

Argonne National Laboratory, with facilities in the states of Illinois and Idaho, is owned by the United States Government and operated by The University of Chicago under the provisions of a contract with the Department of Energy.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor The University of Chicago, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or The University of Chicago.

Available electronically at <http://www.doe.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

ANL-02/29

Argonne National Laboratory
9700 South Cass Avenue
Argonne, IL 60439

PRELIMINARY EVALUATION OF SOLVENT-EXTRACTION
AND/OR ION-EXCHANGE PROCESS FOR MEETING AAA PROGRAM
MULTI-TIER SYSTEMS RECOVERY AND PURIFICATION GOALS

by

John L. Swanson, Candido Pereira, and George F. Vandegrift

Chemical Technology Division

May 30, 2002

CONTENTS

	<u>Page</u>
SUMMARY	1
1. OBJECTIVES	3
2. COMPARISON OF PROCESSES.....	4
2.1 RECOVERY OF URANIUM	4
2.1.1 PUREX Process	4
2.1.2 UREX Process	5
2.2 RECOVERY OF TECHNETIUM.....	6
2.3 RECOVERY OF TRANSURANIC ELEMENTS	6
2.3.1 TRUEX Process	7
2.3.2 DIAMEX Process.....	7
2.3.3 TRPO Process	8
2.3.4 TBP Extraction.....	8
2.3.5 Extraction Chromatography.....	10
2.3.6 Ion Exchange	10
3. SEPARATION OF AMERICIUM AND CURIUM FROM LANTHANIDES	11
4. RECOVERY OF CESIUM AND STRONTIUM.....	14
5. EVALUATION OF PROCESSING SYSTEMS	14
REFERENCES	18
ACRONYMS	19

FIGURES

	<u>Page</u>
1. UREX Process Flowsheet	6

PRELIMINARY EVALUATION OF SOLVENT-EXTRACTION AND/OR ION-EXCHANGE PROCESSES FOR MEETING AAA PROGRAM MULTI-TIER SYSTEMS RECOVERY AND PURIFICATION GOALS

by

John L. Swanson, Candido Pereira, and George F. Vandegrift

SUMMARY

Several potential processes are described and evaluated for their suitability in a multi-tier aqueous-based approach to processing dissolved spent nuclear fuel under the Advanced Accelerator Applications (AAA) program. The evaluation is focused on solvent extraction and ion exchange technologies that have been demonstrated to varying degrees. The goals of the program are to separate uranium (U), technetium (Tc), and the transuranic (TRU) elements from the fission products that are to be vitrified for disposal as high-level waste (HLW). Uranium will be disposed as low-level waste (LLW); Tc and TRU will be transmuted in an accelerator.

A number of processes have been examined. The focus was on liquid-liquid solvent extraction processes because of their relatively high state of development and their suitability for high-throughput-rate processing. Ion exchange processes were also examined. PUREX and UREX were evaluated as options for recovery of uranium; UREX is also an option for Tc recovery. Solvent extraction options examined for TRU recovery included TRUEX, DIAMEX, and TRPO, as well as some based on TBP extraction. Processes for trivalent actinide separation from lanthanides were also examined.

The PUREX processes have been developed over many years, and have been refined to a significant degree. In the first cycle, U and plutonium (Pu) are co-extracted from dissolved spent fuel solutions by TBP in a diluent, selectively stripped, and purified in additional extraction/strip cycles. Neptunium (Np) can be extracted or driven into the raffinate by adjusting the oxidation state. Trivalent actinides and fission products remain predominantly in the raffinate, although a significant Tc fraction will co-extract with the U and Pu.

In the UREX process, the PUREX process is modified by the addition of aceto-hydroxamic acid (AHA) to complex and reduce Pu and Np so that they do not extract along with the U. Also, a low nitric acid concentration promotes efficient extraction of Tc with the U. Selective stripping produces separate U and Tc streams that meet AAA targets.

Several processes have been developed that will recover the TRU elements. The TRUEX, DIAMEX, and TRPO processes all extract all of the TRU elements simultaneously (the lanthanide fission products are also extracted); selective oxidation/reduction and stripping can then be used to separate tetra- and hexavalent ions of Pu and Np from the trivalent ions such as americium (Am) and the lanthanides. Processes based on TBP can be used to selectively extract the tetra- and hexa-valent species of Pu and Np. Extraction chromatography and ion exchange processes can also achieve the desired separations.

The octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide (CMPO) extractant used in the TRUEX process will extract all of the actinides and lanthanides with good selectivity over most fission products (except for the lanthanides). The trivalent actinides and lanthanides can be separated from TRU elements in higher valences by a dilute acid strip. This process has been widely studied and is relatively mature. The DIAMEX process accomplishes the same separations with a diamide extractant. TRU elements are less strongly extracted at moderate acidities, therefore nitric acid or nitrate salt addition would be required if DIAMEX were used in tandem with UREX. The tri-alkyl phosphine oxides (TRPO) process uses a mixture of TRPO to extract the TRU and lanthanide elements at low acid concentrations. Selective co-stripping of the trivalent actinides and lanthanides requires a high acid concentration, a drawback for this process because low acidities are required in subsequent processes to separate this trivalent ions product stream into lanthanides and actinides.

An alternative approach to simultaneous extraction of the TRU elements is selective extraction of tetravalent or hexavalent Pu and Np by TBP, followed by extraction of the trivalent actinides (and lanthanides) by TRUEX, DIAMEX, or TRPO. With choice of appropriate oxidation, reduction, or complexing agents, a number of processing options are possible for TRU recovery by TBP extraction. While such a multi-process approach may be more complicated than a simultaneous extraction approach, it is thought to be more certain of success. The TBP extraction options for recovery of Pu and/or Np might potentially be implemented in an expanded UREX process flowsheet, simplifying the overall system.

Extraction chromatography and ion exchange are judged to be of limited utility. The former is not well suited to large-scale processes, while recovery of Pu and/or Np by anion exchange requires high nitric acid concentrations that may complicate downstream processing.

