, bench-scale batch extraction tests with synthetic and actual CC waste demonstrated that the $D_{f\ \mathrm{TRU}}$ was on the order of 10^2 (Schulz and Horwitz, 1988). The TRU concentration in the effluent was 1 *n*Ci g^{-1}.
- NCRW consists of solids (principally $ZrO_2 \cdot xH_2O$) generated while treating Zircaloy-clad fuels. It contains moderate amounts of TRU elements. A preliminary test with actual NCRW dissolved in HNO_3 or HNO_3–HF solutions using the TRUEX solvent was reported to result in satisfactory uptake of the actinides (Schulz and Horwitz, 1988). At the Pacific Northwest National Laboratory (PNNL), highly encouraging results have been reported for actinide removal by TRUEX treatment of NCRW sludge and of PFP sludge (Swanson, 1991a–c; Lumetta and Swanson, 1993a–c).

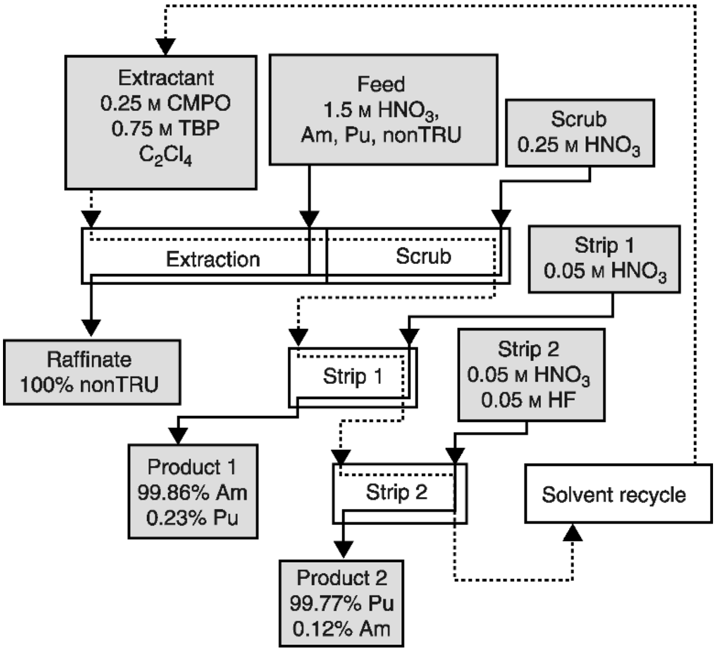


Fig. 24.20 *Generic flow sheet for TRUEX processing of plutonium finishing plant (PFP) wastes.*

- SST waste, a mixture of solid salt cake (e.g. water-soluble sodium salts), solid sludge [primarily hydrated Fe(III) oxide], and a small volume of interstitial liquid containing TRU elements, can also be treated and TRU removed from the acidic solutions, as has been demonstrated using TRUEX on simulated dissolved sludge waste (Schulz and Horwitz, 1988).

The most extensive pilot-scale testing of the TRUEX process has been done at the Idaho National Engineering and Environmental Laboratory under the auspices of the Lockheed Martin Idaho Technologies Co. Several TRUEX demonstration runs have been made on sodium-bearing wastes (Law *et al.*, 1998), a secondary acidic HLW. An optimized TRUEX flow sheet was tested in shielded hot cells at the Idaho Chemical Processing Plant (ICPP) Remote Analytical Laboratory using a 20-stage bank of 2 cm centrifugal contactors.

Stripping of actinides from the loaded process solvent was accomplished with 99.79% efficiency (99.84% for Am, 99.97% for Pu, 99.80% for U) using 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) as the stripping agent. A second demonstration using a dissolved zirconium calcine feed recovered 99.2% of Am (Law *et al.*, 1998). In this case, the HEDPA stripping was less efficient due to problems created by precipitation of zirconium phosphate. The phosphate is believed to be present as an impurity in the HEDPA solution.

Literature reports indicate that such impurities are readily removed by recrystallization of HEDPA from glacial acetic acid (Nash and Horwitz, 1990). The radiolytic stability of this reagent has not been tested, but it is stable in acidic aqueous solutions.

At the Los Alamos National Laboratory (LANL) substantial amounts of waste chloride salts containing moderate concentrations of Pu and Am are generated. These salts, dissolved in HCl, can serve as feed for the separation of actinides using high concentration of CMPO (0.5 M) in C_2Cl_4. If the feed contains large amounts of metal ion impurities that are appreciably extracted by CMPO [e.g. U(VI)], a preceding solvent extraction process employing TBP, TOPO, quaternary ammonium compounds, or some other process must be applied. The *D* values of Th(IV), U(VI), Np(IV), Pu(IV), and Am(III) at varying HCl concentrations in contact with 0.5 M CMPO in tetrachloroethylene have been reported previously (Horwitz *et al.*, 1987). Initial counter-current studies using TRUEX solvent indicated the need for moderate chloride ion concentration in the feed solution for satisfactory extraction of plutonium and americium (Schulz and Horwitz, 1988). Flow sheet for the generic TRUEX process for the removal of actinides from aqueous chloride solutions is given in Fig. 24.21.

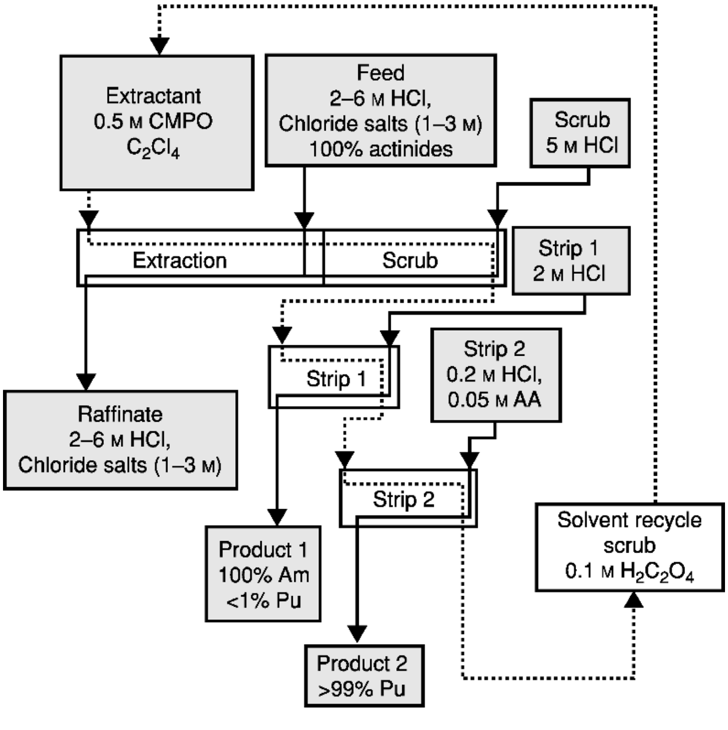


Fig. 24.21 *Generic flow sheet for TRUEX processing of chloride wastes.*

In the European Community R&D program on the management and disposal of radioactive wastes, the Fuel Cycle Dept. ENEA, Rome, Italy, reported that the mixture of TBP and CMPO in chlorinated or aliphatic hydrocarbons achieves a very high D_f for actinides. Batch and counter-current extraction experiments were performed with MOX fabrication liquid wastes. Only batch studies were conducted with simulated solutions of aluminum MTR CANDU high-level wastes of the EUREX reprocessing plant and with analytical wastes from control laboratories of a MOX fabrication plant. Very high D_f values for actinides were obtained without requiring any salting agents and in the presence of many potentially complexing anions (Casarci *et al.*, 1988, 1989).

At Japan's Power Reactor and Nuclear Fuel Development Corporation (PNC), batch and counter-current runs with real high-active raffinate from FBR spent fuel reprocessing have been carried out without adjusting acidity, using 0.2 M CMPO + 1.2 M TBP in *n*-dodecane. The mixer–settler employed in this study had 19 stages for extraction-scrubbing and 16 stages for stripping. The rare earths were extracted along with actinides and some fraction of ruthenium. The D_f for actinides was greater than 10^3. Oxalic acid was added in the feed and scrubbing solutions to improve ruthenium decontamination and effectively lower the D values of zirconium and molybdenum (Ozawa *et al.*, 1992). In another communication from the same laboratory, Ozawa *et al.* (1998) suggested improvements in the TRUEX process flow sheet, specifically, increasing the acidity of the feed to about 5 M to improve Ru decontamination in the actinide fraction, and using salt-free reagents like hydrazine oxalate, hydrazine carbonate, and tetramethylammonium hydroxide for stripping and cleanup steps to obtain a final raffinate that is α-inactive and salt-free. The improved TRUEX flow sheet utilized at PNC is given in Fig. 24.22.

A numerical simulation code for the TRUEX process has been developed to determine the optimum operational conditions for the separation and recovery of TRU elements (Takanashi *et al.*, 2000). With a view to minimize radioactive organic/inorganic waste released from TRUEX process, the electro-redox technique and mediatory electrochemical oxidation using Ag(II)/Ag(I) or Co(III)/Co(II) couples have shown great promise (Ozawa *et al.*, 2000).

