

Progress in Metal Ion Separation and Preconcentration

Solvent Extraction in the Treatment of Acidic High-Level Liquid Waste: Where Do We Stand?

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During the last 15 years, a number of solvent extraction/recovery processes have been developed for the removal of the transuranic elements, ^{90}Sr and ^{137}Cs from acidic high-level liquid waste. These processes are based on the use of a variety of both acidic and neutral extractants. This chapter will present an overview and analysis of the various extractants and flowsheets developed to treat acidic high-level liquid waste streams. The advantages and disadvantages of each extractant along with comparisons of the individual systems are discussed.

During the last few years, several books and symposia proceedings have been published that describe a variety of separation techniques applied to the treatment of radioactive waste for disposal (1-6). Most of these separation techniques have focused on acid-side extraction of the transuranium (TRU) elements from high-level liquid waste. High-level waste (HLW) is defined as liquid waste generated from separating uranium and plutonium from other undesired radioactive elements (7). The TRUs are generally considered to be the most hazardous constituents of the waste due to the fact that they are alpha-emitters with long half lives (5). The objective of this chapter is to present and update the development and testing of acid-side solvent extraction processes for the removal of TRUs from HLW. Although much less effort has been devoted to the acid-side extraction of ^{90}Sr and ^{137}Cs from HLW, significant progress has been made during the last five years in their extraction. Therefore, a brief review and comparison of solvent extraction processes for the removal of Sr and Cs from acidic HLW is also included.

As the title states, this chapter is limited to solvent extraction (SX) processes. Since the introduction of the REDOX process at the Hanford site in January 1952 and the PUREX process at the Savannah River Plant in Aiken, South Carolina in November 1954, SX has been the premier separations technique used in the nuclear fuel cycle. There are a number of features of SX that make it the separation technique of choice for plant-scale processing. Foremost among these features is that SX is a continuous, multistage process with a high rate of throughput. Of equal importance is the availability of a number of extractants with high selectivities and high loading capacities for actinides in the tetra- and hexavalent oxidation states. These extractants (in process solvent formulations) can be readily purified from most of the hydrolytic and radiolytic degradation products and then recycled to the extraction stages. Concurrent with the development of the PUREX process on a laboratory-scale, a variety of equipment was being developed for efficient multistage operation of the process on a plant-scale. Most SX processes involving nuclear materials are carried out behind heavy shielding by remote control.

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When interest began to develop in the mid-1970s on processing HLW for volume reduction purposes, many years of experience had been gained on the operation of the PUREX process, both in the USA and abroad. It is not surprising, therefore, that studies involved with the development of the processes for the removal of the TRUs, Sr and Cs from HLW focused on SX systems.

Two different classes of HLW have been the focus of attention, namely, those wastes referred to collectively as defense nuclear waste and those wastes generated during the reprocessing of spent nuclear fuel from commercial nuclear power plants. The latter are referred to hereinafter as commercial HLW. Defense HLWs have been generated during the operation of SX processes, such as PUREX and REDOX, and the operation of precipitation processes such as bismuth phosphate. All these processes focused on the recovery of uranium and plutonium for defense purposes. Except for waste arising from the bismuth phosphate process, practically all HLW arose from aqueous raffinates from SX processes. At the Hanford Site, the acidic raffinate was made alkaline forming a sludge and an alkaline supernate (7). (Acidic HLW generated at the Savannah River Site has been treated in a similar manner.) This practice has resulted in large volumes of alkaline waste which is stored in underground tanks. The sludge formed during the neutralization contains essentially all of the TRUs and ^{90}Sr together with a small, but significant, portion of the ^{137}Cs . At the Idaho National Engineering Laboratory, acidic raffinate was evaporated and calcined to a mixture of oxides which was then stored in stainless steel bins at the site (8). In other cases, the acidic raffinate and incidental wastes from PUREX were stored without treatment as an acidic nitrate solution in stainless steel tanks. In all cases the elements of interest are the same, namely, the TRUs, Np, Pu, Am (and Cm from commercial HLW) and fission products ^{90}Sr , ^{99}Tc and ^{137}Cs , although the relative amounts may vary significantly depending on the origin and treatment of the waste.

TRU Extraction

The major obstacle in the development of SX processes for the extraction of TRU elements from acidic HLW is the achievement of an efficient extraction of trivalent actinides. To convert high-level waste to Class C low-level waste one must reduce the alpha activity to less than 100 nanocuries per gram of the disposed waste form. Because the major alpha activity in HLW is due to the presence of significant concentrations of ^{241}Am , (and ^{244}Cm for commercial HLW), the key feature of all processes for the treatment of HLW is the removal of Am(III) or both Am(III) and Cm(III). Although the extraction of ^{237}Np and ^{239}Pu are also important, efficient SX systems for their extraction in the tetra- and hexavalent oxidation states from a wide range of nitric acid concentrations has been available and utilized for a number of years.

Two classes of compounds have been utilized in SX processes for the extraction of TRU elements from HLW solutions: (1) the acidic organophosphorus extractants; and (2) neutral extractants, primarily, but not exclusively, of the bifunctional type. Processes utilizing both classes of compounds will be described along with the advantages and disadvantages of each system.

Processes Based on Acidic Extractants. Some of the first processes to be developed used acidic organophosphorus extractants, most likely, because acidic extractants were commercially available at low cost and because of the extensive number of publications describing their fundamental chemical behavior. Three different acidic extractants have been utilized, namely bis(2-ethylhexyl) phosphoric acid (HDEHP) (9-13), diisodecyl phosphoric acid (DIDPA) (14-17) and bis(hexoxyethyl) phosphoric acid (HDHoEP) (18).

Swedish CTH Process. A Swedish team developed and hot tested a process utilizing HDEHP to treat commercial HLW (9-12). The process (called CTH for Chalmers Tekniska Högskola) begins with a HLW solution prepared by adjusting PUREX aqueous raffinate to 6 M HNO_3 and then treating with NO_x . A 1 M HDEHP solution in kerosene is used in the first SX

cycle to remove U, Np and Pu together with most of the Fe, Zr, Nb and Mo. The loaded organic phase is first washed with an HNO_3 -HF solution to remove Zr and Nb and then stripped with ammonium carbonate. A mixture of ammonia and manitol are added to the organic phase before stripping to avoid precipitation of iron. The strip solution is evaporated to recover the ammonium carbonate for recycle and then acidified to recover the U, Np and Pu. Test runs demonstrated that 99.99% of U, 98.9% of the Np and >99.99% of the Pu can be recovered in the first extraction cycle.

The second extraction cycle in the CTH process involves the use of 50% TBP in kerosene to reduce the acidity of the aqueous phase to prepare it for a second low-acid HDEHP cycle. In addition to extracting HNO_3 , TBP also extracts Pd, Ru and Tc leaving Am and Cm plus the light lanthanides in a 0.1 M HNO_3 aqueous raffinate. Nitric acid is recovered by scrubbing with water and then evaporated and distilled to produce ~9 M HNO_3 . The HNO_3 is then reused to prepare the feed for the first extraction cycle. The Tc, Ru and Pd can be recovered from the strip solution by anion exchange.

The third and final extraction cycle in the CTH process consists of the extraction of Am and Cm, together with the light lanthanides, from the raffinate of the second extraction cycle using a solution of 1 M HDEHP in kerosene. At this stage the trivalent actinides can be selectively stripped from the light lanthanides using a diethylenetriamine pentaacetic acid (DTPA)-lactic acid mixture, or the actinides together with the lanthanides can be stripped using 6 M HNO_3 . If the trivalent actinides are partitioned from the lanthanides, a final HDEHP extraction cycle is required to remove the trivalent actinides from the DTPA-lactic acid solution. Another feature of the flowsheet is that Sr and Cs in the raffinate from the third extraction cycle can be sorbed on inorganic ion exchangers such as titanates and zeolites, respectively, for disposal.

The entire CTH process has been successfully tested by processing 20 liters of synthetic HLW feed using a number of small-scale (150 mL) mixer-settlers. Analytical results showed the process behaved as predicted. The major advantage of the CTH process is that it utilizes two commercially available, low cost and well characterized extractants. The major disadvantages of the process are that multi-extraction cycles (at least three) using two different extractants are required and that all strip solutions require further processing to recover the TRUs. In addition, a significant acidity adjustment is required before trivalent actinides can be extracted. A process this complex would be very costly and difficult to operate on a plant-scale.

JRC-ISPRA/HDEHP Process. A team of chemists working at the Joint Research Centre-Ispra Establishment, Italy, have also developed and tested a process to treat commercial HLW (13). The JRC-ISPRA process is somewhat similar to the CTH process. The process begins by performing either an exhaustive TBP extraction or HDEHP extraction of a PUREX raffinate that has been concentrated 10-fold. (Residual U, Np and Pu are removed by the TBP or HDEHP.) The raffinate from the above front-end extraction is denitrated to pH 2 using formic acid. After a clarification step, Am and Cm, together with the light lanthanides, are extracted with 0.3 M HDEHP - 0.2 M TBP in dodecane. Partitioning of Am and Cm from light lanthanides is performed by a Reverse TALSPEAK process, or the actinides and lanthanides can be stripped together using 4 M HNO_3 . Batch extraction tests with actual HLW demonstrated >99% removal of Am and Cm after a single extraction from a feed solution with a pH of 2.76 (13). The Pu left in the precipitate formed during the denitration step after formic and nitric acid washings varied from 2 to 0.6% (13).

The JRC-ISPRA process suffers from the same problems as the CTH process. A multi-cycle process of this type would be most difficult and very costly to operate on a plant-scale. Formation of precipitates of varying alpha contamination is also a drawback.

Japanese/DIDPA Process. The third SX system using an acidic extractant has been developed by a team of chemists from the Japan Atomic Energy Research Institute (14-17). These chemists have utilized a less common acidic extractant called diisodecyl phosphoric acid (DIDPA). The major difference between DIDPA and HDEHP is that the former can extract light trivalent actinides from higher acidities, for example, 0.5 M rather than ≤ 0.1 M HNO_3 required by

HDEHP. As with the CTH process, the major motivation is to reduce the quantity of HLW for disposal. The HLW is generated by reprocessing fuel from commercial nuclear power plants.

The process consists of four steps. The first step is an SX cycle using TBP to remove the small amount of U and Pu left in the raffinate from PUREX. The second step involves a denitration of the raffinate from the first extraction with formic acid. The second step has two objectives; first, to reduce the acidity to pH 0.5 to allow the efficient extraction of Am and Cm with 0.5 M DIDPA - 0.1 M TBP-dodecane; and second, to precipitate zirconium and molybdenum (as $Zr(MoO_4)_2$) that interfere with the subsequent extraction of Am and Cm. The third step involves the extraction of Am and Cm with 0.5 M DIDPA - 0.1 M TBP-dodecane. If the feed for the Am/Cm SX step is made 0.5 to 1 M in H_2O_2 , at least 99% of the Np can also be removed. The fourth and final step of the process involves the selective stripping of Am and Cm with 0.05 M DTPA - 1 M lactic acid. As with the CTH process, the raffinate from step 3 can be treated with inorganic ion exchange materials to remove Sr and Cs. The flowsheet has been tested in a 16-stage bank of mixer settlers using actual commercial HLW. Greater than 99.99% of the Am and Cm were extracted with DIDPA. Overall results showed that the process behaved as predicted.