The separation of the trivalent actinides Am and curium (Cm) from the lanthanides is difficult because of the similarity of chemical properties. Several methods make use of the greater stability of aqueous-soluble complexes of trivalent actinides with organic complexants such as diethylenetriaminepentaacetate (DTPA). In the "direct" TALSPEAK (trivalent actinide lanthanide separations by phosphorus-reagent extraction from aqueous complexes) process, the lanthanides are selectively extracted away from the actinides, which remain in the aqueous phase as complexes. In the "reverse" TALSPEAK process, both the lanthanides and actinides are extracted, and the actinides are selectively stripped away from the lanthanides into the complexant solution. Several extraction systems under development utilize the "reverse" TALSPEAK approach; among these are the so-called DIDPA, SETFICS, and PALADIN processes (see Section 3 for descriptions). Selective complexation has also been employed in cation exchange chromatography (CEC). Similar to reverse TALSPEAK, co-adsorption is followed by selective elution with complexant solutions. The large volume of liquid waste generated limits the utility of the CEC process.

Newer processes being developed for the separation of trivalent actinides and lanthanides employ solvents that selectively extract the actinides away from the lanthanides, without using complexants to keep the lanthanides in the aqueous phase. Such processes are being called SANEX (selective actinides extraction) processes.

UREX is best suited for simultaneously achieving two objectives of the AAA program: >99.9% of the uranium in a stream suitable for disposal as LLW, and recovery of >95% of Tc in a stream that can be converted to transmutation targets. Many potential process combinations following UREX can meet the programmatic TRU element recovery and purification objectives. A processing system that will likely meet AAA program goals with minimal development employs TBP extraction to recover Pu, Np, and residual uranium from UREX raffinate, TRUEX to recover the trivalent actinides (lanthanides are also recovered), and a SANEX process to purify the trivalent actinides. Other approaches are more speculative but lead to simpler-appearing systems. A very simple process system could include recovery of Np and Pu by TBP extraction in an expanded UREX process with recovery and purification of trivalent actinides directly from the expanded UREX raffinate by a SANEX process.

It is felt that development work should center on defining optimal redox reagents for Pu and Np recovery in various processes, development of a SANEX-type process for separation of trivalent actinides from lanthanides, and continued development of process modeling tools.

1. OBJECTIVES

This report describes and evaluates strengths and weaknesses of various solvent extraction and/or ion-exchange processes for meeting multi-tier recovery and purification goals for potential aqueous-based processing in the Advanced Accelerator Applications program. Goals of such processing include:

- A separate U stream, containing >99.9% of the U, that has been sufficiently purified from other actinides and from fission products that it meets the requirements of Class C LLW.
- A separate Tc stream, containing >95% of the Tc, sufficiently pure that the contained impurities amount to no more than 1% by weight.
- <0.1% of all TRU elements remaining in the streams to be vitrified for disposal as HLW.
- Separate TRU element streams to be converted to transmutation targets. Various objectives are possible here, including:
 - Mixed Np, Pu, Am, and Cm,
 - Separate streams for each TRU element (for the present study, however, we are assuming that Am and Cm will not be separated), and
 - Mixed (Np + Pu) and (Am + Cm) streams.

In order for the separate U stream to meet Class C LLW requirements, the U must be decontaminated from both fission products and transuranic elements. Decontamination factors required to achieve this (based on 40-year cooling of the spent fuel) are <100 for Sr-90, Tc-99, and Cs-137; ~3 for Np-237; ~3 x 10³ for Pu-239; and ~3 x 10⁴ for Am-241.

In a typical spent power reactor fuel, the U/Tc weight ratio is ~1,300. Thus, only ~0.001% of the U can be present in the Tc stream in order for the assumed Tc purity objective to be attained; this appears to be an aggressive assumption.

The most difficult separation of TRU elements from fission products will be that of Am and Cm from the lanthanides. The weight ratio of lanthanide element fission products to Am in typical spent power reactor fuel is ~15. Thus, only about 0.07% of the lanthanides can be present in the Am stream in order for the weight of these elements to amount to 10% of the weight of Am.

The objective of <0.1% of each TRU element being in the dissolved spent fuel stream may be difficult to achieve in the case of Np, because of the complex chemistry of this element and because its most stable oxidation state in nitric acid solution, Np(V), is essentially inextractable. So, valence adjustment and control are necessary for Np to be recovered (the chemistry of Pu is also complex, but its most stable oxidation state under normal process conditions is Pu(IV), which is extractable). Perhaps the “<0.1% to HLW” objective should be revised upward for Np.

Another goal of processing reactor fuels under the AAA program is the recovery of >99% of the iodine (I), to be converted to transmutation targets. This goal is not addressed in this report because it will be accomplished by volatilization and trapping of iodine during dissolution rather than by solvent extraction or ion exchange processes.

2. COMPARISON OF PROCESSES

In this section, we will briefly describe methods to accomplish the program objectives by solvent extraction and/or ion exchange processing. Strengths and weaknesses of the various processes will also be discussed. The sections are arranged by recovery of the key components U, Tc, and transuranic (TRU) elements. This is by no means an exhaustive list of processes, but it should touch upon the most developed or most promising of the options available [Nuclear Energy Agency 1997].

A brief section is also included on the recovery of Cs and Sr, the major heat-producing fission products.

2.1 RECOVERY OF URANIUM

2.1.1 PUREX Process

The PUREX process is the “industry standard” for the recovery of U. It was developed to separate and purify U and Pu from dissolved spent fuel, and has been used very successfully for nearly 50 years. The fuel is dissolved in nitric acid; U and Pu are separated from fission products and other actinides by solvent extraction. The solvent used is typically 30% TBP in a hydrocarbon diluent, such as dodecane [Schulz, Burger, and Navratil 1990].

In the dissolved fuel solution, uranium and plutonium are present primarily as U(VI) and Pu(IV). In most applications of the PUREX process, the first cycle has involved co-extraction of Pu and U followed by selective stripping of the Pu by reducing it to the trivalent oxidation state, and then stripping the U into dilute acid. Subsequent extraction/strip cycles are used to achieve the needed degrees of purification of the separate products; in some cases one subsequent cycle is sufficient (a two-cycle process), and in other cases two subsequent cycles are employed.