At the Bhabha Atomic Research Centre in India, basic data were generated for the extraction of actinides and a few fission and corrosion products using TRUEX solvent (0.2 M CMPO + 1.2 M TBP in *n*-dodecane) (Mathur *et al.*, 1992b). Subsequent studies examined the extraction and separation of actinides from synthetic and actual high-level aqueous raffinate waste (HAW), sulfate-bearing high-level waste solutions (SBHLW) at low acidity of about 0.3 M, non-sulfate wastes originating from pressurized heavy water reactor (PHWR), and fast breeder reactor (FBR) both in about 3 M HNO_3, and actual HLW solutions generated from the reprocessing of research reactor fuels at this center. In each study, the compositions of the synthetic waste solutions were reported (Deshingkar *et al.*, 1993, 1994; Mathur *et al.*, 1993a, 1995, 1996a; Gopalakrishnan *et al.*, 1995). The results of batch studies on actual waste solutions are given below:

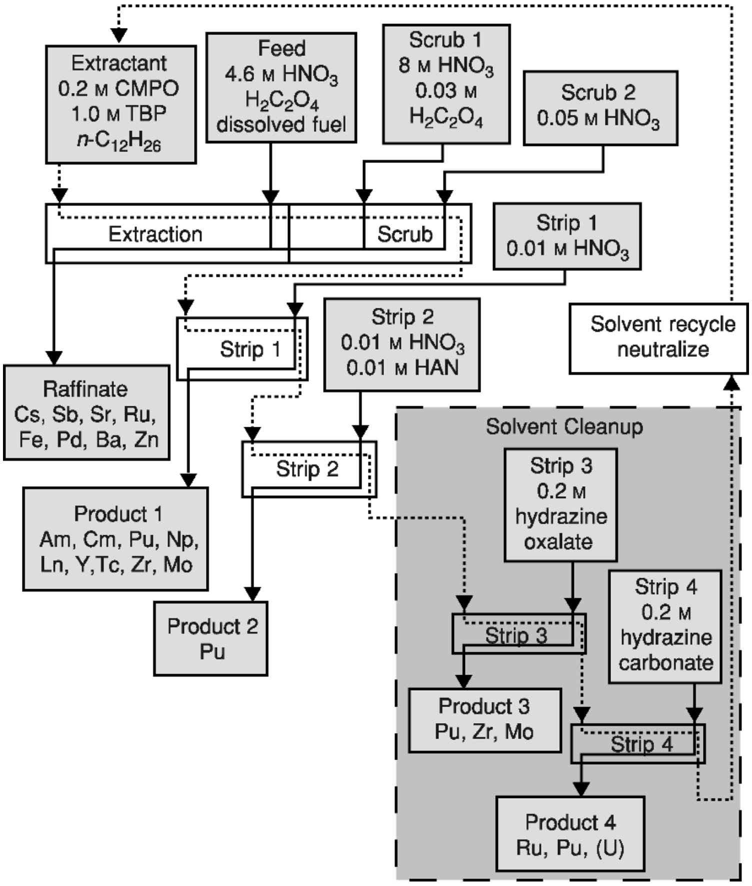


Fig. 24.22 *Generic TRUEX flow sheet for actinide partitioning at JNC.*

- Unmodified HAW was contacted twice with fresh lots of 0.2 M CMPO + 1.2 M TBP in n-dodecane in 1:1 ratio. After two contacts, 99.8% of the α-activity was found in the organic phase. The rare earths (Ce, Pm, Eu, etc.) followed americium, and ruthenium was partially extracted while cesium and strontium were not (Mathur *et al.*, 1993a).
- For extraction of HLW, the feed contains at least ten times higher concentration of uranium, fission and corrosion products than those in HAW. Therefore, one contact with 30% TBP/n-dodecane was made to deplete the uranium content. After this, four contacts were made with 0.2 M CMPO + 1.4 M TBP. The raffinate was found to contain $\sim$ 0.06% of the total α-activity (Mathur *et al.*, 1993a).

- With SBHLW, two contacts were made with 30% TBP followed by four contacts with 0.2 M CMPO + 1.2 M TBP in *n*-dodecane. Even at the low acidity of 0.3 M and ~ 0.16 M SO_4^{2-}, about 99.6% of the total α-activity was removed from the HLW solutions (Gopalakrishnan *et al.*, 1995).

Mixer–settler experiments employing a six-stage unit with synthetic SB- and PHWR-HLW have been reported. After pretreatment with 30% TBP to reduce the concentrations of uranium, neptunium, and plutonium, the raffinate containing the remaining uranium, neptunium, and plutonium and the trivalent actinides and lanthanides (at total acidity of about 3 M) was the feed for a subsequent mixer–settler experiment using 0.2 M CMPO + 1.2 M TBP in *n*-dodecane. In all cases, the HLW raffinate leaving the extraction section showed α-activity near background level. Final analysis indicated that nearly 99.7% of the rare earths are extracted along with the actinides and with about 30% of the ruthenium (Deshingkar *et al.*, 1993, 1994; Chitnis *et al.*, 1998b). The combined flow sheet using 30% TBP and the TRUEX solvent (Fig. 24.23) has been tested with actual HAW solutions generated from the reprocessing of research reactor fuels.

In the first step, with 30% TBP U, Np, and Pu were recovered from HAW and then minor actinides left in the raffinate were extracted with the TRUEX solvent in the second step. Plutonium and neptunium extracted in TBP were stripped together using a mixture of H_2O_2 and ascorbic acid in 2 M HNO_3 and later uranium was stripped from the TBP phase with dilute HNO_3. Actinides extracted in TRUEX solvent were stripped together using a mixture of formic acid, hydrazine hydrate, and citric acid. The final raffinate analysis showed no alpha activity (Chitnis *et al.*, 2000).

(*ii*) *Recovery of Pu from oxalate supernatant*

The solutions resulting from Pu oxalate precipitation (oxalate supernatants) are among the final liquid waste streams in conventional PUREX processing. This waste typically contains ~30 mg $L^{-1}$of plutonium in 3 M HNO_3 and about 0.1 M oxalic acid. TRUEX solvent has proven highly efficient for almost quantitative recovery of plutonium from such a solution in batch solvent extraction studies. Plutonium is stripped from the loaded CMPO phase by 0.5 M acetic acid or by a mixture of oxalic acid, calcium nitrate, and sodium nitrite (Mathur *et al.*, 1994). Plutonium also could be recovered from such solutions utilizing the extraction chromatographic technique in which CMPO adsorbed on Chromosorb-102 (CAC) was used for batch and column studies (Mathur *et al.*, 1993b). When the oxalate supernatant contained large amounts of uranium (10–12 g L^{-1}) along with plutonium, a TBP extraction step followed by TRUEX process solvent step has recovered uranium and plutonium almost quantitatively (Michael *et al.*, 2000).

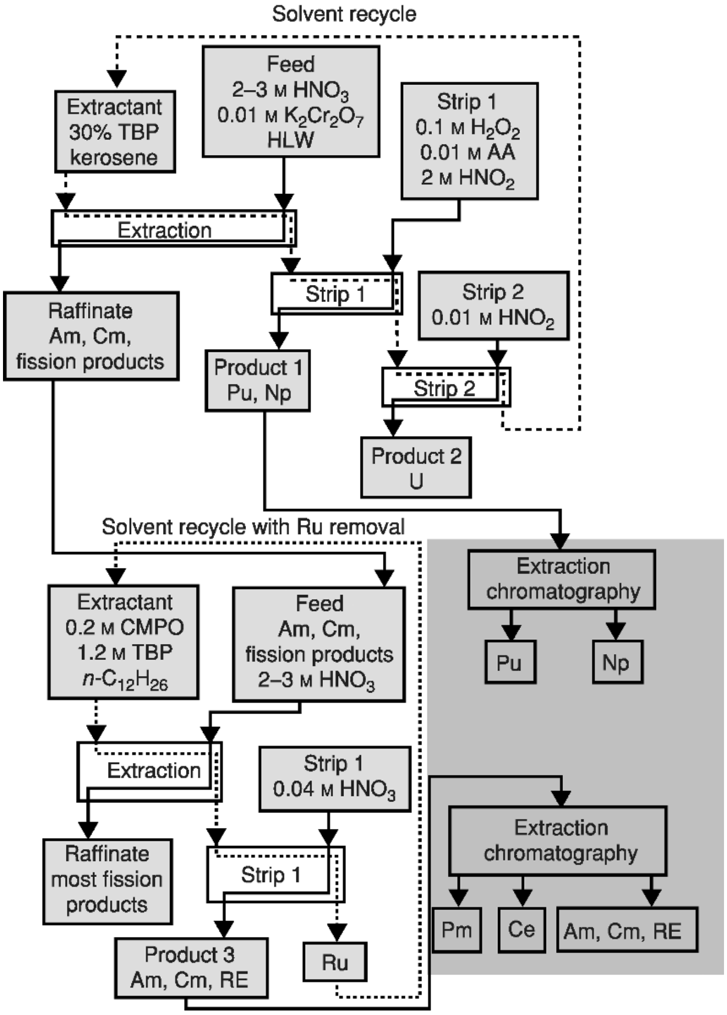


Fig. 24.23 *Generic TRUEX flow sheet for actinide partitioning at BARC.*

(*iii*) *Stripping of actinides from TRUEX solvent*

Oxidation state-specific stripping of actinides from loaded TRUEX solvent can be done in three steps: 0.04 M HNO_3 to remove trivalent actinides, dilute HNO_3–HF mixture (0.05M each), or dilute oxalic acid for selective stripping of tetravalent actinides, and 0.25 M Na_2CO_3 for uranium recovery (and simultaneous reconditioning of solvent for recycle). Horwitz and Schulz (1990) recommend that a solution of either vinylidene-1,1-diphosphonic acid (VDPA) or HEDPA be used for stripping TRUs when they are directly to be vitrified. In similar fashion, coprecipitation of actinides, lanthanides, and a few other fission and corrosion products extracted into the TRUEX process solvent was achieved by using iron(III)ferricyanide as a carrier precipitant. The volume of the precipitate was very small and suitable for vitrification of TRUs (Rizvi and Mathur, 1997). In other reports (Chitnis *et al.*, 1999a,b), a mixture of formic acid, hydrazine hydrate, and citric acid have shown promise for efficient stripping of Am and Pu from TRUEX solvent loaded with simulated HLW in both batch and counter-current modes. Ozawa *et al.* (1998) report that hydrazine oxalate, hydrazine carbonate, and tetramethylammonium hydroxide for stripping of actinides from loaded TRUEX solvent and its cleanup will lead to a salt-free effluent.