The same advantages and disadvantages listed for the CTH and JRC-ISPRA processes apply equally to the Japanese process. In addition, an eight-fold dilution of the HLW may be required to prevent formation of a gelatinous precipitate in the DIDPA process solvent (15) and the percentage of TRU precipitated during the formic acid denitration step can be significant if the pH increases to 1.0 (14). Both of the last two points are major drawbacks to implementing such a process on a plant-scale.

ANL/HDHoEP Process. The Argonne National Laboratory (ANL) process utilizes the strongest acidic organophosphorus extractant of the four systems (18). Bis-(hexoxyethyl) phosphoric acid ($C_6H_{13}OC_2H_4O)_2PO(OH)$, abbreviated HDHoEP, requires no adjustment of acidity up to a nitric acid concentration of 2.4 M. The flowsheet developed and cold-tested by the Argonne Group was based on a PUREX aqueous raffinate generated by processing a light water reactor fuel with a burnup of 3300 megawatt-days per ton (19). A HLW simulant was prepared containing thirty components. The process solvent consisted of 0.5 M HDHoEP in diethylbenzene. The organic to aqueous phase ratio (O/A) in the extraction stages was one. After a 1 M HNO_3 scrub (O/A = 4), Am and Cm were stripped with 6 M HNO_3 (O/A = 2) and Np and Pu together with Zr, Nb, Mo and Fe were stripped with a mixture of 0.35 M oxalic acid and 0.35 M tetramethylammonium hydrogen oxalate (O/A = 2). The process solvent was washed with 8 M H_3PO_4 to remove any U and degradation products. The entire process was operated at 50°C. A three extraction stage batch countercurrent test run removed 93% of the Am and Cm, 97% of the Np and 99.7% of the Pu. Using eight extraction stages, the calculated amount of Am, Np and Pu extracted from the feed would be 99.8, 99.8 and 99.99%, respectively.

The ANL process flowsheet is much simpler than the flowsheets based on HDEHP and DIDPA because it has only one extraction cycle and requires no acidity adjustment of the feed, provided that the HNO_3 concentration in the feed is not above 2.4 M. Nevertheless, the process has several serious drawbacks. For example, the process solvent uses diethylbenzene as a diluent, which is not looked upon favorably because of its low flashpoint. The Am and Cm are recovered in 6 M HNO_3 , which would require extensive evaporation and recovery of concentrated nitric acid. An even bigger drawback of the ANL process is that the Np and Pu fraction would require further processing to remove macroquantities of Fe, Zr and Mo and the 8 M H_3PO_4 solvent wash will be contaminated with U and Y fission products. These last two features make the process much more complicated than it first appears.

Conclusion on the Use of Acidic Extractants. All of the acidic organophosphorus extractants discussed above have major drawbacks. Most important are that the extractants have insufficient selectivity for TRUs (especially trivalent TRUs) over a number of fission products and inert constituents that are present in HLW and that the acidic extractants require low acidities to efficiently extract trivalent actinides. Because the trivalent actinides are the major source of alpha radiation in HLW, this latter drawback is perhaps the most serious of all. Both of these

shortcomings lead to complex multicycle flowsheets and frequently to unfavorable stripping conditions.

Processes Based on Neutral Extractants. Neutral extractants, particularly bifunctional neutral extractants, were developed to overcome the major drawbacks of acidic extractants. Neutral extractants remove metal ions from aqueous nitrate media by the formation of a bond between the electron donor group of the extractant and the nitrate-complexed metal ion. The resultant complexes are usually lipophilic because the donor groups of the extractant enter the inner coordination sphere of the metal ion displacing waters of hydration (20,21). Lipophilic complex formation may also occur by the formation of an ion pair between the extractant and the metal ion nitrate complex. One of the most noteworthy and useful properties of the actinides is their propensity for the formation of nitrate complexes. (The extraction of the nitrate complexes of tetra- and hexavalent actinides is the basis of the PUREX process.) The extraction of trivalent actinide-nitrate complexes using TBP is much more difficult than the corresponding extraction of tetra- and hexavalent actinides. High concentrations of salting out agents, such as aluminum or lithium nitrate, and low acidity are required for efficient extraction of Am(III) by TBP (13).

In 1963-64 Sidall reported the synthesis and characterization of several new classes of compounds that showed vastly improved efficiencies for the extraction of trivalent actinides and lanthanides from high nitric acid concentrations (22,23). Although Sidall's compounds were impure, and in most cases the improvement in extraction efficiencies was insufficient for practical applications, his studies nevertheless opened up a new area of actinide separation chemistry that eventually led to some of the most successful waste processing flowsheets.

Early studies utilizing neutral bifunctional extractants focused largely on dihexyl-*N,N*-diethylcarbamoylmethylphosphonate (DHDECMP) (24-28). (The structure of DHDECMP is shown in Figure 1.) These studies utilized a 30% solution of DHDECMP in diisopropylbenzene (DIPB). Feed solutions were defense HLW at least 3 M in HNO₃. Although these early studies were plagued by the use of an impure extractant (~85% DHDECMP), which led to difficulties with stripping, and by a superficial knowledge of the chemical behavior of this new class of extractants (24,26), the foundation was laid for the development of a more advanced system.

TRUEX Process. The TRUEX process is a generic TRU element extraction/recovery process based on the use of a carbamoylmethylphosphoryl type of extractant, called octyl (phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (abbreviated O(ϕ)DiBCMPO or CMPO for short), dissolved in PUREX process solvent (29-33). The CMPO molecule contains a unique combination of substituents that enable it to extract trivalent actinides, as well as tetra- and hexavalent actinides, over a wide range of nitric acid concentrations. (The structure of O(ϕ)DiBCMPO is shown in Figure 1.) The chemistry of CMPO with particular relevance to the TRUEX process has been discussed (33, and references therein). TRUEX was developed primarily to treat a wide variety of defense high-level and TRU wastes generated at the DOE defense establishments (29-32,34). In order for a TRU extraction/recovery process to be applicable for the treatment of defense waste, it must meet a number of criteria. First, it must be capable of efficiently extracting all TRUs from a wide range of nitric acid concentrations, for example, 1 to 6 M HNO₃, in a single extraction cycle. Second, the process must be selective for actinides in the tri-, tetra- and hexavalent oxidation states over most of the fission products (lanthanide fission products excluded) and inert constituents. Third, stripping of the TRUs should not require high concentrations of acid or complexants. Last but not least, the process must be adaptable to existing processing facilities. The TRUEX process meets all of the above criteria.

The key feature in the TRUEX process is the process solvent formulation. TRUEX process solvent is very similar to PUREX process solvent, with the only major difference being the presence of CMPO in the TRUEX solvent formulation. TRUEX process solvent contains 0.20 M CMPO - 1.2 to 1.4 M TBP in a paraffinic hydrocarbon with a carbon chain length of twelve to thirteen. The quantity of TBP used is a function of the chain length and branching of the paraffinic hydrocarbon. If the average chain length of the hydrocarbon is thirteen and contains no branching,

that is, an *n*-paraffin, then the higher TBP concentration is utilized (29). It is not surprising, therefore, that the physical properties of PUREX and TRUEX process solvents are similar.

One of the major reasons for selecting the octyl (phenyl)-*N,N*-diisobutyl CMPO derivative over the corresponding diphenyl derivative was the solubility of the former in PUREX process solvent. This property of the octyl (phenyl) derivative was considered more important than the fact that the diphenyl derivative has a somewhat more favorable nitric acid dependency for the extraction of Am(III) as shown in Figure 2, which compares the D_{Am} versus nitric acid concentration curves for DHDECMP and the *N,N*-diisobutyl derivatives of $D\phi$ CMPO and $O(\phi)$ CMPO. Because of solubility constraints, the three extractants were compared in 0.75 M TBP- CCl_4 media. Another reason for selecting the octyl (phenyl) derivative was the rather remarkable beneficial effect that TBP has on the behavior of $O(\phi)$ DiBCMPO (33, and references therein). The presence of TBP in CMPO-diluent mixtures increases D_{Am} at high acidities (extracting conditions), decreases D_{Am} at low acidities (stripping conditions), decreases the variation of D_{Am} over the range of 0.75 to 6 M HNO_3 , increases the solubility of CMPO in paraffinic hydrocarbons, decreases third phase formation at high loading and increases radiolytic stability. The nitric acid dependency curve for the extraction of Am using a typical TRUEX process solvent formulation is shown in Figure 3. Conoco (C_{12} - C_{14}) was used as the diluent. (Conoco C_{12} - C_{14} is a mixture of normal paraffinic hydrocarbons with an average carbon-chain length of thirteen.) It is noteworthy that D_{Am} values of ten or greater can be obtained from 0.5 to 7.0 M HNO_3 and that D_{Am} values from 1.0 M to 7.0 M are very insensitive to nitric acid concentration.

Comparisons of DHDECMP and $O(\phi)$ DiBCMPO in TBP-paraffinic hydrocarbon mixtures were also performed in some of the early studies on TRUEX development (34). Although DHDECMP has a number of favorable properties, its much weaker extractant strength prohibits exploiting the beneficial effects of high TBP to extractant concentration ratios. To be comparable to CMPO, the concentration of DHDECMP must be increased to at least 0.5 M to compensate for low D_{Am} values. A 0.5 M solution of DHDECMP would require a TBP concentration of 2.5 to 3 M to eliminate third phase formation. Such a mixture has no room for a diluent (34). Therefore, DHDECMP is most commonly utilized as a 30% solution in DIPB (26,27).

TRUEX and PUREX process flowsheets are very similar, that is, extraction is carried out at high acidities and stripping is carried out at low acidities. However, unlike PUREX, TRUEX can treat feed solutions that vary widely in both acidity and composition. Depending on the composition of the streams, oxalic acid is sometimes added to suppress the extraction of Fe, Zr, Mo and Pd. Reducing agents, such as ferrous sulfamate, may be added to ensure that neptunium is in the tetravalent oxidation state. (It makes no difference if Pu is in the trivalent or tetravalent oxidation state because both are extractable.) Solvent scrubs are usually 0.25 to 1 M HNO_3 or 1.5 M HNO_3 - 0.03 M $H_2C_2O_4$, but if an unusually high concentration of Zr is present in the feed, different scrubbing regimes may be required. Trivalent actinides, together with light lanthanides, are stripped with dilute HNO_3 , whereas tetravalent actinides are stripped with a dilute complexing agent such as 0.05 M HNO_3 - 0.05 M HF or ammonium oxalate to solubilize macroquantities of Pu. Uranyl ion and pertechnetate are removed from the process solvent during solvent washing with dilute carbonate solution. Thus, in one extraction cycle TRUEX can achieve what required multiple steps to achieve using acidic extractants. In addition, trivalent actinides are separated from tetra- and hexavalent actinides and tetravalent actinides may be partitioned from hexavalent actinides using relatively dilute reagents. In most cases Tc also may be recovered, but its recovery, although adequate, is not as high as for the actinides.