In the acidic dissolved spent fuel feed, neptunium is present as a mixture of Np(VI) and Np(V). Np(VI) is extracted by TBP along with the U and Pu in the initial contact. Inextractable Np(V) remains in the aqueous raffinate. The relative amounts of Np(VI) and Np(V) depend on a variety of factors. One of the most important is the concentration of nitrous acid; another is the nitric acid concentration. By careful control at low nitrous acid concentrations, the Hanford PUREX plant was able to recover most of the Np by extraction as Np(VI). Conversely, the Savannah River PUREX plant employed relatively high nitrous acid concentrations to shift the equilibrium toward Np(V) and drive the Np into the raffinate. Other factors that affect Np extraction in the PUREX process include the temperature during the extraction and the loading of the solvent with U [Schulz, Burger, and Navratil 1990].

Most fission products, and the trivalent actinides Am and Cm, are only slightly extractable by TBP and remain in the raffinate (waste) stream of the first cycle. However, fission product Tc is appreciably extracted at moderately low acidities, especially in the presence of U, Pu, and fission product zirconium (Zr).

Little or no attention was given to control of Tc in early PUREX process flowsheets. While Tc was primarily in the raffinate, a significant fraction was typically extracted along with the U and Pu.

2.1.2 UREX Process

In an effort to achieve the U and Tc recovery goals of the AAA program in a simple manner, a process termed the UREX process has been developed by modification of the PUREX process. One major modification introduced in the UREX process is the use of AHA in the extraction cycle scrub solution to complex Pu(IV) and reduce Np(VI) to Np(V) in order to minimize the extraction of these two elements along with the U. The UREX flowsheet also employs relatively low concentrations of nitric acid in the feed and scrub solutions, allowing efficient extraction of Tc. AHA also weakly complexes some important fission products (molybdenum [Mo], Zr) and can limit their extraction (and contamination of the U and Tc products).

The co-extracted U and Tc are separated by stripping the Tc into moderately concentrated nitric acid; the stripped Tc is further purified from U using a TBP scrub stream. The U is then stripped into dilute nitric acid.

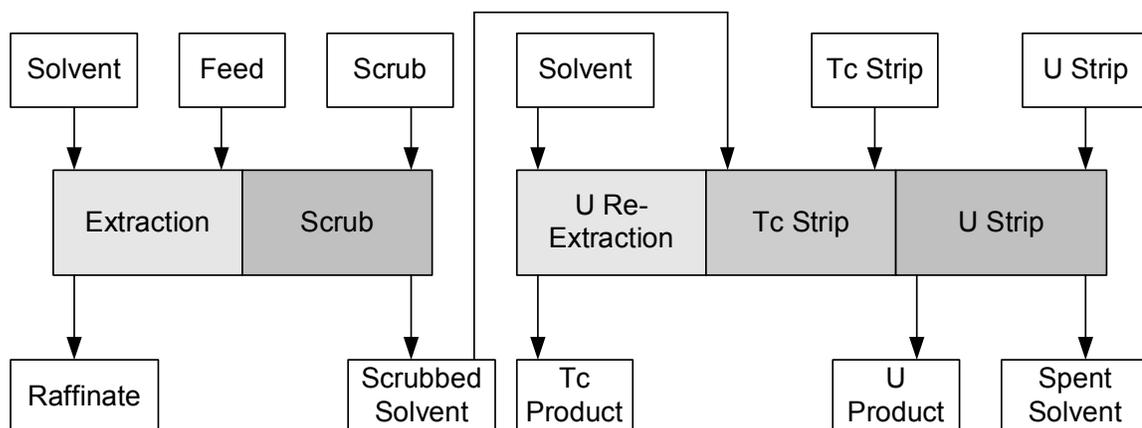


Fig. 1. UREX Process Flowsheet

2.2 RECOVERY OF TECHNETIUM

After dissolution of the spent fuel, a portion of the Tc remains in an undissolved residue that is primarily an alloy of noble metal fission products. The fraction of Tc that remains in this residue is thought to be <5%; thus, the program objective of recovering >95% of the Tc in a separate product stream can likely be accomplished by efficient removal of Tc from the dissolved fuel solution.

Several approaches are feasible for the recovery of Tc from the dissolved fuel solution, or from a HLW raffinate solution. Individual processes could be employed for its separate removal from either of these solutions. However, such processes are not addressed here because of the demonstrated effectiveness, and the simplicity, of the UREX process (described in Section 2.1.2).

In the UREX process, Tc is coextracted with uranium and the two elements are then separated by selective stripping. Tc is first stripped into moderately concentrated nitric acid and U is then stripped into dilute acid. In the UREX tests to date (run in a 2-cm centrifugal contactor with a simulated dissolved spent fuel feed), 97% of the Tc originally present in the feed stream was recovered in the Tc strip stream. The remaining 3% was present in the raffinate from the initial extraction. Modeling results indicated that 99.7% of the Tc could have been recovered in the Tc strip with improved control of process temperatures.

2.3 RECOVERY OF TRANSURANIC ELEMENTS

Several solvent extraction processes have been developed to separate and recover transuranics from PUREX raffinates and other TRU-element-bearing waste streams. Some of these processes are capable of recovering only the TRU elements that exist in tetravalent or hexavalent oxidation states (e.g., Pu and Np), while others can recover the trivalent elements (e.g., Am and Cm) as well [Horwitz and Schulz 1999; Mathur, Stark, and Nash 2001; Schulz and Horwitz 1988].

We will first discuss three processes that are capable of co-extracting all TRU elements at once (TRUEX, DIAMEX, and TRPO), and then will discuss some separation possibilities based on TBP extraction. Finally, we will briefly discuss the use of extraction chromatography and ion exchange for TRU element recovery.

2.3.1 TRUEX Process

The principal extractant of the TRUEX process is CMPO, which is added to TBP in a paraffinic hydrocarbon, typically dodecane (in cases where high concentrations of extractable ions are present, branched-chain hydrocarbon diluents are more effective in preventing third-phase formation). CMPO extracts trivalent, tetravalent, and hexavalent actinides, with good selectivity over most fission products.