(*iv*) *Degradation, cleanup, and reusability of TRUEX solvent*

The hydrolytic and radiolytic degradation of CMPO has been studied in CCl_4 and decahydronaphthalene (decalin) (Chiarizia and Horwitz, 1986), TCE, or a mixture of TBP and TCE (Nash *et al.*, 1988b). Hydrolytic and radiolytic degradation of TRUEX process solvent (0.2 M CMPO + 1.2 M TBP in *n*-dodecane) has been investigated in the presence of 5 M HNO_3 (Chiarizia and Horwitz, 1990) and under dynamic conditions in contact with 3 M HNO_3 or synthetic PHWR-HLW (Mathur *et al.*, 1988). The G values (molecules/100 eV deposited) for the disappearance of CMPO in CMPO–TBP mixture are (1.2 ± 0.3) in *n*-dodecane, (4.5 ± 0.3) in TCE, and (16.4 ± 1.7) in CCl_4 (Nash *et al.*, 1989; Chiarizia and Horwitz, 1990), indicating that more reactive conditions are created upon radiolysis of chlorinated diluents. Hydrolysis generates only acidic compounds while radiolysis produces both acidic and neutral compounds. The degradation products reported are methyl(octyl)phenylphosphine oxide, octyl(phenyl)-*N*-monoisobutylcarbamoylmethyl phosphine oxide, dibutylphosphoric acid, octyl(phenyl)phosphinic acid, octyl(phenyl)phosphinyl acetic acid (Chiarizia and Horwitz, 1990), methyl(phenyl)-*N*,*N*-diisobutylcarbamoylmethylphosphinic acid, and phenyl(diisobutyl) carbamoylnitromethylphosphine oxide (Mathur *et al.*, 1988).

The presence of the acidic extractants as degradation products increases D_{Am} under stripping conditions. Such impurities must be nearly completely removed from the used TRUEX solvent prior to recycle of the extractant. Table 24.16 gives the D_{Am} with an irradiated CMPO mixture under static conditions in contact with 5 M HNO_3 (Chiarizia and Horwitz, 1990) and under dynamic conditions in contact with 3 M HNO_3 (Mathur *et al.*, 1988). The D values at pH 2.0 are quite high and increase with absorbed dose. They also increase in the same fashion at 0.04 M HNO_3, but up to a dose of 200 kGy (~55 W h L^{-1} or 20 Mrad absorbed dose), D is less than 1, hence stripping with 0.04 M HNO_3 should still be possible. Up to an absorbed dose of about 200 kGy, primary cleanup

Table 24.16 *Partitioning of americium* (D_{Am}) *between* 0.2 M *CMPO* + 1.2 M *TBP in* n-*dodecane* and HNO_3 *as a function of absorbed gamma dose.*

	D_{Am}				
	Static condition 5.5 M HNO_3 *Chiarizia and Horwitz* (1990)			*Dynamic condition* 3 M HNO_3 *Mathur* et al. (1988)	
Dose (kGy)	pH 2.0	0.04 M	*Dose* (kGy)	pH 2.0	0.04 M
0	0.011	0.13	0	0.016	–
~70	0.87	0.72	~50	0.55	0.23
~130	0.91	0.61	~110	2.77	0.38
~200	1.33	0.59	~210	16.4	0.81
~280	1.42	0.58	~260	32.7	1.21

D_{Am} only after the wash with respective aqueous phase, no sodium carbonate or alumina treatment.

with 0.25 M Na_2CO_3 will remove most of the acidic impurities. Although the D_{Am} at pH = 2.0 may not match the reference condition, D_{Am} at 0.04 M HNO_3 suggests that continuous counter-current stripping of americium will be efficient. However, at high radiation doses, a secondary cleanup with macroporous anion exchange resin (Chiarizia and Horwitz, 1990) or with basic alumina (Mathur *et al.*, 1988) will restore TRUEX process solvent to near reference condition.

(*v*) *CMPO for extraction chromatography separation of actinides*

Extraction chromatography is fundamentally solvent extraction in which the extractant phase is 'immobilized' on a non-reactive solid support. The technique is generally considered to be most applicable for analytical purposes due to the tendency of the immobilized extractant to 'bleed' from the solid as the aqueous effuent transits the column. However, process-scale applications have been suggested.

The feasibility of using TRU-Resin™ (CMPO + TBP adsorbed on Amberchrom-CG-71 from Eichrom Industries Inc., Darien, Illinois, USA) for separating TRU elements from actual neutralized decladding waste solution (resulting from the removal of zirconium cladding from irradiated fuel) from the Hanford Waste tank has been demonstrated (Lumetta *et al.*, 1993). Actinides (U, Pu, Am) and lanthanides (Ce, Eu) were separated from nitric acid solutions using a column of 0.75 M CMPO in TBP adsorbed on XAD-7. They were subsequently eluted from the column with HCl, oxalic acid, and nitric acid solutions (Yamaura and Matsuda, 1999). Highly encouraging results have been reported for the separation of americium, plutonium, and uranium from acidic waste solutions using several types of extraction chromatographic supports impregnated with CMPO (Barney and Covan, 1992; Schulte *et al.*, 1995a,b, 1996; Barr *et al.*, 2001).

Batch uptake studies have been carried out on the extraction chromatographic behavior of U(VI), Pu(IV), Am(III), and several fission and corrosion products from HNO_3 media using CMPO adsorbed on Chromosorb-102 (CAC) (Mathur *et al.*, 1995). Very high *D* values of actinides and lanthanides as compared to other fission products were obtained. For example, a small CAC column (containing 9.5 g of CAC) was prepared and about 0.5 L of the uranium depleted actual HAW at an acidity of ~1.7 M was passed through it. No α-activity was detected in the effluent. An americium and RE fraction, plutonium fraction, and uranium fraction were subsequently eluted with 0.04 M HNO_3, 0.01 M $H_2C_2O_4$, and 0.25 M Na_2CO_3, respectively. Comparable results were obtained while using a similar column and a synthetic SBHLW (Gopalakrishnan *et al.*, 1995).

A novel silica-based extraction chromatographic support has been prepared by immobilizing styrene–divinylbenzene copolymer in porous silica particles (SiO_2-P) (Wei *et al.*, 2000). Separation experiments using a CMPO/SiO_2–P resin packed column have given good separation of trivalent actinides and lanthanides from fission products like Cs, Sr, and Ru in simulated HLW solutions containing concentrated HNO_3. Also, it has been shown that, using a column packed with freshly purified Cyanex-301/SiO_2–P, americium was completely adsorbed by the resin and only about 1–2% of the Ln(III) were adsorbed from a 1 M $NaNO_3$ solution at pH 3.99 containing trace amounts of ^{241}Am, ^{153}Gd, ^{152}Eu (and 10^{-2} M Eu carrier), and ^{139}Ce. Americium was then eluted in a pure form with 0.1 M HNO_3.

(*vi*) *CMPO in supported liquid membrane separation of actinides*

Supported liquid membrane (SLM) is a technique wherein a microporous film (either as flat sheets or hollow tubes) is impregnated with an extractant and the transport of target metal ions is facilitated from the feed to the stripping solution. A simple schematic description of the SLM system is shown in Fig. 24.24. The salient features of the SLM processes are (1) extractant needed is in small quantities, (2) high feed/strip volume ratio, and (3) very simple

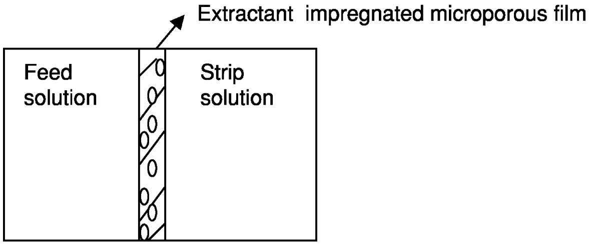


Fig. 24.24 *Schematic description of a supported liquid membrane (SLM) system.*

operation systems. Danesi *et al.* (1983) have used a solution of CMPO/DEB adsorbed onto a 48-μm thick microporous polypropylene film to facilitate the transport of Am(III) from aqueous nitrate solutions to the strip section containing formic acid solution. The transport mechanism suggested consists of a diffusion process in the feed compartment through an aqueous diffusion film followed by a fast interfacial chemical reaction and finally diffusion through the membrane itself to the stripping compartment. The membrane permeability coefficient has been correlated with the diffusional parameters and to the chemical composition of the system.

In another study from the same group (Danesi *et al.*, 1985), an SLM consisting of a mixture of 0.25 M CMPO and 0.75 M TBP in decalin adsorbed on thin microporous polypropylene supports in flat-sheet and hollow-fiber configurations was used for the selective separation and concentration of actinides (Am, Pu, U, and Np) and lanthanides from synthetic acidic nuclear wastes. It has been shown that actinides can be efficiently removed at a level sufficient to characterize the resulting solution as a non-TRU waste. An adjustment developed by Danesi *et al.* (1985) suggested an improvement in the efficiency of actinide removal from waste solutions. Incorporation of a double liquid membrane system, wherein a second SLM containing a primary amine that extracts only HNO_3 from the strip solution, allows near complete removal of actinide and lanthanide metal ions from the feed solution (Chiarizia and Danesi, 1987).

Ramanujam *et al.* (1999) have reported the transport of actinides from nitric acid and uranium-lean simulated samples as well as the actual HLW using CMPO/*n*-dodecane as a carrier and polytetrafluoroethylene as the support. The receiving phase was a mixture of citric acid, formic acid, and hydrazine hydrate. Very good transport of U(VI), Np(VI), Np(IV), Pu(IV), Am(III), and Ce (III) has been achieved. The TRUEX solvent (0.2 M CMPO + 1.2 M TBP/*n*-dodecane) has also been used as a carrier for the transport of Am(III) from nitrate–nitric acid solutions using track-etched polycarbonate plastic membranes (Pandey *et al.*, 2001). For Am(III) transport, these membranes performed at a level comparable to that obtained using commercial membranes.