To aid in designing site- and feed-specific TRUEX flowsheets and in estimating the space and cost requirements for installing a TRUEX process, chemists and engineers at ANL have developed a Generic TRUEX Model (GTM) (35). The GTM is composed of four major sections: (1) SASSE (Spreadsheet Algorithm for Stagewise Solvent Extraction), (2) SASPE (Spreadsheet Algorithm for Speciation and Partitioning Equilibria), (3) SPACE (Size of Plant and Cost Estimates) and (4) INPUT/OUTPUT. All four sections interact together and are executed by Microsoft Excel software. SASSE calculates multistage, countercurrent flowsheets based on

distribution ratios calculated in the SASPE section. SPACE enables one to estimate the space and cost requirements for installing a specific TRUEX process using a variety of different equipment and processing facilities. INPUT/OUTPUT is a menu-driven interface that allows the user to choose which option to run, prompts the user for all the information needed by the GTM before calculations begin and generates reports of results. The GTM has been utilized in designing a number of TRUEX flowsheets described in the following sections.

Experience with TRUEX. A number of laboratories, both in the USA and abroad, have carried out hot test runs with actual waste solutions using the TRUEX process. Although this chapter specifically focuses on HLW, some of the results of test runs on TRU wastes have been included below because they have demonstrated the capability of TRUEX and the utility of the GTM. Table I lists (alphabetically) the laboratories in the USA that have tested TRUEX and the foreign countries that are currently performing studies on TRUEX. The types of waste treated are also shown.

ANL Experience. Except for the initial development studies on TRUEX, which utilized a dissolved sludge waste that simulated the insoluble HLW sludge from a Hanford storage tank (29), all additional studies with real waste solutions carried out at ANL involved testing the TRUEX process by treating the large volumes of TRU analytical waste generated at ANL and the New Brunswick Laboratory. A total of 118 L of TRU nitric acid waste solutions were treated in four process runs (36). A 20-stage bank of 4 cm centrifugal contactors housed in a plutonium glovebox was used to process the wastes. The nitric acid concentration in the feed varied from 1.7 to 4.5 M. Various amounts of other acids, such as HCl, H₂SO₄ and H₃PO₄, were also present in some of the solutions. For example, the phosphoric acid concentration was as high as 1.3 M in one of the waste solutions.

The flowsheets utilized in each of the four processing runs were designed using the GTM. The TRUEX process solvent formulation consisted of 0.2 M CMPO - 1.4 M TBP-*n*-dodecane. Alpha decontamination factors, D.F.s, of the waste solutions ranged from 4.0×10^3 to 6.5×10^4 , which allowed disposal of the process raffinates as low-level wastes. Approximately 18 g of U, 84 g of Pu and 200 mg of Am were recovered. In addition to the high alpha D.F.s achieved, several other features of these processing runs are noteworthy. In one processing run, the Am product contained 99.1% of the Am and only 0.2% of the Pu whereas the Pu product contained 99.8% of the Pu and only 0.9% of the Am. An innovative scrub/Am strip section was designed and tested to reduce the number of stages required for stripping and at the same time to concentrate Am by a factor of ~17. A 0.28 M (NH₄)₂C₂O₄ solution was used to strip Pu and prevent its precipitation. Details of all of the processing runs and flowsheets have been reported (36).

LMITCO Experience. The TRUEX process is being evaluated at the Lockheed Martin Idaho Technologies Co. (LMITCO) for the separation of the actinides from acidic HLW (8,37-40). The treated wastes resulting from TRUEX and subsequent fission product separation processes (discussed below) are anticipated to be grouted and disposed of as non-TRU low-level wastes. The TRUs and lanthanide fission products will be vitrified and disposed of as HLW. Several TRUEX demonstration runs have been performed on Sodium Bearing Waste (SBW) (38, and references therein). The SBW is a secondary acidic HLW (1.5 to 1.7 M HNO₃) containing twelve inert constituents, including Pb and Hg, and the following radioactive constituents: ⁹⁰Sr, ⁹⁹Tc, ¹³⁷Cs, ^{235,238}U, ^{238,239}Pu and ²⁴¹Am. Based on preliminary studies of TRUEX, an optimized TRUEX flowsheet was tested in shielded hot cells at the ICPP Remote Analytical Laboratory using a 20-stage bank of 2 cm diameter centrifugal contactors. The flowsheet, which was designed using the GTM, consisted of six stages of extraction (O/A=0.33), four 0.01 M HNO₃ scrub stages (O/A=1.5), six 0.01 M 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) strip stages (O/A=1.0), two 0.25 M Na₂CO₃ solvent wash stages (O/A=1.0) and two 0.1 M HNO₃ rinse stages (O/A=6.0). HEDPA is a powerful complexing agent that will effectively remove actinides (III, IV, VI) from TRUEX process solvent (41). The process solvent formulation consisted of 0.2 M CMPO - 1.4 M TBP-in Isopar-L. (Isopar-L is a mixture of isoparaffinic hydrocarbons with an average of 12 carbons per molecule.)

In the optimized demonstration run with SBW, 99.79% of the actinides were removed from the waste, resulting in a reduction of alpha activity from 540 nCi/g in the feed to 0.90 nCi/g in the aqueous raffinate (38). This reduction is well below the NRC Class A low-level waste requirement of 10 nCi/g for non-TRU waste. Removal efficiencies of 99.84% for ^{241}Am , 99.97% for $^{238,239}\text{Pu}$ and 99.80% for $^{235,238}\text{U}$ were obtained (38). Although some iron was extracted by TRUEX solvent, it was effectively scrubbed from the solvent, resulting in only 0.7% of the Fe existing in the TRU strip product. Seventy-four percent of the Hg was extracted by the TRUEX solvent but was effectively stripped by the 0.25 M Na_2CO_3 wash. The 0.01 M HEDPA solution back-extracted 99.4% of the actinides, but some additional adjustments in the strip section need to be made to eliminate a slight precipitate from forming. Details of the entire demonstration run have been reported (38).

TRUEX demonstration runs have also been carried out on dissolved zirconium calcine simulant using 2 cm centrifugal contactors (42). Zirconium type calcine was produced from reprocessing zirconium clad fuel. Zirc-Calcine comprises the majority of calcine stored at ICPP. Two liters of spiked simulant were treated in six extraction stages using the same composition process solvent used for SBW. The four-stage scrub section utilized a 0.2 M NH_4F - 1.0 M HNO_3 solution (O/A = 3) to remove extracted Zr. A 0.004 M HEDPA solution was used to concomitantly strip U, Np, Pu, Am and lanthanides. Detailed results of the preliminary demonstration run have been published (42). The major problem encountered in the test run was precipitate formation in the strip section. The precipitate was determined to be zirconium phosphate, which was formed most likely from the excessive amount of Zr carried into the strip section and from the small amount of H_3PO_4 usually present in commercial grade HEDPA. In spite of the problems encountered in the stripping section, >99.2% of the Am was removed from the feed in the extraction section. Although this level of Am removal is not sufficient to ensure the <10 nCi/g TRU content in the low-level waste raffinate, modifications in the flowsheet are being made to suppress the extraction of Zr into the TRUEX process solvent. Based on the highly successful demonstration runs using TRUEX to treat wastes at the Idaho plant, consideration is being given to implementing TRUEX after year 2000. However, further experimental studies need to be carried out to address solvent cleanup and recycle issues and to refine flowsheets.

ORNL Experience. The Radiochemical Engineering Development Center (REDC) at Oak Ridge National Laboratory has tested TRUEX for separation and recovery of macroquantities of Am and Cm from irradiated Mark 42 PuO_2 targets (43). These targets were highly irradiated (>87% fission), therefore, the test runs with TRUEX were carried out in a shielded hot cell. Three banks of 16-stage mixer-settler contactors were used to conduct three test runs using TRUEX. The objectives of the test runs were twofold: (1) to test the performance of the TRUEX process when used to treat a highly radioactive feed solution containing macroquantities of fission products and TRUs and (2) to verify the GTM using gram quantities of Am and Cm and dekagram quantities of Pu. The TRUEX process solvent composition was 0.2 M CMPO - 1.2 M TBP-Norpar-12. (Norpar-12 is a mixture of normal paraffinic hydrocarbons with an average chain length of twelve.)

In general, the design criteria for the process flowsheet were met. The Am-Cm product contained <0.1% of the Pu, and the Pu product contained <1% of the Am-Cm. The losses of TRUs to the aqueous raffinate were low as predicted by the GTM. The major problem area revolved around the stripping section for Pu. In all three test runs, a significant Pu concentration remained in the stripped process solvent. It is believed that the unstripped Pu is most likely retained by acidic degradation products formed in the process solvent.

PNNL/WHC Experience. The first TRUEX demonstration runs performed outside of ANL and the first demonstration runs performed with real waste solutions were carried out at the Plutonium Reclamation Facility (PRF) located at the Hanford Site (30-32). As mentioned above, TRUEX was developed primarily to address the problem of treating the vast quantities and varieties of defense waste generated and stored at the Hanford Site. The first type of waste stream selected for a demonstration run was a TRU waste referred to as Plutonium Finishing Plant (PFP) waste, that was generated at the PRF. The PFP waste consisted primarily of aqueous raffinate

from a SX process using TBP in CCl_4 to recover Pu from scrap materials. In addition, PFP waste may also contain carbonate scrub solution from solvent cleanup operations, distillates from evaporators, HF scrubber waste and miscellaneous laboratory waste. (The PFP waste used for the demonstration did not contain any solvent scrub waste.) The major constituents in PFP waste were Al (0.5 M), Na (0.05 M), Mg (0.3 M), Ca (0.2 M), Fe (0.05 M) and F (0.4 M). The nitric acid concentration ranged from 1.5 to 4.0 M. Typical Pu and Am concentrations in PFP were 0.1 g/L (7,500 $\mu\text{Ci/L}$) and 0.05 g/L (170,000 $\mu\text{Ci/L}$), respectively. Because no flammable solvents were allowed in the PRF plant, the TRUEx process solvent formulation consisted of 0.25 M CMPO - 0.75 M TBP-tetrachloroethylene. This formulation is equivalent, with respect to TRU distribution ratios, to the corresponding formulations that utilize paraffinic hydrocarbon diluents.

Four centimeter centrifugal contactors were used to carry out the solvent extractions. The entire setup including solid-liquid separation equipment, associated tankage and transfer lines was housed in a large glovebox train (31). Five extraction stages, three scrub stages, five dilute nitric acid strip stages and three dilute HNO_3 -HF strip stages were employed in the demonstration runs. The feed/scrub/solvent flows were 250/50/100, respectively. A total of 40 L of clarified PFP waste was treated in four separate runs. In each of the runs, 10 liters of clarified feed were processed through the centrifugal contactor equipment in about 40 minutes. The TRU content of all aqueous raffinates was reduced to well below the 100 nCi/g goal. The Am product contained 96% of the Am and only 7% of the Pu, whereas the Pu product contained 88% of the Pu and only 1% of the Am. (Note that even better Am/Pu partitioning was achieved in the ANL and ORNL demonstration runs that were performed at a later date (36,43).)