Schulz and Horwitz [1988] provide an overview of TRUEX and information on extraction of other species. Selective partitioning of trivalent actinides and lanthanides from tetra- and hexavalent actinides can be achieved by selective stripping of the co-extracted elements. Dilute HNO_3 will strip An(III) and Ln(III) while leaving tetra- and hexavalent species in the organic phase. Stripping of tetra- and hexavalent actinides requires the use of aqueous-phase complexants; alternatively, reductants can be used to reduce Pu(IV) to Pu(III), whose extractability is comparable to that of Am(III), and to reduce Np(VI) to inextractable Np(V). High HNO_3 concentrations enhance extraction of Zr and iron (Fe), while moderate HNO_3 concentrations favor extraction of Tc and palladium (Pd). Co-extraction of Fe and Zr can be suppressed by addition of oxalic acid to the dissolved spent fuel feed.

Problem areas in the TRUEX process include (1) the potential for third-phase formation (more likely with a UREX than with a PUREX raffinate feed because of a much higher Pu concentration), (2) difficult stripping of the tetravalent and hexavalent actinides, and (3) the need for good solvent clean-up processes.

A similar “TRUEX” process developed in Russia uses a different CMPO and achieves similar performance. This CMPO is used along with other extractants, and a different diluent, in the so-called UNEX process that extracts Cs and Sr (and the lanthanides) along with the actinides.

2.3.2 DIAMEX Process

The DIAMEX process is under development in France as an alternative to TRUEX [Horwitz and Schulz 1999; Mathur, Stark, and Nash 2001]. The process utilizes a diamide extractant, typically DMBTDMA dissolved in TPH, to extract actinides from nitric acid solutions. An often-cited advantage of this process is that the extractant contains only elements that, at the end of the extractant’s use, can be converted into gases—thus minimizing secondary waste volumes. Some believe that this is a minor advantage when such wastes are considered in relationship to all the other secondary wastes—especially if the process is to be employed in conjunction with PUREX or UREX, which employ an extractant (TBP) that contains phosphorus.

TRU elements are extracted less strongly at moderate nitric acid concentrations by the DIAMEX solvent than they are by the TRUEX solvent. Typically, efficient extraction of trivalent TRU by DIAMEX solvent requires that the nitrate concentration be ~3 M or higher; thus, acid (or salt) addition would be necessary for efficient extraction from UREX process raffinate (or from raffinates in many PUREX process flowsheets). Of course, the less-strong extractions by the DIAMEX solvent also have a positive side—they allow the extracted materials to be stripped more easily than in TRUEX.

The DIAMEX process also suffers from the fact that fission product Pd is highly extracted, and must be dealt with in subsequent process steps. This is also true to lesser degrees with fission product ruthenium (Ru) and corrosion product Fe.

2.3.3 TRPO Process

The TRPO process [Horwitz and Schulz 1999; Mathur, Stark, and Nash 2001] uses a mixture of tri-alkyl phosphine oxides for extraction of actinides from dissolved spent fuel solutions. The process was developed in China. U, Pu, Np, and trivalent actinides are all recovered by extraction at low (0.7-1 M) nitric acid concentration. Np can be extracted upon electrolytic reduction to Np(IV). The actinides are separated into groups by selective stripping into moderately concentrated nitric acid for trivalent species, oxalic acid for Pu and Np, and sodium carbonate for U.

The fact that the trivalent species are stripped into moderately concentrated nitric acid is a potential drawback for incorporation of the TRPO process into a system that includes separation of the trivalent actinides and lanthanides, because processes for such a separation usually involve low acid concentrations.

2.3.4 TBP Extraction

While all the TRU elements (and residual U) can be co-extracted from UREX (or PUREX) raffinate by the three processes discussed above, such an approach may not provide the best method of achieving the AAA program objectives. For example, the separation of the TRU elements into the desired streams by selective stripping of the co-extractant used in one of these processes might be more difficult to achieve (using unobjectionable stripping agents) than it would be by using selective extraction processes. An obvious extractant to use in such selective extraction processes is TBP [Schulz, Burger, and Navratil 1990], the one used in the UREX and in conventional PUREX processes. In normal process conditions, TBP will extract tetra- and hexavalent TRU elements (and U), but not the tri-valent TRU elements.

One potential advantage of employing a TBP extraction process to recover some of the TRU elements prior to the use of a process that extracts the trivalent TRUs is that TBP extraction will efficiently remove the residual U that is present in UREX or PUREX raffinate. The presence of U can be problematic in a trivalent-TRU recovery process, for example it may cause/contribute to formation of a third phase and it may complicate selective stripping of the TRUs.

TBP extraction can be used, in conjunction with valence-adjusting chemicals and/or complexing agents, to provide a number of possible options for recovery of TRU elements (and U) from UREX (or PUREX) raffinate. Among these options are:

- Recovery of Pu (and U) alone. This can be accomplished by adjusting the oxidation states to Pu(IV) and Np(V); Pu(IV) will extract but Np(V) will not. Pu can be stripped into dilute acid (along with U), or by reduction to Pu(III).
- Recovery of Np (and U) alone. This can be accomplished by adjusting the oxidation states to Pu(III) and Np(IV); Np(IV) will extract but Pu(III) will not. Np can be stripped into dilute acid (along with U) or by oxidation to Np(V).
- Combined recovery of Pu and Np (and U). This can be done by:
 - Oxidizing both Pu and Np to the extractable (VI) oxidation states, followed by stripping into dilute acid (along with the U), or using reductants to strip the Pu and Np away from the U.
 - Maintaining both Pu and Np in the (IV) oxidation state in the feed solution long enough that both can be sufficiently recovered.
 - Maintaining Pu as (IV) and Np(VI). Both are extractable, and both can be stripped by reduction, to the (III) and (V) state, respectively.

These approaches have varying probabilities of success in a practical application.

It is tempting to speculate that at least one of these TBP-extraction options could be implemented by addition to the existing UREX process flowsheet, to give an “expanded UREX process”. Integration of the TBP extraction processes in one flowsheet could simplify the overall processing system.

An important consideration in the use of valence-adjusting chemicals and/or complexing agents must be the extent to which the added materials will impact the volume of vitrified HLW. Evaluation of the quantitative effectiveness of such chemicals and their impact on the volume of vitrified HLW is beyond the scope of this report.

Application of TBP-extraction processes to UREX raffinate would probably require the prior destruction of the AHA complexing/reducing agent that is a key component of the UREX process. Luckily, such destruction should be relatively easy to accomplish; the half-life for AHA destruction in 0.9 M nitric acid at 70 °C has been reported to be 8 minutes. Hopefully, such conditions are moderate enough that precipitation of fission product compounds, which has been observed in boiling PUREX HLW solutions, will not occur to any significant extent.