(*vii*) *CMPO in magnetically assisted chemical separation of actinides*

Pioneering work on the separation and recovery of actinides from waste solutions using magnetically assisted chemical separation (MACS) was performed at the Argonne National Laboratory by Nunez *et al.* (1995a,b). This process gives a selective and efficient separation by chemical sorption followed by magnetic recovery. Magnetic particles (ferrite, magnetite, etc.) are coated with extractants and added to the treatment tank containing dilute TRU waste. The solution can be stirred mechanically or by any other method. Finally, the particles are magnetically separated by imposing a magnetic field around the tank, pumping the solution through a magnetic filter, or introducing a magnet into the tank. Actinide ions can be stripped from the loaded particles with small volumes of suitable stripping agents. This process of recovery of actinides (or any other metal ions) from the waste streams seems to be very simple, compact and, in the proper application, is likely to be cost-effective. Like membrane-based separations, this approach does not involve large amounts of organic solvents and will not produce large volumes of secondary wastes. A conceptual diagram of the MACS process could be visualized as given in Fig. 24.25.

Nunez *et al.* (1995a,b) have used TRUEX solvent (CMPO in TBP) as the active coating on the magnetic particles. The extraction of americium and plutonium from HNO_3 solutions ranging in concentration from 2 to 8 M was found to decrease slowly with increasing acid concentration. The range of K_d values was between 400 and 3000 for americium and between 3900, and 46000 for plutonium. The uptake of the same nuclides was tested using synthetic dissolved sludge waste equivalent to the Hanford site waste. It was concluded that the MACS process could be applied to remediation problems at the Hanford site and other sites only if the waste streams contained low concentrations of TRU elements and lanthanides.

Kaminiski and Nunez (2000) have further studied the separation of U(VI) from HNO_3 and HCl solutions using extractants like CMPO, TBP, TOPO, and HDEHP employing the MACS technique. When magnetic particles were coated with TBP or a mixture of TOPO and HDEHP, partitioning of U(VI) was most efficient from dilute acid environments typical of contaminated ground water. From 2 to 8 M HNO_3, the 1.0 M CMPO in TBP-coated

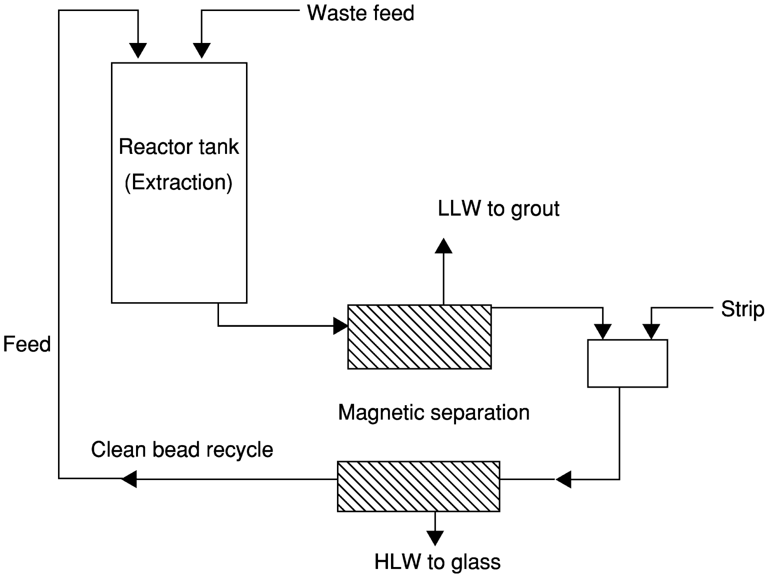


Fig. 24.25 *Schematic diagram of a magnetically assisted chemical separation system (MACS).*

particles gave the highest K_d values for U(VI). From these collected observations, it seems likely that MACS has potential for separating actinides from different actinide-bearing acidic waste solutions using various extractants coated on magnetic particles. Further studies are needed to demonstrate a full-scale operation. The same group has also shown a very high separation between Co and Ni while coating the magnetic particles with a mixture of 0.5 M Cyanex 272 and 0.5 M HDEHP (Kaminski and Nunez, 1999). The other uses of the MACS technique were in pre-analysis separation and concentration of actinides in groundwater (Navratil, 2001), capture of 0.2–0.8 μm PuO_2 particles from very dilute solutions (Worl *et al.*, 2001), and removal of Pu and Am from pH 12 waste waters using magnetic polyamine–epichlorohydrin (Ebner *et al.*, 1999).

(c) Trialkylphosphine oxide (TRPO)

Trialkylphosphine oxide, a mixture of seven alkyl phosphine oxides (Structure r), R being heptyl and octyl alone and a mixture of hexyl, heptyl, and octyl groups[3], has been tested initially in China at the Institute for Nuclear Energy and Technology (Tsinghua University) (Zhu *et al.*, 1983). Tests were continued in a collaborative effort with the European Institute for Transuranium Elements (Karsruhe, Germany) (Apostolidis *et al.*, 1991; Zhu and Song, 1992; Glatz *et al.*, 1993, 1995; Song *et al.*, 1994, 1996; Song and Zhu, 1994; Zhu and Jiao, 1994) for the extraction of actinides, lanthanides, and other fission products from HNO_3 and HLW solutions. The extraction equilibria for the actinide metal ions in their different valency states from nitrate solutions by TRPO can be represented as follows:

$$M^{3+}_{aq} + 3NO^-_{3\,aq} + 3TRPO_{org} \rightleftarrows M(NO_3)_3 \cdot 3TRPO_{org} \tag{24.47}$$

$$M^{4+}_{aq} + 4NO^-_{3\,aq} + 2TRPO_{org} \rightleftarrows M(NO_3)_4 \cdot 2TRPO_{org} \tag{24.48}$$

$$MO^+_{2\,aq} + NO^-_{3\,aq} + TRPO_{org} \rightleftarrows MO_2(NO_3) \cdot TRPO_{org} \tag{24.49}$$

$$MO^{2+}_{2\,aq} + 2NO^-_{3\,aq} + 2TRPO_{org} \rightleftarrows MO_2(NO_3)_2 \cdot 2TRPO_{org} \tag{24.50}$$

From studies in HNO_3 medium with 30% TRPO in *n*-dodecane as the extractant (Zhu and Song, 1992), it was observed that D_{Am} was less than 1 at 3 M and about 10 only at 1 M HNO_3. To achieve an acceptable D_f for Am, the acidity of HLW (typically 3–6 M) must be reduced to less than 1 M. Neptunium extraction is accomplished after electrolytic reduction to Np(IV) in HNO_3 and in simulated HAW solutions. During all of the experiments with concentrated wastes initially 3 M HNO_3, the waste was diluted ten times and the acidity

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[3] Zhu and Song (1992) report approximate composition of 10% hexyl, 50% heptyl and 40% octyl.

then adjusted between 0.7 and 1.0 M. Under such conditions, the recovery of U, Np, Pu, Am, and Cm from HAW using a seven-stage mixer–settler was highly efficient (Zhu and Jiao, 1994). Centrifugal contactor runs (Glatz *et al.*, 1993, 1995; Song *et al.*, 1996) using a battery of 12 extractors with actual diluted HLW has given $D_{\mathrm{f\ actinides}}$ between 10^3 and 10^5. The actinides have in all cases been stripped with 5 M HNO_3 (Am, Cm, rare earths), 0.5 M oxalic acid (Np, Pu), and 5% Na_2CO_3 (U).

Subsequent investigations applied the process to highly saline actual HLW from a Chinese reprocessing plant using 30% TRPO-kerosene. The feed was diluted 2.7 times and the HNO_3 concentration maintained at 1.08 M. This run using miniature centrifugal contactors gave a D_f for total α and ^{99}Tc activities of 588 and 125, respectively. It is claimed that after partitioning the HLW is a non-α waste (Jianchen and Chongli, 2001). The study of γ-irradiation of a 30% TRPO solution in kerosene has shown that above a dose of 2×10^6 Gy phosphonic and phosphinic acids are produced as the radiolytic degradation products along with the formation of polymeric products in the molecular weight range of 500–900 g mol^{-1}. The polymer forms strong complexes with plutonium from which the plutonium is not back-extracted even after five contacts with 0.6 M oxalic acid. This leads to the retention of plutonium in the organic phase (Morita and Kubota, 1987, 1988; Morita *et al.*, 1995; Zhang *et al.*, 2001).

Studies have been carried out with the commercially available TRPO (Cyanex-923, Cytec, Canada Inc., a mixture of four alkyl phosphine oxides R_3PO, R'_3PO, $R_2R'PO$ and RR'_2PO where R = hexyl and R′ = octyl group) to evaluate the effect of phase modifier, TBP, on the extraction of actinides from HNO_3 and synthetic PHWR-HLW solutions (Murali and Mathur, 2001). A series of experiments carried out under various conditions indicated that a mixture of 30% TRPO/20% TBP in *n*-dodecane, when contacted with PHWR-HLW containing ~18 g L^{-1} U at 1 M acidity and an organic to aqueous phase ratio of 5:1, gave highly encouraging results in batch studies. In these experiments, acidity was adjusted with ammonia (a 0.1 L solution of HLW required ~0.02 L of liquid ammonia).

The suitability of TRPO for the partitioning of actinides from HLW solutions has been summarized in Table 24.17. A generic flow sheet is shown in Fig. 24.26. A significant weakness of employing TRPO for actinide partitioning is its comparatively limited capacity and narrow range of nitric acid concentrations that will enable acceptable extraction of trivalent actinides. The dilution of HLW and adjustment of acidity increase waste volume that will create many problems when handling large volumes of HLW.