Several references (31,44-46) describe other Hanford HLW that are amenable to treatment by TRUEx. They include Complexant Concentrate (CC), Neutralized Cladding Removal Waste (NCRW) and Single-Shell Tank (SST) wastes. Chemists at PNNL have recently studied the feasibility of treating NCRW by TRUEx processing (46). The NCRW consists of the solids (principally $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$) that precipitated when the spent $\text{NH}_4\text{F}-\text{NH}_4\text{NO}_3$ waste produced during chemical decladding of Zircalloy-Clad N-Reactor Fuel was made alkaline. There are currently about 2,300 m^3 of NCRW stored at the Hanford site (7,31). A sample of actual NCRW sludge was used to demonstrate TRUEx. The sludge was first washed with 0.1 M NaOH and then dissolved using 12 M HNO_3 and 10 M HF. The dissolved sludge (1.9 M in HNO_3 , 1.0 M in HF and 0.16 M in Zr plus TRUs and fission products) was subjected to a series of batch SX contacts, first using TBP to separate U and then using TRUEx process solvent (0.2 M CMPO - 1.4 M TBP-dodecane) to separate TRUs. Approximately 98% of the U was separated from the TRUs in three stages using 30% TBP allowing the U to be handled as low-level waste. Greater than 99% of the TRUs, together with La, Ce and Nd were extracted in three stages. Three stages of scrub were carried out to remove excess HNO_3 from the solvent. The feed to scrub numbers 1, 2 and 3 to solvent flows ratios were 100/16, 16, 32/48. Stripping was achieved using two stages of 0.01 M $\text{H}_2\text{C}_2\text{O}_4$ (O/A = 3). No attempt was made to partition Am from Pu. A final 0.25 M Na_2CO_3 wash (O/A = 9) was used before recycling solvent. Using the proposed PUREX/TRUEx flowsheet, the number of HLW glass canisters would be reduced from 2,400, if only sludge washing was performed, to approximately 500.

Although test runs using TRUEx to treat a variety of wastes at the Hanford Site have been very successful, no plans have been made to implement the process. The overall problem of waste management at the Hanford Site is under intensive study. TRUEx processing is a possible option but not a favored one at this time.

Japanese Experience/PNC. During the last ten years, researchers from the Power Reactor and Nuclear Fuel Development Corp. (PNC) of Japan have been studying actinide partitioning as part of an advanced reprocessing system. Ozawa et al. (47,48) have been evaluating the option of separating TRUs from PUREX raffinate using the TRUEx process. These studies, which have been performed at the Chemical Tokai-works Processing Facility, have utilized actual HLW generated from an advanced PUREX process. (The PUREX process was carried out on fast breeder reactor spent fuel burned up to 54,000 megawatt-days per ton and cooled for 2 to 4 years.) The HLW was used without adjusting acidity, but small amounts of Pu

and oxalic acid were added. Oxalic acid was added to suppress the extraction of Zr and Mo (29). Countercurrent experiments were conducted in mixer settlers with holdup volumes of 23 mL per stage. Nineteen stages for extraction and scrubbing and 16 to 19 stages for stripping and solvent regeneration were used to test the process flowsheets. The process solvent formulation consisted of 0.2 M CMPO - 1.0 M TBP-dodecane. (Note that a lower concentration of TBP was used than with previously employed process solvent formulations.)

Three countercurrent mixer-settler runs were performed in the early 1990s. The acidity of the feed solutions varied from 4.0 M to 7 M HNO₃. Scrub solutions varied from 0.3 M HNO₃ - 0.1 M H₂C₂O₄ to 7.7 M HNO₃ - 0.03 M H₂C₂O₄ to 0.3 M HNO₃. Strip solutions varied from a single 0.01 M HNO₃ strip to multiple strips using first 0.01 M HNO₃ followed by 0.3 M HNO₃ - 0.1 M hydroxylammonium nitrate (HAN) and then 0.5 M HNO₃ - 0.1 M H₂C₂O₄. A final solvent wash utilized 0.1 M Na₂CO₃. In all test runs, quantitative extraction of actinides resulted in removal of alpha-emitting nuclides with D.F.s >10³. In the stripping section, Am and Cm were effectively stripped with dilute HNO₃; however, significant retention of Pu and Ru by the solvent was observed until the solvent cleanup section, where both are reported to strip very well. Dual scrubbing improved Ru removal from the solvent, but 6% of the initial value was still retained.

The GTM was used to predict concentration profiles for the three flowsheet demonstration runs (49). The agreement between experimental results and those calculated with GTM were quite good, especially for Am, Cm and lanthanide fission products, which once again proved the value of GTM as a computational tool for designing and simulating TRUEX flowsheets.

Recent studies by researchers at PNC have focused on performing a selective partition of trivalent actinides from light lanthanides using TRUEX process solvent (50). The process is called SETFICS, which is an acronym derived from Solvent Extraction for Triivalent f-elements Intra-group separation in CMPO-complexant System (50). A demonstration of SETFICS was carried out in a countercurrent mode using real TRUEX process solvent that was obtained in previous hot experiments. Americium and curium were partitioned from light lanthanides using 0.05 M DTPA - 4 M NaNO₃. The ¹⁴⁴Ce/²⁴¹Am decontamination factor was 72. Although 80% of the lanthanides were rejected from the Am and Cm products, very little of the Sm and Eu were removed from the actinide(III) product. The yield of Am and Cm was rather low because of the lack of achievement of steady state.

India Experience. Scientists at the Bhabha Atomic Research Centre have tested the TRUEX process using HLW generated from PUREX processing of thermal reactor fuels (51-53). Two process solvent formulations were used: 0.2 M CMPO - 1.2 M TBP-dodecane and 0.2 M CMPO - 1.4 M TBP-dodecane. Feed solutions were approximately 2 M in HNO₃. Two demonstration test runs were carried out. In the first, TRUEX processing was carried out directly on the HLW, whereas, in the second test run PUREX processing preceded TRUEX processing. In both sets of experiments TRUEX effectively removed the alpha activity from the feed. For example, in the second test run experiments, the alpha activity left in the raffinate after four contacts (O/A = 0.5) was less than 0.06% of the total in the feed. Stripping in succession with 0.04 M HNO₃, 0.05 M HNO₃ - 0.05 M HF and 0.25 M Na₂CO₃ resulted in the usual actinide partitioning. The stripped and washed process solvent did not contain any detectable activity above background.

Summary of TRUEX. The TRUEX process has been demonstrated in five laboratories in the USA and in two laboratories in foreign countries. It has been shown to be applicable to both defense and commercial TRU and HLW waste. Particularly noteworthy is its adaptability to treat a variety of defense wastes with wide ranging compositions. TRUEX can achieve in a single extraction cycle what requires multiple extraction cycles and cumbersome pH adjustments with acidic extractants. Another major feature of TRUEX is that stripping does not require high concentrations of acids or undesirable complexants. In addition, trivalent actinides can be concentrated many fold through innovative design of stripping sections.

One of the disadvantages of TRUEX is the cost of the CMPO, although manufacturing the extractant on a large-scale would reduce the cost to an acceptable level. Another disadvantage of

the process is that extensive hydrolytic and radiolytic degradation of the process solvent reduces stripping efficiency. Solvent degradation of CMPO and TRUEX process solvent has been investigated at ANL and several methods have been developed and tested to restore the solvent to near pristine conditions (33, and references therein). Another drawback to TRUEX is the poor selectivity for trivalent actinides over Zr and Mo and, to some extent, Fe. However, the addition of oxalic or hydrofluoric acid or the use of special scrubbing reagents improves the selectivity to acceptable levels. It is interesting to note, as will be discussed below, that both acidic and neutral extractants utilized in TRU extraction processes have the same deficiency with regard to the selectivity of actinide(III) over Fe, Zr and Mo.

Russian TRU Extraction Process. Russian chemists have been studying neutral bifunctional extractants for a number of years (54-58). These studies have paralleled somewhat similar investigations carried out in the USA. To extract TRUs from HLW, Russian chemists have adopted a different carbamoylmethylphosphine oxide (CMPO) derivative than used in TRUEX, namely, diphenyl-*N,N*-di-*n*-butyl CMPO which is abbreviated D δ DBCMPO. The structure of D δ DBCMPO is shown in Figure 1. As discussed in the TRUEX section, the diphenyl CMPO derivative is insufficiently soluble in paraffinic hydrocarbon diluents, even in the presence of excess TBP, to be of practical use. Furthermore, diphenyl CMPO derivatives have a strong propensity towards third phase formation. However, Russian chemists found that by using a fluoroether, called Fluoropol-732, as a diluent for the diphenyl CMPO, the unfavorable solubility and third phase formation properties of this derivative could be overcome (59). The D_{Am} versus aqueous HNO_3 concentration curve using a 0.05 M D δ DBCMPO solution in Fluoropol-732 is shown in Figure 3 (60). The data in Figure 3 show that the values of D_{Am} obtained with the D δ DBCMPO-Fluoropol system are significantly higher, using only one-fourth the concentration of CMPO, than those obtained with TRUEX process solvent over the entire nitric acid concentration range.

The Russian TRU extraction process uses a 0.1 M solution of D δ DBCMPO in Fluoropol-732 as the process solvent (59). An 18-stage bank of centrifugal contactors was used to test the TRU extraction flowsheet. Feed solution consisted of a HLW simulant, 5 M in HNO_3 , containing more than 13 g/L of lanthanides and actinides. An interesting feature of the flowsheet is the use of acetohydroxamic acid (AHA) to strip Fe(III), Zr(IV) and Mo(VI), which also extract along with the transplutonium elements (TPEs). A solution of 2 M HNO_3 - 10 g/L AHA was employed for this purpose. The AHA strip solution is apparently contacted with fresh process solvent to remove any traces of TPEs and possibly Pu (59). TPEs and lanthanides were stripped from the process solvent using 0.01 M HNO_3 . Greater than 99.5% of the actinides and lanthanides were recovered and concentrated by a factor of four to six. The reduction of Fe, Zr and Mo from the TPE fraction was >50. Efforts are currently underway to apply the process to a plant-scale operation (60).

A number of the favorable features outlined for TRUEX also apply to the Russian TRU/SX process, namely, efficient extraction of Am(III) over a wide range of HNO_3 concentrations and stripping with low concentrations of acid. The Russian TRU process has the added advantage of using a lower concentration of a less expensive extractant. Radiolytic and hydrolytic degradation is probably less with the D δ DBCMPO-Fluoropol system than with TRUEX process solvent because of the absence of TBP in the former.

There are, however, some major concerns that arise regarding the Russian process. These concerns center around the use of the Fluoropol diluent. Introducing a diluent with physical properties that are radically different from the physical properties of paraffinic hydrocarbons could cause major problems in implementing this process in existing processing facilities that were designed for PUREX or are currently being used to carry out PUREX processing. Other concerns regarding Fluoropol are its radiolytic stability, its corrosive properties in high radiation fields, the adequacy of practical process solvent cleanup techniques, and the environmental issues created when the spent solvent must be discarded.

There are other features of the D δ DBCMPO-Fluoropol system that need comment. For example, because of the very high distribution ratios of Am over a wide range of HNO_3 concentrations, back-extraction of Am requires unusually low acid concentrations as shown in

Figure 3. Low acid concentrations may not be easily attainable under plant operating conditions. Note that the Russian process data in Figure 3 apply to a 0.05 M solution of extractant whereas the process solvent utilizes a 0.1 M solution (59). Assuming at least a second power extractant dependency, the D_{Am} values for the process solvent will be four times higher than the D_{Am} values shown in Figure 3. Most likely, additional low acid scrubs will be required to help reduce the HNO_3 concentration in the organic phase prior to stripping. Even the advantages of the high D_{Am} values attainable at high HNO_3 concentrations are partially negated by the limitations in stage efficiency. In addition, using low extractant concentrations such as 0.05 M to 0.1 M results in a significantly reduced loading capacity of the process solvent. It is important to keep in mind that in evaluating different extractant systems, low distribution ratios in the extraction stages can be compensated for by the addition of one or two extra stages and/or a higher organic to aqueous flow ratio.