An interesting question related to AHA destruction is what the oxidation states of Np and Pu will be following the destruction step. An optimistic suggestion is that both might be in the tetravalent state for a significant period of time, resulting from the reduction of the Np(V) in the

UREX raffinate to Np(IV) during the AHA destruction step, followed by sufficiently slow oxidation back to Np(V). If that were true, the option of maintaining both Pu and Np in the (IV) oxidation state in the feed solution long enough that both can be sufficiently recovered could be relatively easy to implement. If the AHA destruction step itself does not give this desirable result, perhaps other chemicals (e.g., hydroxyl ammonium nitrate) could be added to that step to assist in achieving the desired result.

2.3.5 Extraction Chromatography

The processes described in the preceding subsections are liquid-liquid solvent extraction processes, in which the ions of interest are removed from an aqueous phase by extraction into an organic-solvent liquid phase. Similar removals have been accomplished with the extractants being “fixed” on a solid material; such removals are referred to as extraction chromatography [FitzPatrick 1996].

The chemistry of extraction chromatographic processes is essentially the same as in solvent extraction processes. Distribution coefficients are typically lower than for comparable solvent extraction processes, but the equipment required is simpler. The trivalent actinides can be separated from the tetra and hexavalent actinides by sequential elution with appropriate solutions. Because comparable separations are achievable at much higher throughputs in solvent extraction, extraction chromatography is not as suitable as solvent extraction for large-scale processing.

2.3.6 Ion Exchange

Anion exchange processes can recover Pu and Np, with good separation from most other elements. The two key steps to such recoveries from nitric acid solutions are (1) a high (~7 M) nitric acid concentration, and (2) stabilization of the tetravalent oxidation states. Separate recovery of Np from PUREX raffinate has been accomplished for years at the Savannah River Site, by reducing Np to Np(IV) and Pu to Pu(III); sorbed Np is then eluted with dilute acid. Combined recovery of Pu and Np can be accomplished by stabilizing both elements in the tetravalent oxidation states; it is not easy to do this. One commonly used method that is reasonably successful involves reduction to Pu(III) and Np(IV), followed by addition of nitrite, which oxidizes Pu(III) to Pu(IV) rapidly but Np(IV) to Np(V) slowly. The sorbed Pu and Np can either be eluted together (with dilute acid) or separately (using a reductant for Pu and dilute acid for Np).

The requirement of high nitric acid concentration in the anion exchange process feed can be a major drawback to the use of such processes, especially if they are to be used in a series of processes to recover many elements. For example, a subsequent process to recover Am from the anion exchange raffinate would almost certainly involve a low-acid feed, necessitating dilution or neutralization of the anion exchange raffinate (neither of which is desirable).

3. SEPARATION OF AMERICIUM AND CURIUM FROM LANTHANIDES

In this study, we are assuming that transmutation of Am and Cm will require that these elements first be largely separated from fission products. By far the most difficult separation necessary to achieve this goal is the separation from the lanthanide element fission products; this difficulty arises because of the very similar chemical properties of the trivalent actinides and lanthanides. It may also be desirable to separate the Am and Cm from each other, but we are currently assuming that this separation will not be needed.

Processes that have been studied for the separation of the trivalent actinides from the lanthanides are discussed in this section. They are considered for application to a feed prepared from a mixed trivalent actinide/lanthanide “product” from a TRUEX or DIAMEX process that recovered these groups together from a HLW stream. While future developments may allow some of the processes discussed here to replace TRUEX or DIAMEX, as well as to separate the trivalent actinides from the lanthanides, adoption of such an approach at this time is felt to be overly optimistic.

Early methods for separation of the trivalent actinides from the lanthanides involved ion exchange from chloride solution, with the actinides being less strongly retained because of their more-stable chloride complexes. Similar methods developed subsequently involved anion exchange, other soft-donor complexants such as thiocyanate, and using liquid cation and anion exchangers like sulphonic acids and amines in solvent extraction systems [Nash 2001]. However, none of these methods has been deemed suitable for large-scale application.

Several methods that have been developed more recently for separating the trivalent actinides from the lanthanides make use of the fact that these actinides form more stable complexes with many aqueous-soluble organic complexants than do the lanthanides. For example, both groups can be extracted (or sorbed) in the absence of such complexants, and then separated by selective stripping (or elution) using a complexing agent. The complexant most widely used for this application has been DTPA.

The most-studied solvent extraction process using this approach is one using HDEHP as the extractant; it is termed the TALSPEAK process. In the so-called “direct” TALSPEAK process, DTPA is added to the (low acid) feed, the lanthanides are selectively extracted away from the actinides, and are then stripped into ~5 M HNO₃. The extraction works best at pH ~3, and in the presence of a carboxylic acid such as lactic, glycolic, or citric acid. In the so-called “reverse” TALSPEAK process, extraction of both fractions is accomplished at low acidity in the absence of complexants; the actinides are then stripped away from the lanthanides with DTPA (plus carboxylic acid), and the lanthanides are then stripped into ~5M HNO₃.

A significant drawback to the TALSPEAK approaches is the need for a low acidity in the extraction step. Adjustment to the desired condition can involve undesired dilution and/or formation of salts in a neutralization process. Other potential drawbacks cited by Madic in a recent review [2001] include limited solvent loading for metal ions and difficult solvent cleanup.

The Madic review cited several solvent extraction systems under development that employ selective stripping of the trivalent actinides away from the lanthanides, similarly to the reverse TALSPEAK approach (using DTPA complexing). These approaches are aimed at stripping the actinides from the solvent after it has co-extracted the actinides and lanthanides. These systems are:

- DIDPA process. This process is based on the use of di-isodecylphosphoric acid (DIDPA) as the extractant. As in the TALSPEAK process, extraction is done at low acidity and lanthanide stripping is done at high acidity. This process has been successfully tested in a hot cell (presumably with genuine waste), and possible drawbacks are given as being: (1) required feed acid adjustment, (2) solvent degradation and its delicate cleanup, and (3) limited solvent loading with metal ions [Madic 2001].
- SETFICS. This process is a modification of the TRUEX process based on the use of a different CMPO extractant (di-isobutyl-phenyl-octylcarbamoymethylphosphine oxide). Madic [2001] reported that it had not yet been tested with genuine waste solution, and that its possible drawbacks include: (1) limited stripping efficiency and (2) the management of effluents containing salts and DTPA.
- PALADIN. This process is based on the use of a mixture of extractants—a malonamide (as in the DIAMEX process) and HDEHP (as in the TALSPEAK process). The malonamide functions as the initial actinide and lanthanide co-extractant (from 3-5 M nitric acid) and the HDEHP functions as the extractant in the pH range, where the actinides are selectively stripped with DTPA. This process has been recently successfully tested, and potential process drawbacks are given as being: (1) use of two solvents, (2) need for pH adjustment, (3) co-extraction of numerous ions, and (4) solvent cleanup not yet defined [Madic 2001].