(d) Diisodecylphosphoric acid (DIDPA)

At the Japan Atomic Energy Research Institute, separation of metal ions from the HLW solutions has been classified into four groups: transuranium elements, Tc–platinum group metals, Sr–Cs, and other elements. For the separation of

Table 24.17 *Suitability of TRPO for the partitioning of actinides from HLW.*

HLW, condition	*Reagent composition*	*Inference*
In ~3.0 M acidity, as such	30% TRPO/*n*-dodecane	third phase formation, cannot be used
Zhu and Song (1992) 10 times diluted, $[H^+]$ adjusted, 0.7–1.0 M	30% TRPO/*n*-dodecane	extraction, reported satisfactory
Murali and Mathur (2001) $[H^+] = \sim 1.0$ M	30% TRPO + 20% TBP/*n*-dodecane, org:aq = 5:1	up to six successive contacts, no reflux, reasonably high *D*
Murali and Mathur (2001) $[H^+] = \sim 1.0$ M HLW, diluted in the ratio 1:2 with 1 M HNO_3	30% TRPO + 20% TBP/*n*-dodecane org:aq = 2:1	up to six successive contacts, no reflux, reasonably high *D*

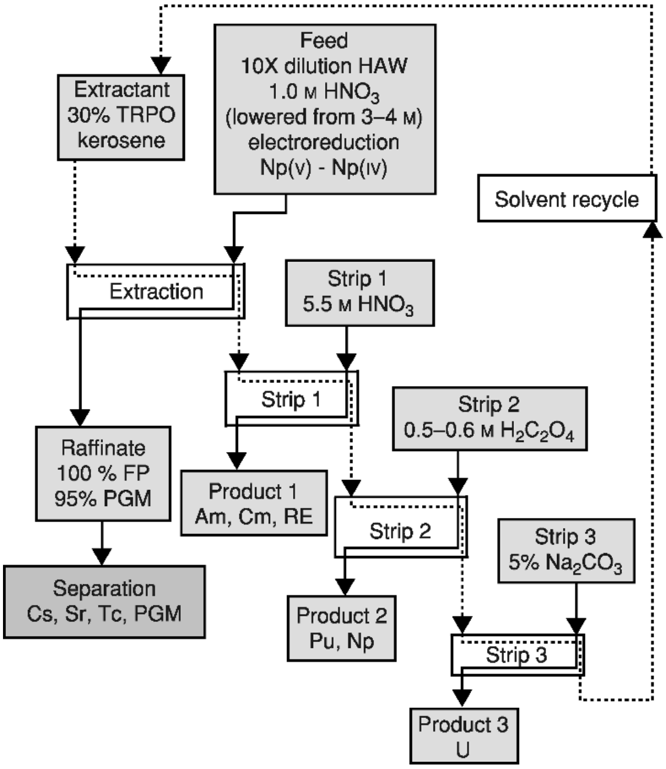


Fig. 24.26 *Generic flow sheet for actinide partitioning using TRPO.*

TRU elements, a mixture of 0.5 M DIDPA + 0.1 M TBP in *n*-dodecane has been proposed with the acidity of the HLW reduced to 0.5 M. Neptunium is reduced from Np(V) to Np(IV) using H_2O_2 and co-extracted with Pu(IV). DIDPA being in the dimeric form (H_2A_2) in *n*-dodecane, the species of the trivalent tetravalent, pentavalent and hexavalent actinides extracted in the organic phase are most likely the electroneutral complexes $M(HA_2)_3$, $M(HA_2)_4$, $MO_2(HA_2)$, and $MO_2(HA_2)_2$, respectively.

Batch as well as counter-current tests using a 16-stage miniature mixer–settler with conditioned synthetic HLW have given very high extraction of actinides including neptunium (flow sheet in Fig. 24.27). During stripping, batch studies with DTPA as a stripping agent gave an Am/rare earths separation factor of greater than 10. After selectively stripping trivalent actinides with DTPA, rare earths could be quantitatively removed with 4 M HNO_3. Neptunium and plutonium are stripped with 0.8 M oxalic acid (Morita and Kubota, 1987, 1988; Morita *et al.*, 1995). In this process, reduction of acidity to about 0.5 M

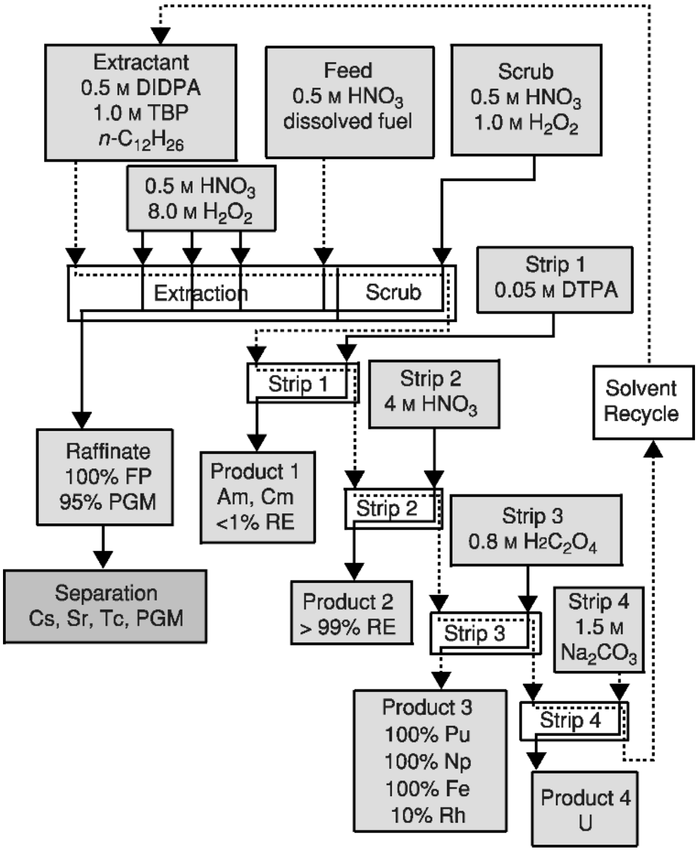


Fig. 24.27 *Generic flow sheet for actinide partitioning in the DIDPA process.*

is accomplished using formic acid. At such low acidity, molybdenum and zirconium precipitate out, carrying about 93% of the plutonium. Filtration units are needed to get a clean HLW solution.

(e) *N*,*N*′-Dimethyl-*N*,*N*′-dibutyltetradecylmalonamide (DMDBTDMA)

One drawback of using organophosphorus extractants is the solid residue that results upon their incineration at the end of their useful life. French researchers have championed the CHON (carbon, hydrogen, oxygen, nitrogen) principle of extractant design (avoiding the use of S or P containing reagents) to minimize the generation of wastes from extractant destruction. This approach to extractant design has generated a much interesting research on a diverse group of reagents.

Among the numerous diamides synthesized and employed for extraction of actinides from nitric acid solutions (Musikas and Hubert, 1983; Musikas, 1987, 1991, 1995; Cuillerdier *et al.*, 1991a,b, 1993; Nigond *et al.*, 1994a,b; Baudin *et al.*, 1995), *N*,*N*-dimethyl-*N*′,*N*′-dibutyl-2-tetradecylmalonamide (DMDBTDMA) has shown the greatest promise. This diamide dissolves in *n*-dodecane, does not give a third phase when in contact with 3–4 M HNO_3, and a 1 M solution gives a D_{Am} of about 10 at 3 M HNO_3. In France, this extractant has been strongly promoted for the partitioning of actinides from HLW solutions (the DIAMEX process).

Investigations of the extraction of uranium, plutonium, americium, and iron by DMDBTDMA at varying HNO_3 concentrations from medium activity liquid waste has given encouraging results. However, some problems have been reported while using this process on tests with high-activity liquid wastes (Baudin *et al.*, 1995). A counter-current centrifugal extractor experiment using a 16-stage battery has been carried out to investigate the hydraulic and extraction behavior of the DIAMEX process using a synthetic HLW solution (Courson *et al.*, 2000) and then finally used for the genuine HLW solution (Malmbeck *et al.*, 2000). With six extraction stages, decontamination factors between 100 and 230 were obtained for lanthanides and above 300 for minor actinides. For back-extraction, four stages were sufficient to recover more than 99.9% of both lanthanides and actinides. The kinetics of lanthanide/actinide extraction (Weigl *et al.*, 2001) and both transient and steady-state concentration profiles in DIAMEX counter-current processing (Facchini *et al.*, 2000) have also been studied. Detailed characterization of these materials and further development of the DIAMEX process continue under the auspices of the PARTNEW European Program (Madic *et al.*, 2002).

(f) Neptunium partitioning during processing

In PUREX processing, consistent control of the flow of neptunium through the system is much more difficult than that of uranium, plutonium, or the trivalent actinides. Dissolution of spent reactor fuel by nitric acid under reflux conditions yields a solution containing principally Np(V) and Np(VI). Flow of neptunium in

PUREX depends on what initial oxidation state adjustments are made to the feed and what steps are taken subsequently to partition plutonium and uranium. Drake (1990) has summarized both the chemistry and process aspects of neptunium control in PUREX. The distribution of neptunium remains a topic of interest in actinide partitioning.