French DIAMEX Process. French chemists at Fontenay-aux-Roses have investigated a number of new amidic extractants as part of a broad strategy for improving the management of radioactive waste (61-65). Two classes of amidic extractants have been investigated. The first class are monoamides of the general structure, $RCONR'R''$, where R, R' and R'' are alkyl groups. Monoamides are monofunctional extractants that only effectively extract tetra- and hexavalent actinides. The second class of extractants are bifunctional amides of the general structure, $(RR'NCO)_2CHR''$, where R and R' are alkyl groups and R'' is an alkyl or oxyalkyl group. The bifunctional compounds are able to extract all actinides, including trivalent actinides, from acidic nitrate media. Only the bifunctional amidic extractants will be discussed in this chapter since they are the basis of the French DIAMEX process (61-64).

French chemists have synthesized and characterized a number of the 1,3- propanediamide (or malonamide) derivatives (62,63). Characterization studies have involved, in addition to the typical SX parameters, speciation and third phase formation (62,63,65). An interesting finding of the speciation studies is that the malonamide compounds form neutral complexes with U(VI) and Pu(IV) nitrates, whereas with Nd(III), a standin for Am(III), both neutral and acidic ion pair complexes are formed, with the latter predominating as the acidity increases (63,65). This behavior with Nd(III) is different from the behavior of the CMPO class of extractants with Nd(III), where only neutral complexes form between the actinide(III) nitrate and the extractant (33, and references therein). As a result of these basic studies, the *N,N'*-dimethyl-*N,N'*-dibutyl tetradecylmalonamide (DMDBTDMA) was selected as the extractant of choice for the DIAMEX process. The structure of DMDBTDMA is shown in Figure 1.

The process solvent in DIAMEX consists of a 0.5 M solution of DMDBTDMA in the aliphatic diluent TPH. The distribution ratio of Am(III) as a function of aqueous nitric acid concentration for DIAMEX process solvent is shown in Figure 3 (63). These data show that DMDBTDMA requires very high nitric acid concentrations (≥ 3 M) to extract Am(III). If 0.05 to 0.2 M $H_2C_2O_4$ is present in the feed to complex Fe, Zr and Mo, the HNO_3 concentration should be 5 M (63).

The DIAMEX process flowsheet is similar to, but somewhat simpler than, the TRUEX and the Russian TRU process flowsheets (61-64). Feed solutions are 5 M in HNO_3 with oxalic acid usually present to complex Fe, Zr and Mo. The O/A in the extraction stages is one. Scrub solution consists of 2 M HNO_3 and stripping is achieved using 0.1 M HNO_3 - 0.2 M hydroxylammonium nitrate, O/A = 1, for Am and Pu, 0.5 M $H_2C_2O_4$ for Np(V), and 0.01 M HNO_3 for U.

The most noteworthy features of the DIAMEX process are that the process solvent is incinerable and that back-extraction is extremely simple and efficient. Most impressive is the fact that radiolytic and hydrolytic degradation of the process solvent do not interfere with stripping (63). Therefore, no involved periodic solvent cleanup step would be required, as with the CMPO extractants. Also, ruthenium extraction was not a problem as in the TRUEX process.

The major disadvantage of the DIAMEX process is that very high HNO_3 concentrations are required to obtain efficient extraction of Am. Furthermore, the acid dependency of D_{Am} , as depicted in Figure 3, is extremely sensitive to the HNO_3 concentration below 4 M. This feature could cause operational problems when carried out on a plant-scale. However, because the French

utilize high acidities in their PUREX processing flowsheets or would utilize equally high acidities in flowsheets where TBP is replaced by a monofunctional amidic extractant, the high HNO_3 concentrations required for feed solution in the DIAMEX process should not be a problem. Another disadvantage of the DIAMEX process is that the extraction of Tc along with the actinides does not appear to occur, as was the case with TRUEX. This feature is most likely due to the high HNO_3 concentration of the feed solutions. The cost of DMDBTDMA relative to the cost of the CMPO class of extractants is difficult to assess because none of these compounds has been prepared on a large scale. Although significant improvements have been made in the preparation of DMDBTDMA, the final step involves purification of the extractant on an adsorbent to eliminate traces of a phase transfer catalyst (62). On the other hand, both of the CMPO compounds are readily purified by crystallizations.

TRPO Process. In 1989 a cooperative program was established between Tsinghua University, Beijing, China and the European Institute for Transuranium Elements, Karlsruhe, Germany to develop a new TRU solvent extraction process to treat HLW (66). The key ingredient in the new process is a mixture of trialkylphosphine oxide extractants (abbreviated TRPO) (66-69). The TRPO mixture consists of seven different, primarily straight chain, phosphine oxides with six to eight carbon atoms per chain. The most abundant phosphine oxides are $(\text{C}_7\text{H}_{15})_3\text{PO}$, 27%, $(\text{C}_7\text{H}_{15})_2(\text{C}_8\text{H}_{17})\text{PO}$, 24%, and $(\text{C}_7\text{H}_{15})(\text{C}_8\text{H}_{17})_2\text{PO}$, 16%. A general structure for the TRPO is shown in Figure 1.

The TRPO-dodecane system has been extensively characterized with respect to the uptake of actinides (III, IV, V, VI) and with respect to selected fission products and Fe. In addition, speciation, loading capacity, third phase formation and radiolytic stability have been studied. Details of all these studies have been reported (69, and references therein). The most important data from these studies are the distribution ratio of Am(III) as a function of aqueous nitric concentration, which is shown in Figure 3 for 30 vol % TRPO in kerosene. The data show that Am is only effectively extracted between 0.05 M to 1 M HNO_3 . The extraction of Am(III) may best be represented by the formation of a neutral complex containing three TRPO molecules coordinated to $\text{Am}(\text{NO}_3)_3$ (69). The behavior of TRPO with respect to speciation more closely resembles that of the CMPOs than that of the DMDBTDMA. This is not surprising since the TRPOs and CMPOs are both phosphine oxides.

Hot demonstration runs of the TRPO process were carried out on real commercial HLW originating from WAK, Karlsruhe. Composition of the HLW can be found in (70). The HLW solutions were centrifuged to remove solids, treated with Fe(II) sulfamate along with HAN to reduce Np(V) to Np(IV) and diluted ten-fold with H_2O . The nitric acid concentration was adjusted to 0.7 M for one test run and 1.4 M for another test run. Process solvent consisted of 30 vol % TRPO in kerosene.

The demonstration runs were carried out in two separate parts. The first consisted of the extraction and stripping of Am. After the first part reached steady state, 200 mL of loaded organic phase (with Am removed) was fed into clean centrifugal contactors to carry out the second part of the process, which consisted of stripping Np, Pu and U. In all, 22 stages were used for the entire process.

The phase ratios in the extraction and 1 M HNO_3 scrub stages were 0.44 and 3.0, respectively. Americium was stripped with 5.5 M HNO_3 , O/A=1. Np and Pu were stripped with 0.6 M $\text{H}_2\text{C}_2\text{O}_4$, O/A=1, after the organic phase was given a preliminary scrub with 0.1 M HNO_3 to reduce the concentration of HNO_3 in the process solvent. Finally, U was stripped with 5% Na_2CO_3 , O/A=1.

More than 99.97% of the Am was extracted in seven stages. All TRUs were effectively stripped from the loaded organic phase. Cross contamination of the TRU elements among the three different product solutions was very low. Technetium-99 was also effectively extracted from the feed with D.F.s of >1400. However, Zr, Mo and, of course, lanthanides were also extracted. The lanthanides were stripped along with Am, Zr and Mo were stripped with Np and Pu and Tc most likely was stripped with U (70).

Additional hot demonstration runs were carried out with a highly salted HLW that was obtained from reprocessing facilities in China (71,72). Nonradioactive nuclides such as Na, Al, Cr, Fe and Ni contributed 88% of the total mass, whereas the TRUs and ^{99}Tc contributed only 0.31% of the total mass. Greater than 99% of the total alpha activity was from Am and Pu and <1% of the alpha activity was from Np. Test runs were carried out in a hot cell using a 50-stage bank of 1-cm miniature centrifugal contactors. To avoid third phase formation due to the enhanced extraction of Fe from salting-out effects, the feed solution was diluted 2.7 times. The final HNO_3 concentration of the feed was 1.2 M. The flowsheet used to extract and recover TRUs from highly salted HLW was essentially the same as the flowsheet used for the extraction and recovery of TRUs from commercial HLW, except for the number of stages employed (71). The decontamination factors achieved were 650-700 for Am and Pu, 15 for Np, 10^4 for U and 125 for Tc. Additional processing of the raffinate from the TRPO process for Sr recovery was also carried out. This subject will be discussed below under Sr and Cs Extraction/Recovery.

Noteworthy features of the TRPO process are: (1) it utilizes a relatively inexpensive extractant, (2) the process solvent has very high radiolytic and hydrolytic stability, (3) the partitioning of tri-, tetra- and hexavalent actinides from each other is relatively simple and easy to control and (4) very high removal of Tc is achievable. Disadvantages of the process are: (1) Am is not efficiently extracted from even moderately high HNO_3 concentrations, (2) Am back-extraction requires very high HNO_3 concentrations and (3) Am is not significantly concentrated in the stripping section relative to its concentration in the feed. Because of the first disadvantage, most HLW streams would require adjustments in acidity, primarily dilutions. These adjustments would most likely cause precipitations to occur, especially in attempting to treat dissolved HLW sludges. The second and third disadvantages would create major problems because the Am product would have to be significantly concentrated and the nitric acid recovered before further treatment, such as Am/rare earth separation or vitrification, could be carried out.

Conclusion on the Use of Neutral Extractants. All of the neutral extractants, whether monofunctional or bifunctional, have the same major advantages over acidic extractants. Foremost among these is that neutral extractants (with the exception of TRPO) are able to extract TRUs from much higher acidities and release them at low acidities. This behavior is due to the fact that neutral extractants coordinate to TRU nitrates, therefore, extraction is directly dependent on nitrate (or nitric acid) concentration. Acidic extractants, on the other hand, are inversely dependent on hydrogen ion concentration and coordinate to the bare (dehydrated) metal ion. An outgrowth of this difference in complexing behavior of the two classes of extractants is responsible for another major advantage of neutral extractants, namely, their significantly superior selectivity for TRUs over fission products (lanthanides excluded) and over the inert constituents usually present in HLW.

Although the four different types of neutral extractants, namely, $\text{O}(\phi)\text{DiBCMPO}$, $\text{D}\phi\text{DBCMPPO}$, DMDBDTMA and TRPO, show major differences in D_{Am} vs. nitric acid dependencies, they all can be effectively utilized in TRU extraction processes. Frequently, the specific types of HLW treatment problems that are being addressed, for example, commercial vs. defense wastes or highly acidic raffinates vs. dissolved sludges, dictate the choice of the extractant.