Madic [2001] also listed several processes that are under development to selectively extract the trivalent actinides away from the lanthanides (as opposed to selective stripping after co-extraction in the processes described in the preceding paragraph). They have been termed SANEX (for selective actinides extraction) processes; they offer significant advantages in that they do not involve the use of aqueous-phase complexants, and some of them can operate with ~1 M nitric acid in the feed. Such processes have been developed using both S-containing and N-containing extractants.

The SANEX processes employing acidic S-containing extractants are:

- CYANEX 301 process. The extractant for this process is a dialkyldithiodiphosphinic acid (R₂PSSH). It has been tested with genuine An(III)/Ln(III) mixtures and has shown a high separation efficiency [Madic 2001]. The need to adjust the feed to pH 3-5 is given as a drawback. Solvent cleanup is also given as a weak point.
- ALINA process. To cope with the feed pH problem in the CYANEX 301 process, the ALINA process uses a synergistic mixture of bis(chlorophenyl)dithiophosphinic acid and trioctylphosphine oxide to extract the trivalent actinides away from the lanthanides

[Madic 2001]. This mixture allows feed nitric acid concentrations as high as 1.5 M, which is a large positive factor, even though this solvent gives lower separation factors than those observed with CYANEX 301. Stripping of the extracted actinides is accomplished with dilute nitric acid. This process was successfully tested with genuine waste. Possible drawbacks were given as: (1) solvent cleanup process not yet defined and (2) the generation of P- and S-bearing wastes (from the degraded extractants) to be managed. This process is referred to as the SANEX-IV process in the final report of the NEWPART contract of the European Union [European Union 2000]. The authors of that report consider the successful results to represent a breakthrough in the field of trivalent actinide/lanthanide group separations. While this may indeed be true, several drawbacks remain to be addressed. In addition to those mentioned by Madic [2001], there is the high extraction of Pd, and the need to remove it from the solvent before re-use.

SANEX processes employing neutral N-bearing extractants are:

- BTPs. Bis-triazinyl-1,2,4 pyridines (BTPs) have been found to have astonishing properties for trivalent actinide/lanthanide separation [Madic 2001]. Highly efficient separations were achieved in hot tests with n-propyl-BTP. An important feature of this extractant is that it can be used at feed nitric acid concentrations at least as high as 1 M; the actinides are subsequently stripped into dilute nitric acid (~0.05 M), which is another nice feature. Madic [2001] reported that an instability of the extractant was observed, and that efforts were underway to modify the formulation to address this drawback. This process is referred to as the SANEX-III process in a comprehensive report from the European Union [2000]. The successful results are considered by the authors of that report to represent a breakthrough in the difficult field of minor actinide partitioning. However, they note that Pd can present problems because of its high extractability and the resultant need to remove it from the solvent before re-use. High extraction was also observed for Fe, which could be present as a result of corrosion of equipment.
- TMAHDPTZ + octanoic acid. A synergistic mixture of the terdentate N-ligand, 2-(3,5,5-trimethylhexanoylamino)-4,6-di-pyridin-2-yl)-1,3,5-triazine (TMAHDPTZ) and octanoic acid has been tested on genuine effluent with good efficiency [Madic 2001]. Drawbacks are given as being: (1) required pH adjustment of the feed and (2) not-yet-defined management of secondary wastes.

Selective complexation by complexants such as DTPA has also been used extensively in ion exchange processes to accomplish separation of the trivalent actinides from the lanthanides (and also separation of the individual elements of the groups). In such processes, which are often called cation exchange chromatography, the trivalent actinides and lanthanides are first sorbed on a cation exchange resin, and are then separated by sequential elution using complexing agents (DTPA or other) in the pH acidity range. So-called “barrier ions” such as Ni are often used to sharpen the separations. Very good separations have been achieved in such processes, not only between the trivalent actinide and lanthanide groups, but also between the individual members of these groups. This approach suffers from operational difficulties and the generation of large volumes of salt-containing liquid waste.

4. RECOVERY OF CESIUM AND STRONTIUM

Recovery of cesium (Cs) and strontium (Sr) from HLW solution is not necessary to meet the current objectives of the AAA program. However, it could become an objective in the future, from the standpoint of decreasing the heat-load on the HLW repository. Several processes have been investigated to accomplish the removal of these elements from acidic waste solutions. Some of these processes involve sorption on inorganic ion-exchange materials, or solvent extraction with crown-ether or calix-crown extractants [Madic 2001]. Another approach is thought to be worthy of special mention here.

A solvent extraction process that allows extraction of Cs and Sr along with actinides (plus lanthanides) from acidic waste solutions has been developed [Law et al. 2001; Romanovskiy et al. 2001]; this process has been termed the UNEX process (for universal solvent extraction). The UNEX process solvent consists of chlorinated cobalt dicarbollide for the extraction of Cs, polyethylene glycol for the extraction of Sr, and diphenyl-N,N-dibutylcarbamoyl phosphine oxide for the extraction of actinides; the preferred diluent is phenyltrifluoromethyl sulfone.

Stripping of the elements extracted by the UNEX solvent can be done sequentially (in groups) or all in one step. Sequential stripping can involve nitric acid solution containing guanidine for Cs and Sr, complexant (such as DTPA) solution in the presence of buffer additives for TRU elements (and lanthanides), and carbonate solution for U [Romanovskiy et al. 2001]. One-step stripping can be done with a guanidine carbonate plus DTPA solution [Law et al. 2001].