At the Bhabha Atomic Research Centre, the recovery of neptunium from the HLW along with uranium was attempted using a 30% TBP extraction step. The sample was pretreated with 0.01 M $K_2Cr_2O_7$ to oxidize both neptunium and plutonium to the hexavalent state. Both are subsequently co-extracted with U (VI) into 30% TBP. The extraction behavior of neptunium was tested with three types of synthetic wastes and finally with an actual HLW solution. More than 90% of uranium, neptunium, and plutonium could be removed in a single contact. Stripping of neptunium was achieved using a mixture of 0.01 M ascorbic acid and 0.1 M H_2O_2 in 2 M HNO_3 (Mathur *et al.*, 1996b). The kinetics of Np(VI) extraction and stripping under the above conditions while taking synthetic PHWR-HLW as the feed using the AKUFVE technique (Andersson *et al.*, 1969; Johansson and Rydberg, 1969; Reinhardt and Rydberg, 1969; Rydberg, 1969) has demonstrated that the reaction kinetics are fast enough to avoid problems in mixer–settler contacts (Chitnis *et al.*, 1998a). A counter-current study using PHWR-HLW has confirmed the entire process of neptunium extraction and stripping (Chitnis *et al.*, 1998b).

Recent work at the British Nuclear Fuels Limited (BNFL) has focused on the development of an advanced PUREX process. Control of neptunium partitioning in such a system can be accomplished through its interactions with hydroxamic acids. Taylor *et al.* (1998, 2001a,b) report that both formo- and acetohydroxamic acids selectively complex tetravalent actinides and rapidly reduce Np(VI) to Np(V). These characteristics could be used to separate neptunium from plutonium or uranium depending on the approach taken for neptunium extraction. Selected alkyl hydroxylamine species have also been evaluated as reductants for Np(VI) and Pu(IV).

A similar approach to neptunium selectivity using reduction of Np(VI) by butyraldehydes has been suggested by Uchiyama *et al.* (1998). In the partitioning conundrum (PARC), process, the separation of neptunium from plutonium and uranium is proposed in steps prior to Pu/U partitioning in the first extraction cycle of PUREX. Np(VI) is rapidly reduced to Np(V) by *n*-butyraldehyde. This reagent has no effect on the oxidation state of either Pu(IV) or U(VI). Flow sheet development demonstrated partial success in neptunium, technetium, and uranium partitioning. Further work is required to optimize the process.

(g) Trivalent actinide/lanthanide group separation

As noted in Section 24.3.9, separation of trivalent actinides as a group from the lanthanides has been a topic of great interest since the time of discovery of the transplutonium elements. However, setting aside waste volume minimization considerations, this separation is most important as a problem for hydrometallurgical separations only if the actinides are to be transmuted. Neutron economy in transmutation requires the substantial removal of neutron-absorbing lanthanides. In the PUREX process, as in most new processes being developed for actinide partitioning from HLW, the stripped fraction containing the trivalent actinides (Am and Cm) also contains the trivalent lanthanides. If all actinides are to be recycled as fuel (or targets for transmutation) in a current generation reactor, it is essential to separate americium and curium from trivalent lanthanides to avoid the strong absorption of thermalized neutrons by the lanthanides. Due to the similarities in chemical properties and behavior of Am(III) and Ln(III) reagents, extractants or complexing agents containing soft-donor atoms such as N, S, Cl, etc. are required for reliable group separations (Nash, 1994). A number of techniques and reagents have been developed to achieve separation of trivalent actinides and lanthanides. Among these, a few important existing methods and those being newly developed will be discussed.

(*i*) *TRAMEX process*

Solution of concentrated LiCl at an acidity of 0.02 M HCl in contact with a tertiary amine solution in kerosene or diethyl benzene is the basis of the TRAMEX process for plant-scale separation of trivalent actinides from fission-product lanthanides (Baybarz *et al.*, 1963). In this process, the feed solution is 11 M LiCl (0.02 M HCl) containing trivalent actinides and the fission products; the organic phase employed is 0.6 M Alamine 336 (a mixture of tertiary C6–C8 alkyl amines) in diethyl benzene. The scrubbing solution is 11 M LiCl (0.02 M HCl). Trivalent actinides are extracted into the organic phase, while the trivalent lanthanide fission products remain in the raffinate. The actinides are subsequently stripped from the organic phase with 5 M HCl. The TRAMEX process flow sheet is shown in Fig. 24.28. In a single extraction contact, trivalent actinides (Am, Cm, Bk, Cf, Es, and Fm) as a group have a separation factor of about 100 from the trivalent lanthanides (Ce, Nd, Eu, Tb, Ho, and Tm). The order of extraction for the actinides is reported to be Cf > Fm > Es > Bk > Am > Cm.

Several tertiary amines also have been investigated for the extraction of americium and europium from 8 M LiCl/2 M $AlCl_3$/0.02 M HCl using 0.5 M amine in diethyl benzene. The separation factor between americium and europium followed the order: triisoheptyl- (151.7) > triisooctyl- (124.5) $\sim$ trilauryl- (124.1) > Alamine 336 (108). The distribution ratios of americium and europium increased with a decrease in the carbon chain length of the amines. Although separation factor between americium and europium was lowest with Alamine 336, this extractant was preferred because of its easy availability and satisfactory extraction characteristics.

In another study, extraction of trivalent Pu, Am, Cm, Cf, Eu, and Tm from 11.9 M LiCl at pH 2.0 was done with quaternary amines (Aliquat-336 and

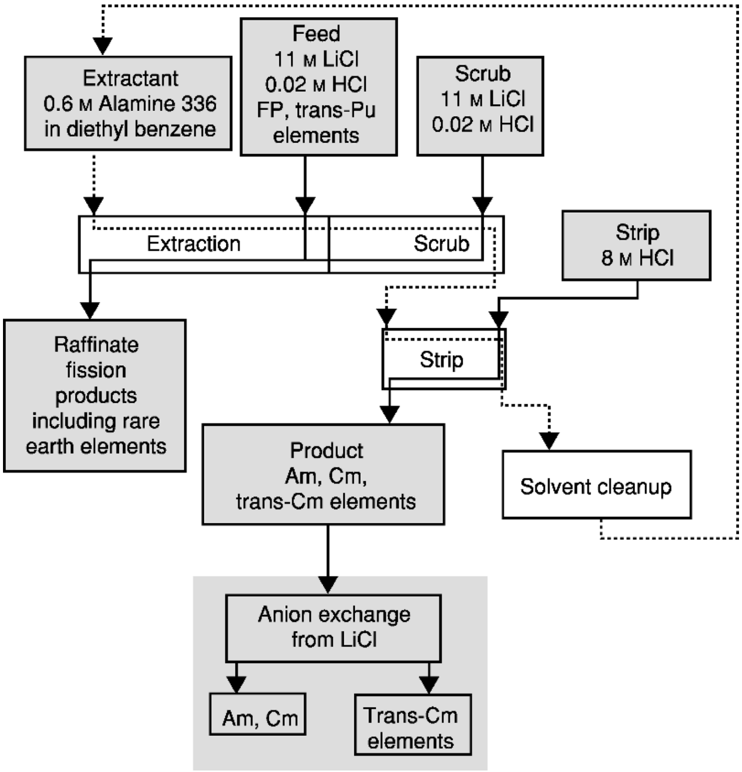
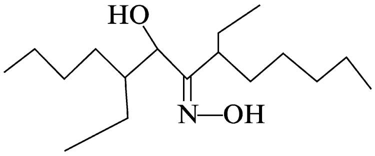


Fig. 24.28 *Generic flow sheet for the TRAMEX process* (*adapted from King* et al., 1981).

tetraheptyl ammonium chloride) and tertiary amines (triisooctyl amine, tri-*n*-octyl amine, Alamine-336 and trilauryl amine) in xylene (Khopkar and Mathur, 1981). The authors have obtained very low separation factors between trivalent actinides and lanthanides when quaternary amines were used whereas they are moderately high while using the tertiary amines. From the absorption spectra of americium and neodymium extracted by the above amines, it was established that the higher separation factors between actinides and lanthanides with tertiary amines are a result of the formation of octahedral hexachloro complexes as compared to the predominantly lower chloro-complexes extracted by the quaternary amines.

(*ii*) *Separation using LIX-63*

The extractant 5,8-diethyl-7-hydroxydodecane-6-one oxime (LIX 63, Structure aa) gave a separation factor ($D_{\mathrm{Am}}/D_{\mathrm{Eu}}$) of 2.9 in a batch extraction study (Hoshi *et al.*, 2001). Using this extractant, separation of americium from lighter lanthanides has been achieved using high-speed counter-current chromatography with a small-coiled column. The coiled column was filled with polytetrafluoroethylene impregnated with a hexane solution of LIX 63. The mobile phase (0.1 M $NaNO_3$/0.01 M morpholinoethane sulfonic acid) contained neodymium and europium (each 10^{-5} M) and radiotracer ^{241}Am. The sample gave a very clear peak for lanthanides when the pH of the mobile phase was 5.60. ^{241}Am was eluted at a pH of 4.60.The authors claim that separation of micro amounts of americium from macro amounts of lanthanides (Hoshi *et al.*, 2001) is possible using this technique. Further work needs to be done to complete the evaluation of the method.



Structure aa

(*iii*) *TALSPEAK process*

The chemistry of the TALSPEAK process has been discussed in detail in Section 24.3.9. Though not deployed as such for accomplishing lanthanide–trivalent actinide separations at process scale, the critical reagent in TALSPEAK, aminopolycarboxylic acids, have repeatedly been employed in the conceptual development of actinide–lanthanide hydrometallurgical separation processes. In the DIDPA and SETFICS processes (described in the next section), the separation of 4f and 5f elements is accomplished in a reverse-TALSPEAK stripping with 0.05 M DTPA (see Fig. 24.11). In the context of modern process design, the aminopolycarboxylates are acceptable reagents, as they are composed of only C, H, O, and N, and hence are fully incinerable. It should be noted, however, that this class of compounds are known to cause difficulties in storage, as hydrogen generation in waste tanks at Hanford has taught (Babad *et al.*, 1991; Meisel *et al.*, 1991; Pederson *et al.*, 1992).