Strontium and Cesium Extraction

Strontium-90 and cesium-137 are the two major generators of heat and β/γ radiation in HLW. Their presence, therefore, greatly complicates waste handling and disposal. The state of separations technology for the removal of ^{90}Sr and ^{137}Cs prior to the mid 1980s has been summarized (73). The conclusion stated in (73) was that improved extraction/recovery processes for Sr and Cs from acidic waste streams are sorely needed. It is not the objective of this chapter to review all of the prior systems that have the potential to extract Sr and Cs from acidic media. Our

objective is to focus on those systems that have actually been demonstrated in process flowsheets to remove Sr and Cs from moderate to highly acidic HLW.

Strontium(II) and cesium(I) are large cations with low charge densities. Consequently, there are relatively few systems capable of efficiently extracting these cations selectively from highly acidic aqueous solution into a nonaqueous medium. Two systems that can achieve this extraction and serve as the basis of process flowsheets are: the bis-dicarbollylcobaltate anion (referred to hereinafter as cobalt(III) dicarbollide or dicarbollide) and the macrocyclic polyethers (referred to hereinafter as crown ethers). The structures of cobalt(III) dicarbollide and a crown ether used for Sr extraction are shown in Figure 4.

Cobalt(III) dicarbollide. Fundamental studies on the extraction of Cs and Sr by cobalt(III) dicarbollide have been carried out primarily in the Czech Republic and are summarized elsewhere (74, and references therein). Application of the dicarbollide technology to HLW processing has been performed in Russia (75,76). Figure 5 shows the nitric acid dependencies for the extraction of Sr and Cs using a 0.01 M solution of cobalt(III) dicarbollide and 0.01 M polyethylene glycol (PEG-400) in nitrobenzene (77).

Plant-scale demonstration runs utilizing a process solvent consisting of 0.15 M chlorinated cobalt dicarbollide (ChCoDiC), 3% PEG-400 dissolved in *m*-nitrobenzotrifluoride were carried out in August 1996, at Mayak, UE-35 Facility, Chelyabinsk, Russia (78,79). The feed was a HLW solution with 2 M HNO₃. In all, 320 m³ of waste solution was treated.

Demonstration runs have also been carried out in the USA at INEEL, by a team of chemists and engineers from the Khlopin Radium Institute, St. Petersburg, Russia and LMITCO (78,79). Initial investigations were performed using a sodium bearing waste (SBW) simulant as the feed and a 0.15 M ChCoDiC - 3% PEG-400 in Fluoropol (78). Two flowsheets were tested on a continuous basis with a 24-stage bank of 2 cm centrifugal contactors. Eleven extraction stages followed by two stages of solvent scrub with 1.0 M HNO₃ were used. The stripping section was comprised of six stages of a proprietary reagent followed by five stages of solvent wash. Cesium and Sr removal efficiencies were 98.6% to 98.9% and 99.89%, respectively (78).

Additional demonstration runs were carried out with actual SBW using 0.15 M ChCoDiC in Fluoropol. Polyethylene glycol, which is added to the dicarbollide solution to enhance Sr extraction, was not added to the process solvent. This was done to evaluate the process strictly as a Cs removal technology (79). The flowsheet consisted of twelve extraction stages, two scrub stages, six strip stages, three concentrated HNO₃ wash stages, and one dilute HNO₃ wash stage. One molar HNO₃ was used for the scrub and a proprietary reagent was used for the strip. The activity of ¹³⁷Cs was reduced from 236 Ci/m³ in the feed to <0.003 Ci/m³ in the aqueous raffinate. Other components in the waste that also extracted were K (50% extracted) and Hg (34% extracted), but both were effectively stripped along with the Cs.

The cobalt(III) dicarbollide and its chlorinated derivative are obviously very effective Cs extractants. With the addition of PEG-400, the ChCoDiC is also an effective Sr extractant. The dicarbollides have high selectivity over Na, which is the major metal ion constituent in SBW, and have high chemical and radiation stability (74,77, and references therein). The cost of the extractant appears to be quite low (77). The major drawbacks of the dicarbollides are the poor solubility in paraffinic hydrocarbons and the need to use stripping reagents that would be looked upon very unfavorably in most countries. Although the use of a Fluoropol diluent is an improvement over *m*-nitrobenzotrifluoride, the concerns raised about Fluoropols in the Russian TRU process also apply with the dicarbollide system. The fact that dicarbollides function as acidic extractants, and thus have inverse hydrogen ion dependencies, causes D_{Sr} and D_{Cs} to increase as acidity decreases. Stripping, therefore, has to be carried out at high nitric acid concentrations or by utilizing mass action effects of other chemicals. Both of these approaches give solutions of Cs and Sr that will require further treatment.

Crown Ethers/SREX. A new Sr extraction/recovery process was developed by chemists at ANL in the early 1990s for the removal of Sr from HLW (80). The new process is based on the

use of an 18-crown-6 derivative dissolved in 1-octanol. The first version of the process utilized a 0.2 M solution of dicyclohexano-18-crown-6, DCH18C6, (primarily the *cis-syn-cis* isomer) dissolved in 1-octanol as the process solvent (80). Efficient extraction occurs from 3 M to 6 M HNO₃ and efficient stripping from 0.01 to 0.1 M HNO₃. The crown ether-octanol process solvent formulation was tested in a countercurrent mode by Chinese chemists at Tsinghua University in Beijing, China using a HLW simulant (71,72). The feed solution contained only 1 M HNO₃ but was very high in nitrate salt. The composition of the high salt waste solution is reported in (71). The process solvent consisted of a 0.1 M solution of DCH18C6 in 1-octanol. Approximately 99% of the Sr was removed from the feed in ten stages (O/A = 0.67).

A second generation Sr extraction/recovery process called SREX was developed by the ANL team to overcome the problem of aqueous solubility of DCH18C6. The SREX process solvent contains a mixture of isomers of 4,4'(5')-di-*t*-butylcyclohexano-18-crown-6 (DtBuCH18C6) dissolved in 1-octanol (81). The structure of DtBuCH18C6 is shown in Figure 4. Once again the most important isomer of the crown is the *cis-syn-cis* derivative (81). Chemists at the Idaho Chemical Processing Plant (ICPP) batch-tested SREX on a SBW simulant. A 0.15 M solution of DtBuCH18C6 in 1-octanol was used as the process solvent (82). Although the results were very favorable, 1-octanol was not looked upon favorably by engineers at ICPP. Meanwhile, further improvements were being made with the SREX process solvent (83). The new process solvent formulation is a modified PUREX process solvent of the following composition: 0.2 M DtBuCH18C6 - 1.2 M TBP-Isopar-L. The nitric acid dependency for the extraction of Sr using 0.05 M DtBuCH18C6 - 1.2 M TBP-Isopar-L is shown in Figure 5. Although the data shown in Figure 5 were obtained using a mixture of the Sr extractant and a Cs extractant, to be discussed below, D_{Sr} is not significantly affected by the presence of the Cs extractant.

During the last few years, chemists at ICPP have performed a number of investigations on the SREX process using the modified PUREX solvent (84-90). These studies focused on the behavior of matrix components including Na, K, Ca, Fe, Zr, Hg and Pb (85-87) and on preliminary flowsheet demonstration runs with SBW simulant (87). The process solvent consisted of 0.15 M DtBuCH18C6 - 1.2 M TBP-Isopar-L. The preliminary studies demonstrated proof-of-principle and identified potential stripping problems with Pb and Hg, which are extracted along with Sr (87). Improvements in the SREX flowsheet were then made and tested in a countercurrent mode to gain valuable operational data for more elaborate flowsheet testing to be carried out in hot cells (88,89).

Radiolytic degradation of SREX process solvent exposed to gamma radiation has also been studied at ICPP. Exposures varied from low doses up to 1000 KGy (90). It was found that radiation had very little effect on the extraction and stripping performance of the process solvent. Exposure of the process solvent to gamma radiation in the presence of solutions of nitric acid and simulated waste solutions also resulted in no change in D_{Sr} . Calculations show that SREX process solvent in continuous contact with SBW would receive a total dose of 8.8 KGy/year (90).

Based on recent studies (84-90), more elaborate countercurrent flowsheet testing of SREX process was performed at ICPP using 24 stages of 2 cm diameter centrifugal contactors that were installed in the Remote Analytical Laboratory hot cell (91). The process solvent consisted of 0.15 M DtBuCH18C6 - 1.5 M TBP-Isopar-L. Demonstration runs were carried out with both SBW simulant and actual SBW. The flowsheet consisted of ten extraction stages (O/A=1), two 2 M HNO₃ scrub stages (O/A=4), four 0.05 M HNO₃ strip stages (O/A=0.5), four 0.1 M ammonium citrate strip stages (O/A=1) and four 3.0 M HNO₃ solvent wash stages (90). The extraction/stripping behavior of actinides, fission products and numerous non-radioactive elements was evaluated. Removal efficiencies of 99.995% for Sr and >94% for Pb were obtained with actual SBW (90), which resulted in reducing the activity of ⁹⁰Sr in the raffinate to 0.0089 Ci/m³. This level of ⁹⁰Sr in the raffinate is well below the NRC Class A low-level waste limit of 0.04 Ci/m³. Further ⁹⁰Sr decontamination would have been achieved if the centrifugal contactors used for testing did not contain residual contamination from previous actinide flowsheet test runs (91). The strip sections of the flowsheet also performed extremely well, with 99.99% of the Sr and <6%

of the Pb exiting with the 0.05 M HNO₃ strip and 0.007% of the ⁹⁰Sr and 93% of the Pb exiting with the 0.1 M ammonium citrate strip (90,91).

The behavior of actinides using the modified PUREX solvent is also very interesting. Only 1.9% of the ²⁴¹Am extracted with the SREX process solvent whereas 99.94% of the Pu and 99.6% of the U were extracted. The extraction of the Pu and U was due to the presence of TBP. In all, 94% of the total alpha activity was removed from the actual SBW (90,91). Other constituents that extracted to some degree are Na (0.5%), K (37%), Ba (64%), Zr (>82%) and Hg (>99%) (90,91). Sodium and K, and most likely Ba, were effectively stripped along with Sr, whereas only 9.5% of the Hg was stripped from the solvent by 0.05 M HNO₃ and the 0.1 M ammonium citrate. The remaining 90.5% of the Hg remained in the solvent.

References (90,91) summarize all the work performed at ICPP on the SREX process. The SREX flowsheet has been recommended to serve as the basis for further feasibility studies and/or facility design studies (91). Further improvements in the flowsheet need to be developed with regard to back-extracting Hg from the process solvent and possibly minimizing K levels in the Sr strip (91).

Combined CSEX-SREX. Efforts have been underway during the last few years to combine SREX with a Cs extraction/recovery process (92,93). The key ingredient in the Cs extraction process, referred to hereinafter as CSEX, is a dibenzo-18-crown-6 derivative of proprietary composition. The distribution ratios of Sr and Cs as a function of aqueous nitric acid concentration using the Combined CSEX-SREX process solvent are shown in Figure 5 (92,93). The Combined CSEX-SREX process solvent consists of 0.1 M Cs extractant - 0.05 M Sr extractant - 1.2 M TBP in Isopar-L. Five volume percent of laurionitrile is added to the process solvent to solubilize precipitates that sometimes form from the interaction of macroconcentrations of Sr and Ba with DtBuCH18C6. The data in Figure 5 show that extraction occurs at high acidity and stripping at low acidity. The acid dependency curves for both Cs and Sr are typical of situations in which nitrate complexes of metal ions are extracted by neutral extractants.