Testing of the UNEX process has progressed from work with simulated wastes, through small-scale tests on actual Idaho National Engineering and Environmental Laboratory tank waste and dissolved calcine, to a recent 80-hour test on actual Russian high-activity waste. Results are very encouraging.

5. EVALUATION OF PROCESSING SYSTEMS

Design of an overall process system needs to consider optimization of the interactions between the individual recovery and purification processes, aimed at simplification of the overall system. For a system involving preparation of transmutation targets and waste-disposal forms, compatibility between the recovery and purification processes and the target- and wasteform-preparation processes should also be considered, but that is not done in this preliminary evaluation.

The UREX process appears to be very well suited, and simple, for efficiently achieving the two program objectives of (1) recovery of >99.9% of the U in a stream that can be disposed of as low-level waste and (2) recovery of >95% of the Tc in a stream that can be converted to transmutation targets. Accordingly, consideration of subsequent processes will be centered here on processing the raffinate waste stream from a UREX process.

There are many potential process combinations to meet the TRU element (Np, Pu, Am, and Cm) recovery and purification objectives of the AAA program. Amenability of incorporating one process into a suitable overall system is an important criterion in choosing a proper combination of processes. One thing that should be remembered in this regard is that the UREX raffinate could contain a significant concentration of U (even though only a small fraction of the total U), and the presence of this U can impact the TRU element recovery flowsheets.

Some of the TRU recovery processes involve co-extraction of all of these elements (and U) in one step; separation into individual fractions can be accomplished by selective stripping. Notable examples of such processes are TRUEX, DIAMEX, and TRPO. TRUEX is considered here to be the most suitable for inclusion in the AAA program system. In addition to its more-advanced stage of development, TRUEX has a major advantage over DIAMEX in that it can efficiently extract the TRUs at lower nitrate concentrations than DIAMEX (the UREX raffinate has a low nitric acid concentration). A major advantage of TRUEX over TRPO arises from the fact that the AAA program system requires that the trivalent actinides (Am and Cm) be separated from the lanthanides that co-extract in all three of these TRU recovery processes; trivalent actinide/lanthanide separation processes generally require low acidities, and trivalent actinides (and lanthanides) can be stripped into dilute acid in TRUEX (TRPO strips them into relatively concentrated acid).

The use of TRUEX (or DIAMEX or TRPO) to simultaneously extract all the TRUs and then separate them into desired fractions by selective stripping is certainly appealing, but it may not be easy to achieve in a practical process. The very fact that allows co-extraction of all the TRUs together (a strong extractant) makes stripping of the Pu and Np (and U) difficult. Complexants are often used to efficiently strip these elements, but such complexants often contain materials that can complicate subsequent processing and/or waste disposal operations.

An approach that avoids the use of complexants, and that involves less complicated operation of solvent extraction equipment (though perhaps more equipment), is to remove the Pu and/or Np (and U) from the UREX raffinate in one process, and then remove the Am and Cm (and possibly either Pu or Np) in another process. An obvious choice for such Pu and/or Np (and U) removal process is TBP extraction.

TBP is used in the UREX process to extract U (and Tc) away from TRUs (and fission products); the key feature of this process is the addition of AHA to complex and/or reduce the Pu and Np so that they do not co-extract. Thus, the use of TBP-extraction to recover Pu and/or Np would require prior destruction of the AHA. Fortunately, that can be accomplished quite readily by heating the UREX raffinate to 70 °C or so.

A processing system that is thought to offer a high probability of success in meeting the AAA program objectives with only a relatively limited amount of development work includes the following processes:

- The UREX process as it currently stands, to give sufficient recovery and purification of the U and Tc, a U stream to be solidified and disposed of as LLW, and a Tc stream to be converted into transmutation targets.
- TBP extraction processing to recover Pu and Np (and the residual U) from the UREX raffinate, following destruction of the AHA that prevented extraction of these elements in the UREX process. The recovery of Pu and Np might involve (1) simultaneous co-extraction (which requires valence adjustment and control) and stripping, (2) simultaneous co-extraction followed by separation by selective stripping, or (3) sequential extraction and stripping of the two elements based on valence adjustments. The stripped Pu and Np would be converted into transmutation targets, and any residual U would be disposed of as LLW (or recycled to the UREX process).
- The TRUEX process to recover the trivalent actinides (Am and Cm) from the TBP-process raffinate. The fission product lanthanides are recovered along with the actinides. The actinides and lanthanides are co-stripped with dilute acid to provide a feed to an additional separation process.
- The SANEX-III or SANEX-IV process to recover and purify the trivalent actinides from the actinide/lanthanide product stream of the TRUEX process. In these SANEX processes, which are similar but use different extractants, the trivalent actinides are extracted from the lanthanides at ~1 M nitric acid, and are then stripped into more dilute acid. These SANEX processes are much less developed than the UREX, TBP extraction, or TRUEX processes, but the early development results are very promising. The apparent advantages of these processes over earlier, better-developed (but not very appealing) trivalent actinide/lanthanide separations processes are thought to be sufficiently large that their development should be emphasized. The SANEX-III process appears to have more appeal than the SANEX-IV process at this time.

Another approach would involve more-simple TBP extraction processing by leaving either Pu or Np in the raffinate, to be recovered in the TRUEX process. In such an approach, it would probably be preferable to have Np be the element sent to TRUEX, because (1) its much lower concentration would be less likely to contribute to third phase formation, and (2) it is likely easier to strip (e.g., by reduction to Np(V)) than Pu would be.

A more simple, but also more speculative, system for meeting the separations objectives of the AAA program could include:

- An expanded UREX process that includes additional cycles to recover Pu and Np by TBP extraction, in addition to the U and Tc that are recovered in the current UREX process.
- A SANEX-like process that recovers and purifies the trivalent actinides directly from the raffinate of the expanded UREX process, instead of from a trivalent actinide/lanthanide “product” stream of the TRUEX process.

These considerations suggest that development work for the AAA program be centered in the areas of (1) definition of optimum redox reagents for Np and Pu recovery and purification in various processes, while minimizing impact on other processes or on the volume of vitrified HLW, (2) development of a SANEX-type process for separation of trivalent actinides from lanthanides, first with a "TRUEX product" as feed, and later as an alternative to TRUEX for the recovery of trivalent actinides from a process raffinate, and (3) continued development of process-modeling tools.