24.4.5 Methods under development

The considerable knowledge that has been developed during decades of fundamental studies of actinide separations supports a number of fresh approaches to important separations processes. It is expected that future efforts to minimize the volume of wastes derived from spent-fuel processing will benefit from this scientific legacy as well. An example of the use of well-understood science being applied in process development is the use of DTPA for La/An partitioning in the DIDPA extraction process for the TRU elements (Morita *et al.*, 1995, 2002). In this case, the stripping of trivalent actinides from the loaded 0.5 M

DIDPA + 0.1 M TBP solvent gave in a batch experiment (after adjustment to pH 3.6) a separation factor of americium from the lanthanides of 10.

A report from JNC has suggested the separation of trivalent actinides and lanthanides applying DTPA in a TRUEX-based process known as SETFICS (Solvent Extraction for Trivalent F-elements Intragroup Separation in CMPO-Complexant System) (Koma *et al.*, 1998, 1999; Ozawa *et al.*, 1998). Using this process, a counter-current experiment was done with an actual TRUEX product solution employing 0.05 M DTPA/4 M $NaNO_3$ (pH 2.0) as the strippant. Americium and curium were successfully recovered using SETFICS. $^{144}Ce/^{241}Am$ decontamination factor has been reported to be 72. Though 80% of the lanthanides were rejected from the Am–Cm fraction, samarium and europium were poorly separated from the actinide fraction (Koma *et al.*, 1998).

(a) Employing soft-donor extractants

By comparison with oxygen donor extactants, soft-donor extractant molecules offer greater potential for more efficient trivalent actinide–lanthanide group separations. For example, Ensor *et al.* (1988) reported Am/Eu separation factors of greater than 100 using the synergistic combination of 4-benzoyl-2,4-dihydro-5-methyl-2-phenyl-3H-pyrazol-3-thione (BMPPT) and 4,7-diphenyl-1,10-phenanthroline (DPPHEN). Independently, neither extractant is particularly effective for the extraction of americium or europium. Musikas and Hubert (1983) reported a high $S^{M'}_{Am}$ between americium and rare earths for their extraction from dilute nitric acid into an extractant mixture of TPTZ and dinonylnaphthalenesulfonic acid (HDNNS) in CCl_4. It was further proposed that HDNNS could be replaced by α-bromocapric acid in an aliphatic diluent. Work on solvent extraction procedures using TPTZ (and related complexants) continues (Cordier *et al.*, 1998; Drew *et al.*, 1998, 2000).

To overcome the considerable aqueous solubility of TPTZ while conforming to the CHON principle, development of nitrogen-containing extractant molecules continues. In a multinational effort funded by the European Commission's research program on nuclear fuels reprocessing for the future (NEWPART), polyaza ligands, BTPs, have been characterized for selective extraction of trivalent actinides from 1.9 M HNO_3/NH_4NO_3 solutions (Kolarik *et al.*, 1999). The extracted complexes have the stoichiometry $M(NO_3)_3 \cdot HNO_3 \cdot 3BTP$ and the Am/Eu separation factors average 100–120. The extraction and separation efficiency is strongly dependent on the diluent. The *n*-propyl derivative self-associates (forming dimers and trimers) in a solution of branched alkanes with 2-ethyl-1-hexanol present as a phase modifier. Counter-current testing of the SANEX-BTP process with real radioactive materials at the Atalante facility in France demonstrated that the *n*-propyl derivative was susceptible to air oxidation with HNO_2 catalysis. Branching in the hydrocarbon side chain improves stability.

(b) Employing Cyanex 301 and other dialkyldithiophosphinic acids

Though Musikas (1985) indicated potential for effective separation of trivalent actinides from lanthanides using thiophosphoric acid extractants, the instability of such extractants towards hydrolysis reduced their utility. However, dithiophosphinic acids, represented by the commercially available extractant Cyanex 301, are somewhat more stable (Sole *et al.*, 1993). Basic features of these systems have been discussed in Sections 24.3.5 and 24.3.9. In a counter-current fractional process having three extraction and two scrubbing stages, more than 99.99% of americium can be separated from a trace amount of europium with less than 0.1% extraction of the latter (Zhu, 1995; Zhu *et al.*, 1996; Chen *et al.*, 1997; Hill *et al.*, 1998).

In another study, a mixture of 0.5 M purified Cyanex 301 and 0.25 M TBP/kerosene has been used in a counter-current experiment to separate americium from lanthanides (Pr, Nd, and Eu) at concentrations of 0.1–0.6 M. A separation factor of around 200 between americium and the lanthanides has been obtained and the extraction can be performed at a pH of 2.7–2.8. This pH value is about 1 unit lower than that needed when Cyanex 301 is used alone. Americium was successfully (>99.998%) separated from macro amounts of lanthanides with only less than 0.04% lanthanides co-extracted (Wang *et al.*, 2001).

The alternative to the SANEX-BTP process that relies instead on dialkyldithiophosphinic acid extractants has been examined as the SANEX-DTP or ALINA process. Initial investigations with a solvent composed of Cyanex 301 in combination with TBP or TOPO as phase modifiers proved inadequate in testing due to the instability of Cyanex 301 under representative conditions. Aromatic derivatives were synthesized in an effort to enable the separation from more acidic media and improve radiation stability. The bis(*p*-chlorophenyl) dithiophosphinic acid (DClDPDTPA) synthesized by Modolo and Odoj (1999) accomplishes both of these objectives. The SANEX-IV process currently under development relies on DClDPDTPA in combination with TOPO as phase modifier. This solvent is reported to extract trivalent actinides from 0.5 to 1.5 M nitric acid.

Apart from the solvent extraction technique for the separation of trivalent actinides from the lanthanides employing Cyanex 301, other techniques like supported liquid membrane and column chromatography have also been utilized (Hoshi *et al.*, 2000; Mimura *et al.*, 2001). A selective and preferential transport of americium across a supported liquid membrane containing highly purified Cyanex 301 has been achieved in the product solution while most of europium remained in the feed solution (Hoshi *et al.*, 2000). Also, micro-capsules enclosing Cyanex 301 were prepared by employing a biopolymer gel, alginic acid, as an immobilization matrix. The chromatographic separation of americium and europium was accomplished by gradient elution with 0.1 M (H, Na)NO_3 (pH 2.0) for europium and 0.1 M HNO_3 for americium while using the column packed with the above micro-capsule (Mimura *et al.*, 2001).

Although Cyanex 301 has not yet been used for the separation of americium and curium from the rare earths in the fraction stripped by 0.04 M HNO_3 in the TRUEX process, this process appears to have great potential, though radiation stability and the nature of degradation products represent a concern.

24.4.6 Comparison of extractants being proposed for actinide partitioning

A comparison of the different extractants, their concentration, diluent, phase modifier, best conditions for extraction and stripping of americium is given in Table 24.18. Each system has both positive and negative features. Based on cost of the extractant, the DIDPA and TRPO are clearly superior. However, processes based on the TRPO and DIDPA extractants require, respectively, a ten-fold dilution of the aqueous feed and/or denitration with formaldehyde impacting the volume of wastes generated. Only the DMDBTDMA extractant is completely incinerable. Furthermore, degradation products of DMDBTDMA do not interfere with stripping of americium, while those of CMP and CMPO can. However, the malonamide requires higher concentrations of HNO_3 for efficient extraction of americium, has a comparatively steep nitric acid dependence on the extraction side, and a lower radiolytic stability than that of TBP. Phase modifiers (TBP) are required for both CMP and CMPO extraction systems to prevent third-phase formation, but the TBP apparently increases the stability of the primary extractant. Extraction in the CMPO/TRUEX system is moderately independent of the concentration of HNO_3, simplifying feed preparation. As a complement to PUREX, TRUEX has an advantage, as no adjustment of the aqueous raffinate from PUREX would be required to

Table 24.18 *Comparative features of partitioning of actinides* (*with data for Am*(*III*)) *with various extractants.*

Extractant concentration (M)	*Diluent*	*HNO_3 conc., for extraction* (M)	*HNO_3 concentration for stripping* (M)
CMP, 0.75	aliphatic hydrocarbon + 0.5 M TBP	>2	<0.15
DIDPA, 0.5	*n*-dodecane + 0.1 M TBP	0.5, denitration or dilution of HLW	4
CMPO, 0.2	*n*-dodecane + 1.2 M TBP	2–3, any HLW as such	0.04
TRPO, 30% (V/V)	*n*-dodecane	0.7–1.0 M, HLW diluted 10 times	>4
TRPO, 30% (V/V)	*n*-dodecane + 20% TBP	~1.0 M, no major dilution	>4
DMDBTDMA, 1.0	*n*-dodecane	>2	<0.5

make successive TRUEX extraction stages compatible. Several new options for trivalent actinide/lanthanide separations by solvent extraction are also emerging. It is clear that, like the decision of whether to process irradiated fuels or not, countries having irradiated nuclear fuels clearly have numerous viable options for processing those fuels should the P&T option be pursued.

Actinide partitioning if and when incorporated at the back-end of the nuclear fuel cycle will considerably reduce the long-term radiological risks and therefore increase the safety of the disposal of nuclear wastes in a geologic repository. Whether actinides are recycled to a reactor (or accelerator) for transmutation or disposed of in a repository, a significant reduction in the hazard associated with the wastes (with transmutation) or the cost (without transmutation) can be achieved through the deployment of actinide partitioning technologies. Though there is no universal consensus on the desirability of actinide partitioning for radioactive waste disposal, continuing research around the world offers an ever-increasing number of potentially viable options for accomplishing partitioning based on solvent extraction, extraction chromatography, supported liquid membranes, or magnetically assisted chemical separations. The continued development of more options relying on the proven technology of solvent extraction may assist immeasurably in securing the public acceptability of nuclear power as the most viable strategy for combating global warming. More advanced options may emerge as work progresses on alternative media like supercritical fluids, room temperature ionic liquids, or the various pyrometallurgical processing options.