The Combined CSEX-SREX process offers several features of potential importance in chemical processing schemes for high-level waste treatment. First, if the Combined CSEX-SREX process is applied as the first step in chemical pretreatment, the radiation level for all subsequent processing steps (e.g., TRUEX) will be significantly reduced. Thus, TRUEX could most likely be carried out in a glovebox. Second, the recovered Cs-Sr fraction could be partitioned from the TRUs and therefore will decay to low-level waste after a few hundred years. Finally, combining Cs and Sr extraction into a single process will reduce the amount of equipment and space required to pretreat the waste. This latter point should reduce the cost of pretreating HLW.

The Combined CSEX-SREX process was tested at ANL in a batch countercurrent mode in 1995 using a zirconia calcine waste simulant obtained from chemical engineers at INEEL (92). The results were sufficiently favorable to carry out a hot test run in a continuous countercurrent mode using centrifugal contactors (93). A 24-stage bank of 2 cm contactors housed in a plutonium glovebox was used for the test run. The Zirc-Calcine waste simulant was 3.8 M in nitric acid. Millicurie quantities per liter of ⁸⁵Sr, ^{99m}Tc, ¹³⁷Cs and ²⁴¹Am were added to the waste simulant. The composition of the waste and the exact concentrations of radioisotopes added to the waste are reported (93). The flowsheet consists of two stages of solvent preconditioning with 4.0 M HNO₃ (O/A=1), nine extraction stages (O/A=2.4), four 4 M HNO₃ scrub stages (O/A=4.3), eight 0.1 M HNO₃ strip stages (O/A=1.3) and one carbonate wash stage (O/A=3.2).

Overall, the hot test continuous countercurrent run was highly successful. The removal efficiencies of Cs and Sr from the raffinate were 4.5×10^5 and $>2.6 \times 10^5$, respectively. Greater than 99.99% of the Cs and Sr were stripped from the organic phase. As expected, ²⁴¹Am remained entirely in the aqueous raffinate. The concentration of ²⁴¹Am in the Cs and Sr strip solution was $<1 \times 10^{-9}$ M. The distribution of Tc throughout the flowsheet is difficult to describe because Tc never appeared to reach steady state. The results indicate, however, that the combined process will not effectively remove Tc from the feed solution.

In summary, SREX and CSEX-SREX are highly effective systems for the extraction and recovery of Sr and Cs and Sr, respectively, from acidic HLW. The similarities between the CSEX-SREX, SREX, TRUEx and PUREX processes are noteworthy. All involve extraction from high nitric acid concentrations and back-extraction from low nitric acid concentrations. All process solvents contain TBP in a similar concentration range, utilize a paraffinic hydrocarbon diluent and have similar physical properties. Radiolytic degradation is somewhat similar for all four process solvents because TBP is a major constituent in each. Although TBP is not noted for its radiolytic and hydrolytic stability, the technology for its cleanup from degradation products is well established.

The major drawback of SREX and CSEX-SREX is the cost of the crown ethers. Both crown ethers are commercially available and are quite costly. However, the price of the crown ethers would decrease substantially if production were increased. It is unlikely that the cost of the extractant would be a significant item in the overall cost of pretreating waste. Another disadvantage of SREX and CSEX-SREX processes is that the process solvents are multicomponent systems. PUREX process solvent is a simple two component mixture but the CSEX-SREX process solvent has five components, namely, two extractants, two phase modifiers, and a diluent. Maintaining control of the composition of such a complex mixture on a plant-scale could present a major problem.

Combined TRU-Fission Product Processes

The significant success achieved during the last ten years in developing efficient TRU, Sr, Tc and Cs extraction/recovery processes has led quite naturally to attempts to develop systems that achieve the simultaneous extraction of TRUs, lanthanides, Sr and Cs (94). For example, chemical engineers at ICPP in collaboration with Russian chemists have tested, with some success, a process solvent containing 0.08 M Co(III) dicarbollide - 0.05 M D₂DBCMPPO in xylene (79). Studies at ANL have focused on developing a TOTAL RADIONUCLIDE EXTRACTIOn/RECOVERY process, called TOREX, based on a modified PUREX solvent (95). The entire topic of combining SX processes for actinide and selected fission product separations has been discussed (95). At this time it is debatable whether such processes simplify the overall pretreatment scheme. Two separate processes carried out in tandem may be simpler to operate on a plant-scale, particularly if the combined process requires multipartitioning steps to separate, for example, TRUs from U, Pu from Am and Sr and Cs from TRUs.

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TABLE I. Experience with TRU EX

<u>Laboratory</u>	<u>USA</u> <u>Type of Waste Processed or Studied</u>
Argonne National Laboratory (ANL)	TRU-Analytical Waste
Lockheed Martin Idaho Technologies Co. (LMITCO)	Sodium Bearing Waste, Calcine Waste
Oak Ridge National Laboratory (ORNL)	Irradiated ^{242}Pu Targets
Pacific Northwest National Laboratory (PNNL) Westinghouse Hanford Co. (WHC)	Neutralized Cladding Removal and Waste (NCRW) and Plutonium Finishing Plant (PFP) Waste

INTERNATIONAL

<u>Country</u>	<u>Laboratory</u>	<u>Type of Waste</u>
India	Bhabha Atomic Research Centre	Commercial and Defense HLW
Japan	Power Reactor and Nuclear Fuel Development Corp.	Commercial HLW

Figure Captions

Figure 1. Structures of neutral bifunctional and monofunctional extractants.

Figure 2. Comparison of octyl (phenyl)- and diphenyl-DiBuCMPO and DHDECMP in the presence of TBP at 25°C as extractants for Am(III) in nitric acid
(Adapted from ref. 33.)

0.25 M CMP or CMPO - 0.75 M TBP - CCl₄.

Figure 3. Comparison of TRUEX, Russian TRU, DIAMEX and TRPO process solvents as extractants for Am(III) in nitric acid
(Adapted from refs. 33, 60, 63, 69.)

TRUEX process solvent (0.02 M O(ϕ)DiBCMPO - 1.4 M TBP-Conoco (C₁₂-C₁₄)),

T = 30°C

Russian TRU process solvent (0.05 M D ϕ DBCMPPO-Fluoropol-732), T = 23°C

DIAMEX process solvent (0.5 M DMDBTDMA-TPH), T = 25°C

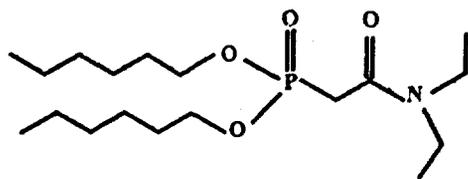
TRPO process solvent (30 vol % TRPO-Kerosene), T = 25°C

Figure 4. Structures of Cs and Sr extractants. (Adapted from refs. 77,92.)

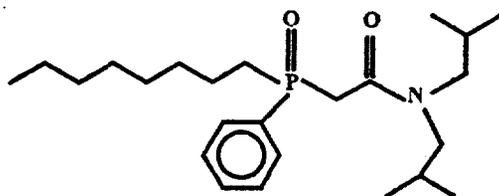
Figure 5. Nitric acid dependencies of Cs and Sr extraction using dicarbollide and crown ether extractants. (Adapted from refs. 77,92,93.)

Dicarbollide (0.01 M cobalt(III) dicarbollide - 0.01 M PEG-400-nitrobenzene)

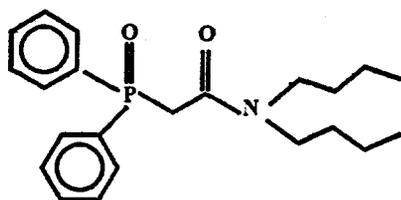
CSEX-SREX (0.1 M Cs extractant - 0.05 M Sr extractant - 1.2 M TBP-Isopar-L - 5 vol % laurionitrile)



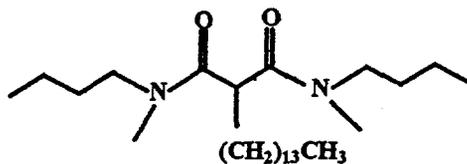
Dihexyl-*N,N*-diethylcarbamoylmethylphosphonate (DHDECMP)



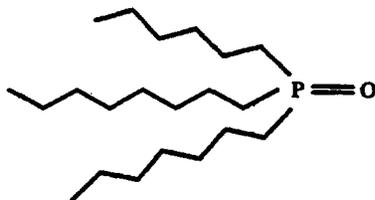
Octyl(phenyl)-*N,N*-diisobutylcarbamoylmethylphosphine oxide (O(φ)DiBCMPO)



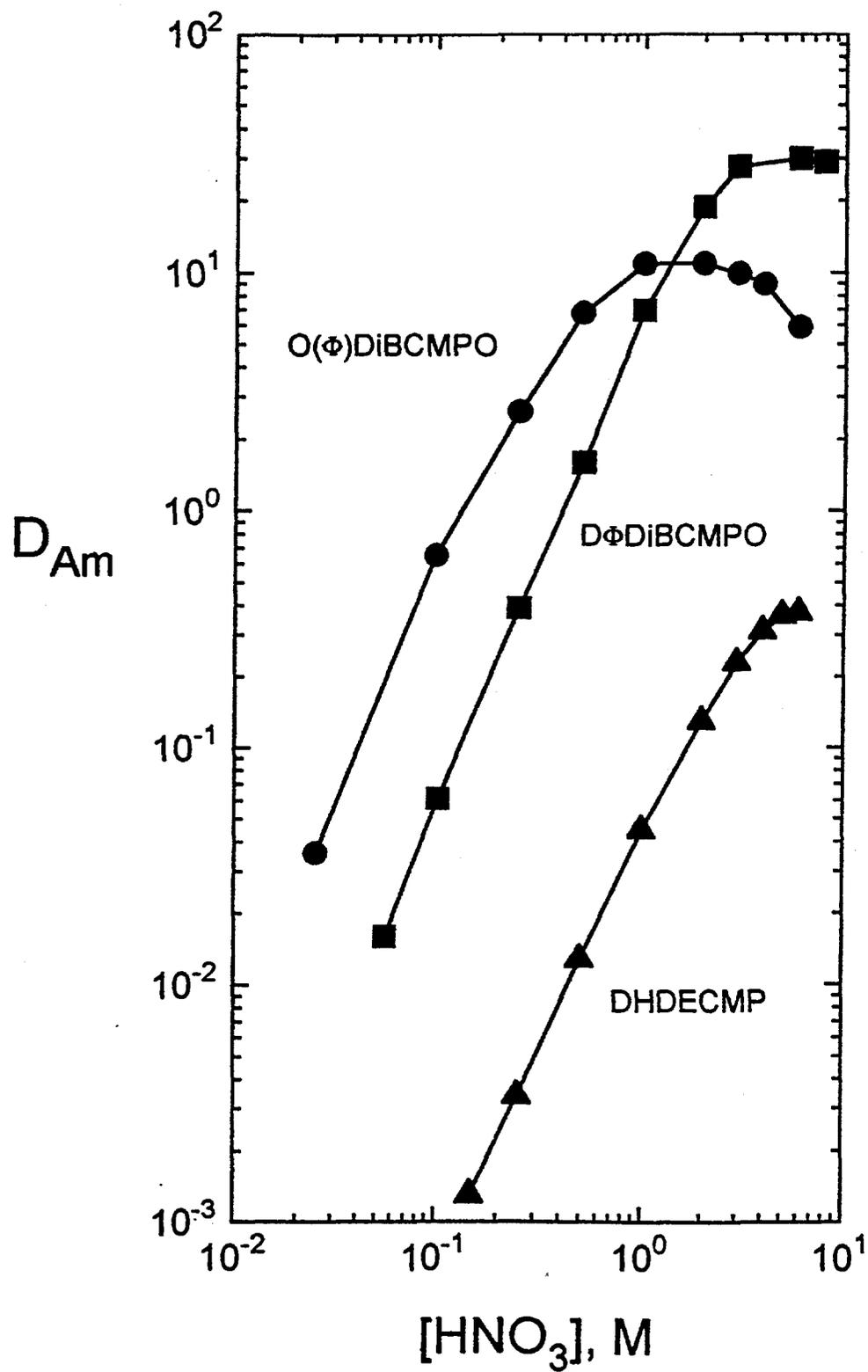
Diphenyl-*N,N*-di-*n*-butylcarbamoylmethylphosphine oxide (DφDBCMPO)