REFERENCES

- European Union. 2000. Partitioning Techniques for Minor Actinides. Report EUR 19149 EN.
- FitzPatrick, J.R. 1996. Adsorption and Ion Exchange Processes. Pp. 77-90 in *Separation Techniques in Nuclear Waste Management*, T.E. Carleson, N.A. Chipman, and C.M. Wai, eds. CRC Press, Boca Raton, Florida.
- Horwitz, E.P., and W.W. Schulz. 1999. "Solvent Extraction in the Treatment of Acidic High-Level Liquid Waste: Where Do We Stand?" pp. 20-50 in *Metal Ion Separation and Preconcentration, Progress and Opportunities*, A.H. Bond, M.L. Dietz, and R.D. Rogers, eds. ACS Symposium Series No. 716.
- Law, J.D., et al. 2001. The Universal Solvent Extraction (UREX) Process II: Flowsheet Development and Demonstration of the UNEX Process for the Separation of Cesium, Strontium, and Actinides from Actual Radioactive Waste. *Solvent Extraction and Ion Exchange* 19(1):23-26.
- Madic, C. 2001. Overview of the Hydrometallurgical and Pyro-Metallurgical Processes Studied Worldwide for the Partitioning of High Active Nuclear Wastes. Transactions of the 6th International Exchange Meeting, "Actinides and Fission Product Partitioning and Transmutation", Madrid, Spain, December 11-13, 2000
- Mathur, J.N., M.S. Stark, and K.L. Nash. 2001. Actinide Partitioning—A Review. *Solvent Extraction and Ion Exchange* 19(3):357-390.
- Nash, K.L. 2001. A Comparison of New Reagents and Processes for Hydrometallurgical Processing of Actinides. Paper presented at Global 2001, September 9-13, 2001, Paris, France. American Nuclear Society.
- Nuclear Energy Agency. 1997. Actinide Separation Chemistry in Nuclear Waste Streams and Materials. NEA/NSC/DOC(97)19, NEA Nuclear Science Committee Report, Nuclear Energy Agency Organization for Economic Co-operation and Development.
- Romanovskiy, V.N., et al. 2001. The Universal Solvent Extraction (UNEX) Process I: Development of the UNEX Process Solvent for the Separation of Cesium, Strontium and the Actinides from Acidic Radioactive Waste. *Solvent Extraction and Ion Exchange* 19(1):1-21.
- Schulz, W.W., and E.P. Horwitz. 1988. The TRU EX Process in the Management of Liquid TRU Waste. *Separation Science and Technology* 23(13&13):1191-1210.
- Schulz, W.W., L.L. Burger, and J.D. Navratil, eds. 1990. *Science and Technology of Tributyl Phosphate, Vol. III*. CRC Press, Boca Raton, Florida, pp. 1-146.

ACRONYMS

AAA	(Department of Energy) Advanced Accelerator Applications Program
AHA	Aceto-hydroxamic acid
BTP	Bis-triazinyl-1,2,4 pyridines
CEC	Cation exchange chromatography
CMPO	Octylphenyl-N,N-di-isobutyl carbamoylphosphine oxide
DIAMEX	Diamide extraction
DIDPA	Di-isodecylphosphoric acid
DMDBTDMA	N,N'-dibutyl tetradecylmalonamide
DTPA	Diethylenetriaminepentaacetic acid
HDEHP	Di(2-ethylhexyl)phosphoric acid
HLW	High-level waste
LLW	Low-level waste
PUREX	Plutonium and uranium recovery by extraction
SANEX	Selective actinides extraction
TALSPEAK	Trivalent actinide lanthanide separations by phosphorus-reagent extraction from aqueous complexes
TBP	Tributyl phosphate
TPH	Total petroleum hydrocarbons
TRPO	Tri-alkyl phosphine oxides
TRUEX	Trans-uranium extraction
UREX	Uranium extraction

Distribution for ANL-02/29

Internal (Printed and Electronic Copies):

S B. Aase	K. V. Gourishankar	M. C. Regalbuto
D. P. Abraham	D. J. Graziano	M. K. Richmann
H. A. Arafat	J. J. Laidler	J. Sedlet
A. J. Bakel	R. A. Leonard	G. F. Vandegrift (15)
D. L. Bowers	W. E. Miller	M. A. Williamson
P. J. Finck	L. Nuñez	J. L. Willit
E. C. Gay	C. Pereira	

Internal (Printed Copy Only):

V. A. Davis
M. J. Steindler
S. K. Zussman (5)

Internal (Electronic Copy Only):

Y. I. Chang
M. R. Hale, TIS
D. Lewis

External (Printed and Electronic Copies):

E. D. Arthur, Los Alamos National Laboratory, Los Alamos, NM
D. Bennett, Los Alamos National Laboratory, Los Alamos, NM
J. C. Bresee, USDOE, Office of Civilian Radioactive Waste Management, Washington, DC
E. D. Collins, Oak Ridge National Laboratory, Oak Ridge, TN
F. J. Goldner, U. S. Department of Energy, Germantown, MD
N. Haberman, USDOE Washington, DC
T. Rudisill, Westinghouse Savannah River, Aiken, SC
N. Schroeder, Los Alamos National Laboratory, Los Alamos, NM
J. Swanson, Richland, WA
K. Thomas, Los Alamos National Laboratory, Los Alamos, NM
T. A. Todd, Idaho National Engineering and Environmental Laboratory, Idaho Falls, ID
M. Thompson, Westinghouse Savannah River Company, Aiken, SC
G. J. Van Tuyle, Los Alamos National Laboratory, Los Alamos, NM

External (Electronic Copy Only):

M. A. Buckley, Library-E

E. S. Sackett, Library-W

Chemical Technology Division Review Committee Members:

H. U. Anderson, University of Missouri-Rolla, Rolla, MO

R. A. Greenkorn, Purdue University, West Lafayette, IN

C. L. Hussey, University of Mississippi, University, MS

M. V. Koch, University of Washington, Seattle, WA

V. P. Roan, Jr., University of Florida, Gainesville, FL

J. R. Selman, Illinois Institute of Technology, Chicago, IL

J. S. Tulenko, University of Florida, Gainesville, FL