24.4.7 Actinide separations around the world – past, present, and future

In the last 20 years, significant emphasis has been put on partitioning and transmutation (P&T) of actinides present in TRU waste generated from various operations involving actinides and also from the HLW solution generated from the reprocessing of nuclear reactor fuels. The International Atomic Energy Agency (IAEA, Vienna) held several advisory group meetings and coordinated research programs on the P&T option. These meetings served as a forum for discussion among several participating countries regarding various extractants, processes developed earlier, or those being developed for partitioning of actinides from HLW solutions. Some of the extractants and developed processes have been discussed above. Here the work that has been carried out and brought to mixer–settler or centrifugal contactor stage of testing will be discussed emphasizing the status of activities in those countries involved in the process, noting that international collaboration is important in this field

(a) United States

In the U.S. after a large amount of work on the extraction of trivalent actinides and lanthanides with several carbamoylmethylphosphonate and phosphine oxides, OΦCMPO was adjudged as the best extractant for this purpose.

For process applications, a mixture of 0.2–0.25 M OΦCMPO and 1–1.4 M TBP in *n*-dodecane, called the TRUEX solvent has been judged as optimum. Although actual HLW generated from the fuel reprocessing plants have not been treated with TRUEX solvent on a large scale in the U.S., different TRU wastes generated have been treated. For example, large volumes of waste generated at the Argonne National Laboratory and the New Brunswick Laboratory have been treated. At Lockheed Martin Idaho Technologies Co., the TRUEX process has been evaluated for the separation of actinides from sodium-bearing waste and calcine waste. At the Oak Ridge National Laboratory, separation and recovery of macro quantities of americium and curium from highly irradiated (> 87% fission) ^{242}Pu targets has been achieved employing the TRUEX process. Other TRU wastes treated with TRUEX solvent at different laboratories in the U.S. are neutralized cladding removal waste (Pacific Northwest National Laboratory), plutonium finishing plant waste (Westinghouse Hanford Co.), and TRU wastes containing chloride salts (Los Alamos National Laboratory). Successful demonstration of a very high efficiency of recovery of TRU elements from the above-mentioned types of wastes is a unique feature for CMPO as an extractant.

Recently, new work has been initiated in the U.S. on the evaluation of possible future nuclear fuel cycles with the commencement of the Advanced Fuel Cycle Initiative. This program is progressing more-or-less in tandem with work on future reactor designs (Generation IV program). In addition, a considerable amount of work has been done in the U.S. investigating pyrometallurgical processing of spent nuclear fuels. Though much work remains to be done to fully enable pyroprocessing, there is no denying that this option has some attractive features and additional work to improve the process is justified.

(b) Japan

At the Japan Atomic Energy Research Institute, 0.5 M DIDPA + 0.1 M TBP in *n*-dodecane has been proposed for the separation of TRU elements from HLW solutions. To employ this acidic extractant for spent fuel reprocessing, the acidity must be reduced to 0.5 M to obtain an efficient recovery of actinides. Work has been done in batch and counter-current tests using synthetic HLW. At Power Reactor and Nuclear Fuel Development Corporation, the TRUEX solvent, i.e. 0.2 M CMPO + 1.2 M TBP in *n*-dodecane, has been utilized for actinide partitioning in batch and counter-current runs with a real high-active raffinate from FBR spent fuel reprocessing. Pyroprocessing and supercritical fluids extraction are also under active consideration in Japan, as are alternatives to the DIAMEX process.

(c) Russia

At the Khlopin Radium Institute, St. Petersburg, efforts have been directed towards using a modified PUREX process to recover actinides such as neptunium and the other actinides, possibly including the trivalent ions by using a neutral organophosphorus extractant like isoamyldialkylphosphine oxide. Scientists in this laboratory have developed a Russian TRUEX process, based on diphenyl-*N*,*N*-dibutyl CMPO which is less expensive and gives higher D_{Am} values as compared to O(Φ)CMPO. It does not need TBP as the phase modifier but the diluent used is a fluoroether. Very high recoveries and separations of trivalent actinides have been achieved from waste solutions. A variation on this process has been incorporated by scientists in the U.S. at the Idaho National Engineering and Environmental Laboratory in the development of the UNEX process for radioactive waste processing.

(d) China

In China, the main emphasis has been on the extractant trialkylphosphine oxide (TRPO), which is easily synthesized and inexpensive. Actinide recovery and separation from HLW solutions carried out within international collaborations had to be done at acidity of ≤ 1 M and the HLW diluted considerably in this process. However, batch studies, mixer–settler, and centrifugal contactor runs have given highly encouraging results.

(e) France

French chemists have concentrated on the CHON (carbon, hydrogen, oxygen, and nitrogen) principle to design the new extractants of the class amides and diamides. After significant efforts in synthesizing various diamides with different combinations of substituents at R_1, R_2, and R_3 (Structure n), the compound DMDBTDMA was prepared, which is soluble in aliphatic diluent like *n*-dodecane and has respectable *D* values for trivalent actinides and lanthanides at 3–4 M HNO_3. More recently, the tetradecyl backbone substituent has been replaced (in the baseline process) by an ethoxy hexyl (ether) group to improve phase compatibility characteristics. Batch studies, mixer–settler, and centrifugal contactor runs with synthetic as well as actual high-active wastes have given satisfactory results for the recovery of actinides. A great deal of effort has been expended in France on new reagents and processes for minor actinide partitioning and lanthanide/actinide separations and on investigating phase compatibility issues in solvent extraction. Creativity and innovation highlight both the technology and R&D efforts in France on the closed-loop nuclear fuel cycle.

(f) India

Scientists at Bhabha Atomic Research Centre have tested the TRUEX solvent for batch and mixer–settler runs using synthetic high-active waste, stored sulfate bearing waste, and PHWR-HLW. A uranium depletion step with 30% TBP/*n*-dodecane followed by TRUEX process has been suggested for highly efficient separation and recovery of all the actinides. Batch studies with actual HAW and HLW of research reactor fuels and mixer–settler runs with actual HAW of research reactor fuels have been performed. The raffinate from the mixer–settler runs with synthetic as well as actual wastes had α-activities at the background level. Also, work has been done with Cyanex 923 (a commercially available TRPO) and its mixture with TBP in *n*-dodecane. The batch studies suggest that even with the combination of Cyanex 923 and TBP, the acidity has to be brought down to about 1 M but it may not be necessary to dilute the HLW to a great extent for achieving high separation efficiencies of the actinides. Preliminary studies have been carried out on the extraction of Am(III), U(VI), and Pu(IV) with DMDBTDMA from nitric acid and PHWR-HLW solutions.

(g) Sweden

The research group at Chalmers University developed a three-stage process called CTH (Chalmers Tekniska Hogskola) for separation and recovery of all the actinides from HLW solutions (Svantesson *et al.*, 1979, 1980; Liljenzin *et al.*, 1980). In the first step, acidity of HLW is adjusted to 6 M and uranium, neptunium, and plutonium are extracted with 1 M HDEHP/kerosene. This step also extracts most of the Fe, Zr, Nb, and Mo. In the second step, the acidity of the raffinate is considerably reduced by contacting with 50% TBP/kerosene. Finally in the third step, americium, curium, and rare earths are extracted with 1 M HDEHP. From all the loaded organic phase, the actinides are stripped with suitable reagents. The entire process has been tried with synthetic waste using small-scale mixer–settlers. Because of the problems associated with significant acidity adjustment in the entire process, this may not be cost-effective on a plant scale.

(h) Other countries

In the UK, though British Nuclear Fuels Ltd. actively reprocesses commercial fuels to recover uranium and plutonium, little has been done in the field of actinide partitioning. It appears likely that if the United Kingdom ultimately decides to partition actinides, an appropriate process from the variety of options being developed elsewhere will most probably be adopted. Among the other countries, at the European Commission Joint Research Centre–Ispra Establishment, Italy, a process has been developed by first extracting uranium, neptunium, and plutonium with TBP or HDEHP, diluting the raffinate to a pH of 2 and extracting trivalent americium, curium, and rare earths with a mixture of 0.3 M HDEHP + 0.2 M TBP in *n*-dodecane (Cecille *et al.*, 1980). This process has the same limitations mentioned above for the CTH process. Within Europe, wide international collaboration on actinide partitioning is supported by the European Commission in the frame of its successive Research Framework Programs.

24.5 WHAT DOES THE FUTURE HOLD? FUTURE DIRECTIONS IN ACTINIDE SEPARATIONS

Actinide separations for plutonium processing (in connection with either weapons production or as a part of a plutonium recycle program) and uranium recovery involve 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 plutonium 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 renewed interest in closing the fuel cycle and by the need for waste cleanup and environment restoration for legacy materials. Current issues in actinide separations are defined by the physical and chemical state of actinides as they occur and the motivation for carrying out the separation.

24.5.1 Alkaline wastes in underground storage tanks

One legacy of 50 years of plutonium production for defense purposes is a large volume of mixed wastes (containing TRUs, long-lived fission products, and non-radioactive but chemically hazardous materials) (Horwitz *et al.*, 1982). Their presence in underground waste tanks or storage bins represents a potential threat to the surrounding environment and so demands attention. 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: improving sludge washing procedures that can 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.

24.5.2 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 energy value of the actinides. Clearly, transmutation also eliminates weapons proliferation concerns as well. 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 fast reactor concept and pyrometallurgical separation process, and the development of new soft-donor extractants and aqueous complexants for actinide/lanthanide separations. Some of the less developed unconventional materials and techniques (RTILs and sc-CO_2, and volatility-based methods in particular) may ultimately have an important role to play in solving this challenging problem.

24.5.3 Actinides and 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 inhibit their entry into the hydrosphere/biosphere.

In the earliest days of actinides separations, discovery and plutonium production dominated the landscape. Sixty years later as we approach the end of the age of fossil fuels, actinide separation could play a central role in the preservation and restoration of the planetary environment. 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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