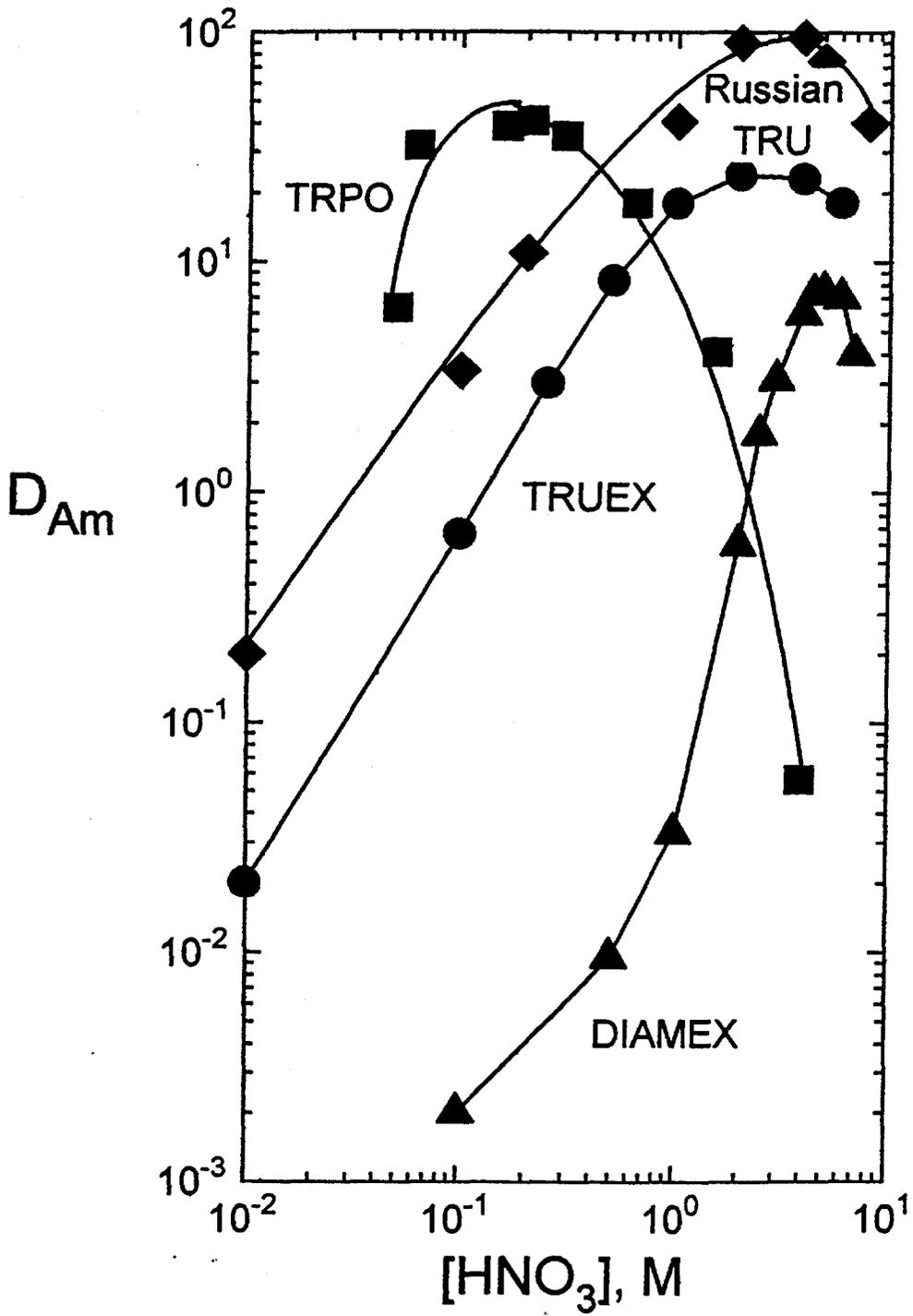


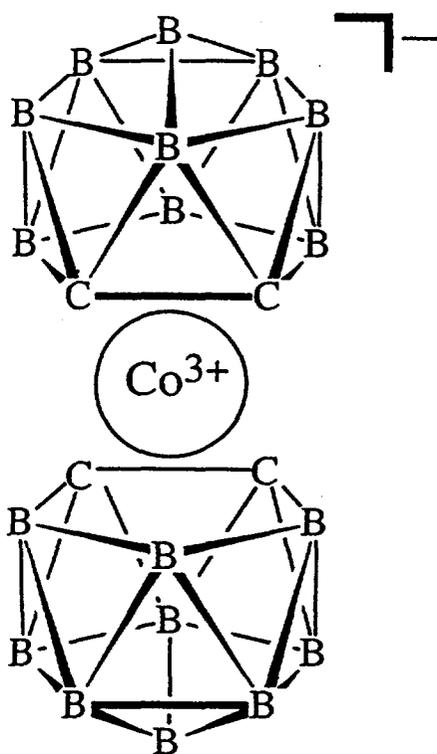
Dimethyldibutyltetradecylmalonamide (DMDBTDMA)



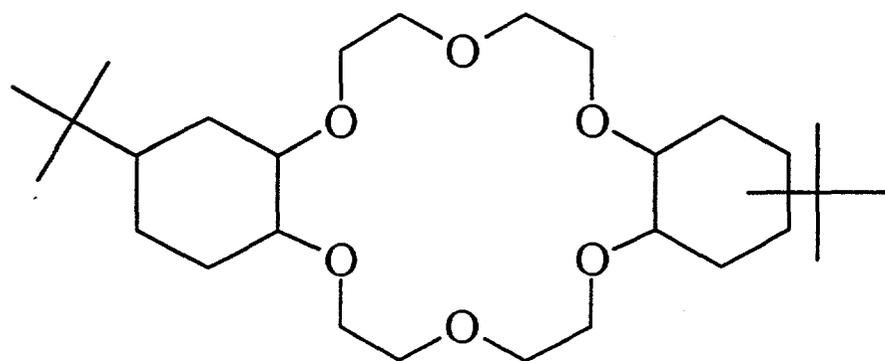
Trialkylphosphine oxide (TRPO)



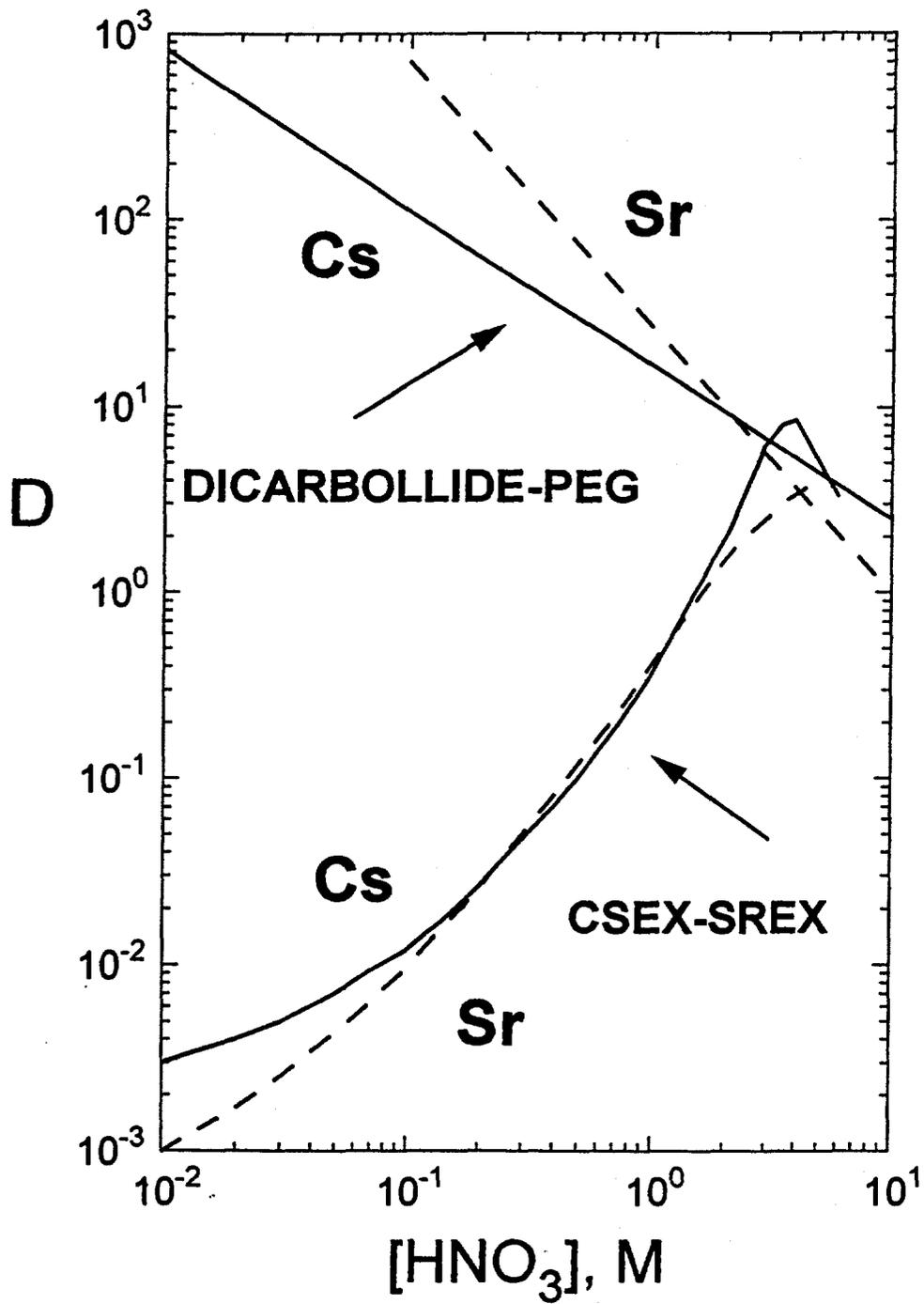




Cobalt(III) Dicarborollide Anion



Bis-4,4'(5')-(*t*-butylcyclohexano)-18-crown-6



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